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Development of membrane extraction systems for measuring trace level organic compounds in water

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ABSTRACT

DEVELOPMENT OF MEMBRANE EXTRACTION SYSTEMS FOR MEASURING TRACE LEVEL ORGANIC COMPOUNDS IN WATER

By
Xuemei Guo

The presence of volatile organic compounds (VOCs) in ground and surface water resources poses a threat to public health. The measurement of these trace level contaminants in water is of significant importance. Conventional methods for analysis of trace volatile organic compounds in water include purge and trap, head space analysis, and solid phase microextraction (SPME). While these are excellent laboratory techniques, none of them can be used for continuous, on-line monitoring of water streams. Membrane separation of organic compounds from water provides an exciting possibility for on-line extraction and analysis. In previous investigations, water continuously flowed on the feed side of the membrane and the analytes were continuously removed by an inert gas stream or a vacuum. The measurement was based on steady state permeation. This approach has several limitations. For example, the steady state can not be reached instantly, resulting in a long analysis time. Another limitation is that this instrument can not be used for analyzing small discrete samples.

In this study, a novel approach, referred to as pulse introduction membrane extraction (PIME), is presented. This technique eliminates steady state requirements and can be used for continuous monitoring, as well as for discrete analysis of trace levels of VOCs in water. Water samples are introduced as a pulse into a membrane module. An eluent is used to transport the sample onto the membrane. The permeated organic compounds are

extracted by an inert gas, concentrated in a micro-sorbent trap and injected into a GC for analysis.

An aqueous boundary layer which forms at the membrane surface due to the poor mixing of water with the membrane appears to be the major resistance to mass transfer for the permeation process. Boundary layer effects were reduced by nitrogen purge of the membrane, and by an alternative membrane module design. A mathematical model which takes into account the aqueous boundary layer effects was developed to describe the non-steady state, pulse introduction process. A qualitative model of extraction efficiency is also presented here to illustrate the factors that affect analytical sensitivity.

The combination of system optimization, nitrogen purge and improved module design results in higher sensitivity and faster response than other methods reported in the technical literature. Detection limits are at ppb levels, precision and extraction efficiency are excellent. As the result of this research, the capability of continuous monitoring of trace levels of organic compounds in water has been demonstrated.

The PIME system was compared with previously reported steady state membrane permeation system. The advantages of the PIME system include higher sensitive and faster response and can also be used for discrete sample analysis. Comparison of the PIME with the purge and trap technique, which is currently the most popular method for VOCs analysis, showed that the results are in good agreement. Contaminated ground water samples from the Naval Engineering Research Station were analyzed to demonstrate the practicality of the PIME system.

This study was extended to the analysis of semivolatile organic compounds (SVOCs) in water. Continuous monitoring of SVOCs in water using membrane extraction and on-

line HPLC analysis was explored. The system was based on continuous extraction rather than pulse introduction. It demonstrated the capability for enrichment of SVOCs from water into a solvent. Continuous monitoring of SVOCs was demonstrated at ppb level using HPLC. System parameters which affect the enrichment factors were studied.

DEVELOPMENT OF MEMBRANE EXTRACTION SYSTEMS FOR MEASURING TRACE LEVEL ORGANIC COMPOUNDS IN WATER

by
Xuemei Guo

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Somenath Mitra, Lizhong Zhang, Naihong Zhu and Xuemei Guo "Characteristic of On-Line Membrane Extraction Microtrap GC System as Applied to Air and Water Monitoring" *Journal of Microcolumn Separation*, vol. 8, no. 1, pp. 21-27, 1996.

Somenath Mitra, Xuemei Guo and Naihong Zhu, "Membrane Sample Introduction for Gas Chromatography" *Eastern Analytical Symposium and Exposition*, Nov. 1996. Somerset, NJ.

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To my mother Zhangzhen Xiao who is in heaven now
and my father Cuibin Guo

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NOMENCLATURE

Roman Letters

A membrane surface area, cm^2

C concentration, mol/cm^3

d diameter of the hollow fiber, cm

D diffusivity, cm^2/s

ΔE_d activation energy of diffusion, J/mol

ΔE_s heat of solution, J/mol

f gas fugacity, kPa

F Enrichment factor in chapter 7 and permeation rate across membrane, mol/s, in the rest of the thesis

ΔH heat of absorption, J/mol

I mass transfer resistance

J flux, mol/ cm^2-s

K mass transfer coefficient

k phenomenological coefficient defined by equation (1-24) in chapter 1 and partition coefficient in the rest of the thesis

k_D Henry's law constant

l membrane thickness, cm

L membrane length, cm

M system response in page 65 and molecular weight in the rest of the thesis

p partial pressure, kPa

NOMENCLATURE
(Continued)

P permeability, mol/cm-s

Q water flow rate, cm^3/s

r distance along membrane diameter, cm

R_c universal gas constant

R fiber radius, cm

Re Reynolds number

S solubility, mol/cm^3

t_L time lag, s

t time, s

T temperature, °C

Δt sample duration on membrane, s

V sample volume, cm^3

w' weight fraction of analyte

x distance along membrane thickness, cm

z distance along membrane length, cm

Subscripts

b boundary layer

e & s inlet and outlet, respectively

i & j molecule i and j, respectively

NOMENCLATURE
(Continued)

m membrane matrix

r reduced (normalized) value

v vapor phase

w water sample

0 standard state

1 & 2 incoming outgoing position respectively

* equilibrium state

Greek Symbols

α membrane selectivity

β constant in equation 1.13 and 1.14

γ activity coefficient

δ cohesive energy density

λ mean jump length

μ chemical potential in page 22-24 and viscosity (millipoise) in the rest of the thesis

ν velocity, cm/s

ρ density, gm/cm^3

σ boundary layer thickness, cm

NOMENCLATURE
(Continued)

Abbreviation

BTEX	benzene, toluene, ethylbenzene and xylene
EE	extraction efficiency
FTIR	Fourier transform infrared spectrometry
GC	gas chromatography
HPLC	high performance liquid chromatography
L-L	liquid-liquid extraction
MDL	method detection limit
MEK	methyl ethyl ketone
MIMS	membrane interface with mass spectrometry
MS	mass spectrometer
OLMEM	on-line membrane extraction microtrap
PIME	pulse introduction membrane extraction
Re	Reynolds number
RSD	relative standard deviation
USEPA	US Environmental Protection Agency
UV	ultraviolet
VOCs	volatile organic compounds
SPE	solid phase extraction
SVOCs	semivolatile organic compounds
TCA	1,1,1-trichloroethane

CHAPTER 1

INTRODUCTION

1.1 Organic Pollutants in Water and Their Measurements

1.1.1 Water Pollution

The contamination of ground and surface water generally occurs from contaminants that find their way into water from industrial waste releases, agricultural runoff and atmospheric deposition. Some contaminants are also formed during the treatment of water supplies, a good example being the disinfection by-products. Between 1988-91, the US Environmental Protection Agency (USEPA) reported numerous cases of ground and surface water contamination due to the presence of organic pollutants. EPA phase I investigations reported the presence of cis/trans-1,2-dichloroethylene contamination in 205 ground water sites, dichloromethane in 294 sites, ethylbenzene in 107 sites, tetrachloroethylene in 447 sites and toluene in 222 sites [1]. From an analytical point of view, the organic pollutants in water generally are classified as volatile organic compounds (VOCs), and semivolatile organic compounds (SVOCs). The VOCs are defined by EPA as the molecules with vapor pressures greater than 0.01 kPa at 25 ^{o}C.

The presence of organic compounds in water pose a direct threat to public health because many of the compounds are toxic or carcinogenic. For example, benzene is a carcinogen, and tetrachloroethylene damages central nervous system and causes kidney malfunction. Some of these compounds, for example the carcinogens, are regulated based on zero toxicity thresholds, which means that any exposure is associated with some kind of health risk. The exposure routes could be dermal absorption, inhalation or direct

ingestion. The bioaccumulation of trace level organics also increases human exposure to these toxicants. Therefore, measurement of trace level organic compounds in water is of significant importance.

1.1.2 Conventional Measurement Methods

The measurement methods of organic compounds in water include liquid-liquid (L-L) extraction, purge and trap, head space analysis, solid phase extraction, solid phase microextraction and large volume injection. These methods are tedious and expensive in terms of time and labor involved. In L-L extraction, a large amount of solvent is used, generating a large quantity of hazardous waste. Moreover, an additional concentration step is needed during which volatile organic compounds could be lost. In head space analysis, a certain amount of aqueous sample is sealed in a vial with head space. Once equilibrium is reached, a head space sample is drawn and analyzed. This method is insensitive, has poor precision and accuracy and is usually used as a screening method. Large volume injection [2] is a relatively new technology for analysis of liquid samples. In this technique, 100-400 µl water sample is directly injected into a GC column. The analytes are eluted as sharp bands during concurrent solvent evaporation. Large-volume injection is also attractive for coupled HPLC-GC system in which the clean-up eluent fraction containing analytes from the preparative HPLC are injected on-line to GC for analysis [2]. Solid phase extraction appears to be the common method for analysis of SVOCs. Analytes in a sample are selectively adsorbed onto an adsorbent disk and washing and desorption are applied to the disk prior to instrumental analysis.

Currently, purge and trap is the leading method for analysis of VOCs. The schematic diagram of purge and trap is shown in Fig. 1.1 [3]. Here an inert gas is used to purge an aqueous sample. The purged organics are concentrated on a sorbent trap. Thermal desorption is then applied to desorb the organics, which are refocused in a cryogenic trap at the head of a GC column. Another thermal desorption step is needed for GC injection and analysis. In purge and trap, the analysis time is long because purging, and heating/cooling of the sorbent trap take time. The moisture from aqueous sample often blocks the cryogenic trap by forming ice and affects the GC analysis.

In all of these techniques, the measurement process is comprised of several distinct steps, such as, sampling at site, transportation, storage, sample preparation and analysis. These are slow processes and are susceptible to errors such as sample loss and cross contamination. Laboratory analyses that involve significant amount of manual sample handling are expensive, thus limiting the number of the samples that can be analyzed. In an environmental process, such as waste discharge, pollutant concentration and/or composition varies with time. The sampling followed by laboratory analysis approach can easily miss some of these concentration dynamics. Consequently, in a guidance document for the Great Lakes system [4], for highly volatile, hydrolyzable, or degradable compounds, EPA strongly recommended the use of only flow-through tests in which the concentrations of test compounds in test solutions are measured using acceptable analytical methods. A flow-through test is a test in which test solutions flow into constant-volume test chambers either intermittently (e.g., every few minutes) or

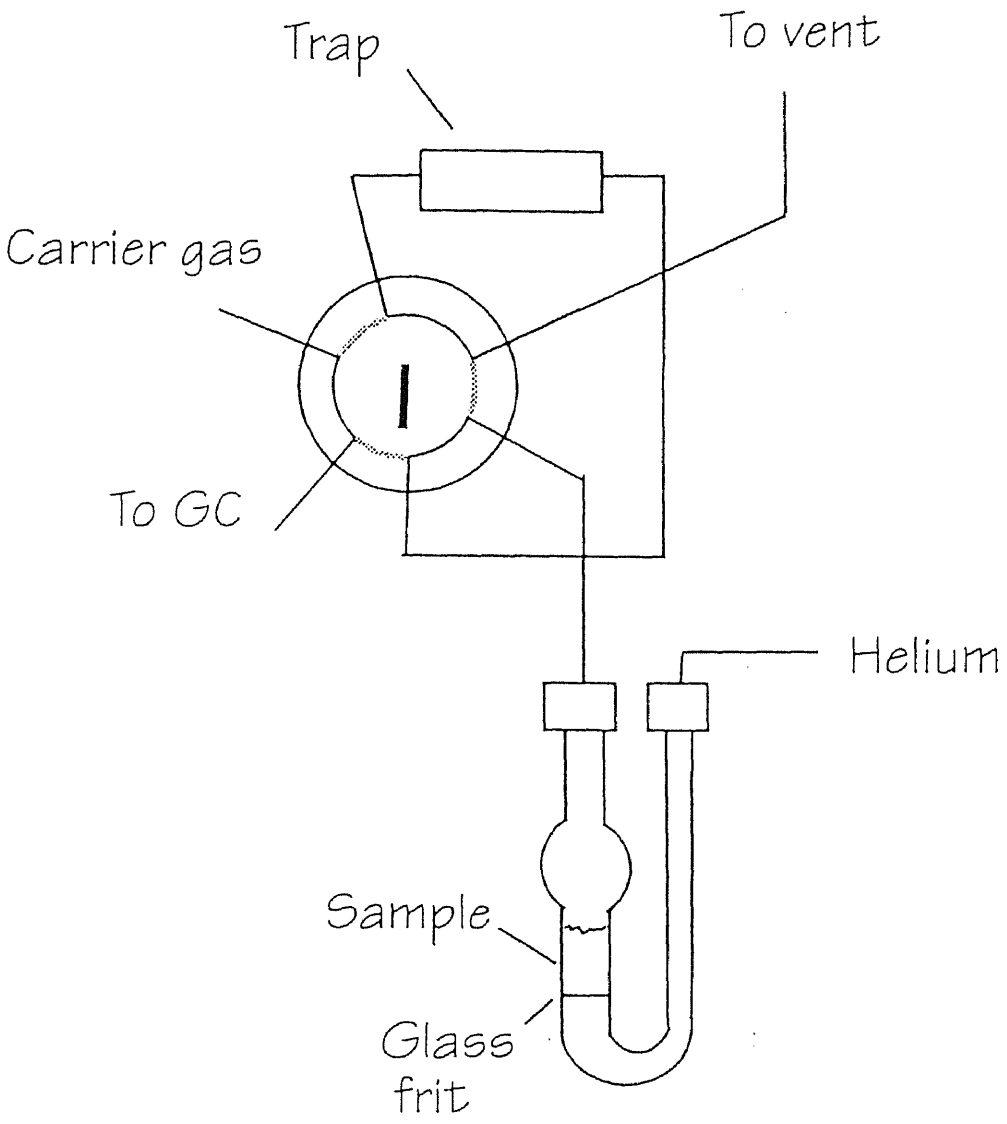


Fig. 1.1 Schematic diagram of purge and trap system. (from reference 3)

continuously, with the excess flowing out. However, such tests are currently unavailable for all analytes.

At present, there is a need for instrumentation providing fast analysis, low detection limits and the capability of analysis for continuous on-line monitoring of water streams. This instrumentation also should have a simple and rugged design and low cost for application on real water monitoring. Continuous on-line analysis combines the distinct steps in sample preparation and analysis process into an integrated instrument. It is capable of the warning of imminent problems, and provides immediate analysis results while the site investigation for ground water contamination is going on. It also allows a process such as water recycle to be monitored continuously. The increasely stringent analytical requirements of low detection limits required by evolving regulations poses a real challenge to on-line environmental measurements.

1.1.3 Instrumentation of Continuous Measurements

Much effort has been put in recently to develop instrumentation for continuous on-line measurement of pollutants in the environment. Fourier Transform Infrared (FTIR) Spectrometer has high accuracy, precision, and rapid data acquisition and handling rates. FTIR has formed applicability for continuous monitoring of air emission [5-8]. FTIR and near IR (NIR) have also been used in real time measurement of industrial process, such as, polymer production [9], and reaction kinetic [4]. GC separation coupled with FTIR has been used for multiple analyte analysis, and one of the earliest studies was reported by Liebman et. al. for monitoring combustion and pyrolysis products [10]. FTIR is more

applicable for qualitative analysis of simple mixtures since the IR fingerprint spectra tend to be low resolution. However, the frequent nonadherence to Beer's law and the inability to interpret complex spectra limits the application of IR methods in many analyses. Moisture in the analytes seriously effects the analysis due to the strong absorption in middle IR, limiting its application to environmental samples which are usually associated with moisture. The detection limits of sub ppm for organics also limits its application of analysis of environmental samples for trace levels of ppb [11].

The ultraviolet spectrometer is a popular detector for organic analysis. Overlapping absorption band resulted from the superposition of vibrational transitions on the electronic transitions limits the qualitative analysis. Background absorption often interferes in the analysis. A UV detector has been used for continuous detection of aqueous contaminants using in situ corona reaction [12]. This approach used a chemical reaction to reduce the background absorption and measured the total UV absorption of contaminants. The reaction was induced in situ via highly reactive species generated in a high voltage, point-to-liquid corona discharge. By continuously measuring the absorption before and after the contactless, electroreagent corona reaction, suppression of the background of nonreacting species was obtained, and continuous measurement of the total absorption of components of interest was achieved. This method has detection limits at the ppm level.

The mass spectrometer has been used for continuous measurements. Direct sample introduction into the mass ionization chamber is a simple configuration for continuous monitoring. However, it is associated with high detection limits and low sensitivity.

Membrane interface with mass spectrometer (MIMS) was reported for continuous monitoring [13-22]. Hoch and Kok published the first article on membrane separation for analysis of organics in 1963 [13]. In MIMS, a selective membrane interfacing with water or air sample and vacuum of the ionization source was used for analyte permeation thus a certain degree of enrichment was provided. The permeated VOCs were directly vacuumed into the mass spectrometer for analysis. Membrane interface with mass spectrometer has been used in continuous monitoring of water and air streams [14-19]. Continuous in vivo mass spectrometric determination of selected organics in blood with a membrane probe has also been reported [21]. The MIMS increases the analysis sensitivity, improves the detection limits and combines the separation, concentration and analysis into one step. It appeared to be capable for direct trace level analysis for organic compounds. However in most cases environmental pollution is so complex that the analysis results are difficult to interpret without chromatographic separation. In some mass analysis cases, a gentle ionization has be used to obtain simple mass spectrum for measurement in order to avoid the interference in the mixture.

Continuous extraction of organics from water via membrane coupled with GC analysis has also been studied where an adsorbent was used as the interface between membrane module and GC [23-39]. The adsorbent trap or cryogenic trap was used as the preconcentrator and GC injector. An on-line membrane extraction microtrap system (OLMEM) [23] has been developed in our laboratory over the last few years for continuous introduction of VOCs from a liquid stream directly into a GC. This system

has demonstrated low detection limits (ppb levels), high selectivity and the ability to continuously monitor VOCs in water.

In these membrane-GC or MS continuous monitoring techniques, the membrane was continuously in contact with the sample and the measurements were made at equilibrium state, which can take a fairly large amount of time to reach [39]. Therefore the system response lags behind the sample concentration change. Another disadvantage is that the continuous membrane extraction is not suitable for discrete small sample analysis because a large amount of sample is needed to reach steady state.

SVOCs are not readily vaporized, so they pose an additional challenge to analysis. Although much effort has been made in membrane extraction of VOCs from water, very limited data are available for membrane extraction of SVOCs. Recently, laser desorption of SVOCs from the membrane interface in membrane introduction mass spectrometry has been reported [40]. The laser directly heated the membrane surface resulting in rapid desorption of the SVOCs and desorbed SVOCs are vacuumed into the ionization source of a mass spectrometer. Study on dialysis with semipermeable membrane as an efficient method for lipid removal in the analysis of bioaccumulative chemicals has also been published [41]. In this study, the membrane is used as an nondestructive media to separate lipid from organochlorine contaminants. The cleaned-up analytes were then analyzed using MS as regular samples. A membrane concentrator for SVOCs in water was designed by H. Nomura, J. Ahn, et al. [42] where a water stream continuously flowed through a membrane module, and a certain amount of organic solvent continuously circulated through the membrane module. After about 110 minutes of equilibration, an

eighty fold enrichment was obtained. In this approach, the extractant solvent was circulated to extract the analytes. Therefore, when the sample concentration changes, the extractant concentration can not represent real the sample concentration.

1.2 Membrane Separation

Environmental analysis is challenging because the pollutant concentration in the real world can be in trace level of parts per billion (ppb) range and environmental matrices are complex and variable. The preconcentration and separation techniques are critical in the analysis process and directly affect the performance in terms of accuracy, precision, linearity calibration curve and detection limit.

For a fast separation of organic compounds from an air or water matrix, membranes have received some attention [14-39] because membranes can be used for selective extraction of organics from water, or air. Membranes have been used in different industries for gas separation, dialysis, osmosis and biochemical compound separation [43]. The first application of membranes in analytical chemistry appeared in the 60's [12]. More efforts on membrane analysis of organic compounds research were carried out in 80's and 90's, since the membrane structures with high selectivity and permeation rate were developed by then. The membrane module can be made from flat sheets or hollow fibers. The later was found to provide higher surface area per unit of volume. Since its introduction to analytical chemistry by Westover et al [14], many applications of hollow fiber for sampling have been reported [16-39].

1.2.1 Historic Review

Membrane separation was first studied by J. K. Mitchell in 1831 who observed the membrane's selective solvation and the diffusion of molecules. Around the same period, A. Fick formulated Fick's law [44] which states that diffusion flux is proportional to the concentration gradient.

$$J = -D\,(\delta C/\delta X) \tag{1-1}$$

where J is flux, D is diffusivity, C is concentration and X is the distance along membrane thickness.

Professor Graham in University College London made a major contribution to membrane separation. He studied gas permeation through porous membrane and proposed the Graham's law [43]:

$$F_i/F_j = \sqrt{\frac{M_i}{M_j}} \tag{1-2}$$

where F_i and F_j are the permeation rate of molecule i and j respectively. M_i and M_j are molecular weight for i and j respectively.

Graham also proposed the theory for nonporous membrane now referred to as "molecular solution and diffusion" [44] which is still the accepted theory for membrane permeation. The "solution and diffusion" theory describes membrane permeation to be comprised of the following processes:

1. Molecules first dissolve in membrane.

2. The dissolved molecules thermally diffuse under concentration gradient utilizing the activation energy of the molecule and the polymer segments. The molecule rotates the

segment creating a suitable size vacancy and jumps in. The total jumping direction is the direction of concentration gradient.

3. The molecules desorb from the membrane surface to the other media.

Granham noted that the solvation of the molecule depends on the nature of the molecule and determined a series of relative permeation rates across the membrane for a number of gases.

In 1920, H. A. Dayne [45] studied unsteady state diffusion in membranes and substantially improved the membrane theory. He established the dynamic methods for measuring the diffusivity, solubility and permeability and developed the mathematical solution for measuring diffusivity. After solving the Fick's second law under appropriate initial and boundary conditions, he demonstrated that the extrapolation of the line obtained, after steady-state conditions are established, to the time axis gives a time lag t_L as shown in Fig. 1.2 that is directly related to the diffusion coefficient [44, 46]:

$$t_L = l^2/6D \tag{1-3}$$

where t_L is time lag, l is membrane thickness. This equation was fully developed by Barrer for use [47].

Over the years, several comprehensive review papers and books [48, 49, 43, 44]] have been published on the mechanism of membrane separation, interaction of polymer segment and solutes, the utilization of the thermal energy by molecules for permeation, and the relationships between permeability, diffusivity and solubility. Although the theory of membrane separation has been known for more than a century, industrial applications were not developed till late 70's and early 80's when the thin membrane with high

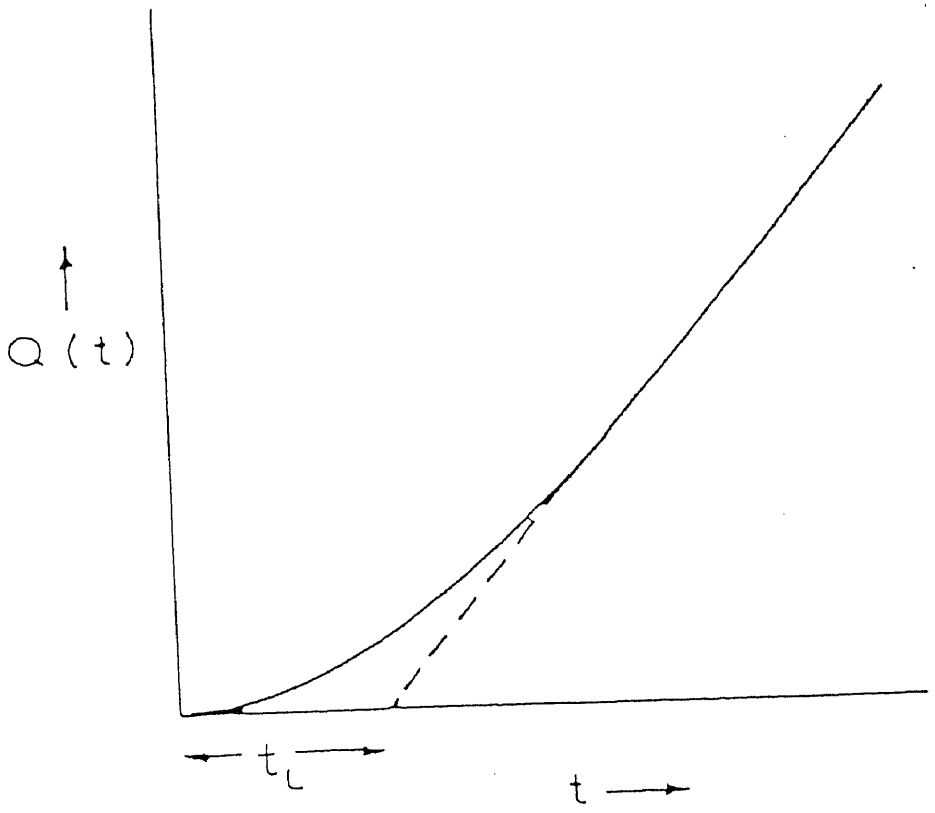


Fig. 1.2 Typical results of a permeation experiment, showing the time lag t_L. (from reference 44)

diffusivity and selectivity were manufactured. As the milestone of the modern membrane synthesis technology, Monsanto introduced Prisom system for air separations in 1983. Following that, Union Carbide developed Innovative Membrane Systems for gas separation. In the last 30 years, membrane separation processes have been widely adopted in other industries, such as, waste water treatment, biomedical separation and dialysis, electrodyalysis, and dehumidification.

1.2.2 Theory of Membrane Separation

1.2.2.1 Fundamental Parameters: As noted above, transport through a nonporous membrane is typically described by a solution-diffusion model. The solution of low molecular weight permeants into the membrane is similar to permeant's sorption into liquid. Solubility indicates the amount of analytes that can be taken up by membrane. It is an equilibrium process that is affected by polymer-permeant interactions. The sorption of low molecular weight permeants in rubbery membrane is defined as [44]:

$$S = C/f = C/(\gamma_p\, p) \approx C/p \qquad (1\text{-}4)$$

where S is solubility, f is gas fugacity, γ_p is activity and p is partial pressure. At sufficiently low permeant concentration, analytes behave ideally (f = p, γ_p = 1). In these cases, the absorption can be described by Henry's law [43]:

$$C = S \times p = k_D \times p \qquad (1\text{-}5)$$

where k_d is Henry's law constant.

Conditions such as high concentration, interaction of permeant and polymer, multilayer adsorption where deviation from Henry's law occurs are seldom of interest for analytical membrane separations.

The average diffusivity measures the mobility of the permeant in the membrane matrix. It is kinetic in nature and is largely determined by polymer-permeant dynamics. The diffusional energy is required principally for the rotation and translation of the polymer segments. Several models for describing the relationship between D and activation energy (E) have been proposed [48]. Brandt's model is one of them [50]:

$$D = k \nu_T \lambda^2 \sum_g [\rho_g \frac{(E_z/RT)^{g-1}}{(g-1)!}] \exp(-\frac{E_z}{RT}) \quad (1\text{-}6)$$

where k is a geometric factor, ν_T is the thermal frequency of vibration of the diffusing molecules, λ is mean jump length, E_z is the total energy, g is the number of backbone chain bonds in the bent segments, and $\rho_g = 1/2^g$.

The membrane separation is based on the different permeability of solutes which is controlled by the diffusivity and solubility. In other words, the membrane's intrinsic selectivity is a ratio of permeability which is comprised of the two parameters:

$$\alpha_{i/j} = P_i/P_j \quad (1\text{-}7)$$

and

$$P = S \times D \quad (1\text{-}8)$$

thus

$$\alpha_{i/j} = (S_i/S_j)\,(D_i/D_j) \quad (1\text{-}9)$$

where $\alpha_{i/j}$ is selectivity of molecule i and j, P is permeability.

1.2.2.2 Effect of Temperature: Temperature can have a large effect on the permeability of small permeants in polymeric membranes. The temperature dependence of solubility follows an Arrhenius-type relationship [48]:

$$S = S_0 \exp. (-\Delta E_s / R_c T) \quad (1\text{-}10)$$

and

$$\Delta E_s \cong V_1(\delta_1 - \delta_2)^2 V_2^2 \quad (1\text{-}11)$$

S_0 is solubility at standard condition, ΔE_s is heat of solution, R_c is gas constant, T is temperature, V_1 and V_2 are volume fraction at state 1 and state 2 respectively, δ_1 and δ_2 are cohesive energy density at state 1 and 2 respectively. Therefore, for permanent gases, the heat of solution is small and positive, and solubility increases with temperature. For other gases and vapors the heat of solution is negative, the solubility decreases with increasing temperature.

The diffusivity exhibits a similar behavior [43]:

$$D = D_0 \exp. (-E_d / R_c T) \quad (1\text{-}12)$$

the E_d is apparent activation energy and always positive thus diffusivity increases with temperature.

Therefore the variation of permeability with temperature depends on the magnitude of the solubility and diffusivity change. For most VOCs in water, in 25° C to 50° C range, diffusivity change dominates permeability which increases with increasing temperature.

1.2.2.3 Concentration Dependence: Virtually in every case where significant interaction occurs between permeant and membrane, both diffusivity and solubility vary with concentration according to [48]:

$$D = D_0 \exp. (\beta_d C) \quad (1\text{-}13)$$

and

$$S = S_0 \exp. (\beta s C) \quad (1\text{-}14)$$

where β_d and βs are constants for the molecule. However, no satisfactory relationship between β_d or β_s and interaction force is available. In analytical application at trace levels, the exponential term can be viewed as 1 and it is safe to assume that concentration doesn't affect permeability.

1.2.2.4 Diffusion Flux: As noted above, steady state diffusion is governed by Fick's first law:

$$F_{ss} = -A\ D\ (dC/dx) = A\ D\ C_0/l \quad (1\text{-}15)$$

where F_{ss} is permeation rate at steady state. A is membrane active surface area. C_0 is sample concentration on membrane.

Non-steady-state diffusion is governed by Fick's second law:

$$\delta C(x, t)/\delta t = -D(\delta^2 C(x, t)/(\delta x^2) \quad (1\text{-}16)$$

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

The mathematical solution for diffusion of one step change of concentration is [15]:

$$F_t = F_{ss} \{1+[2\Sigma(-1)^n \exp. (-(n\pi/l)^2 Dt)]\} \quad (1\text{-}17)$$

For 2 step concentration change, the boundary conditions are as follows:

when x = 0, at t = 0, concentration C changes from 0 to C_0

at t = 0 to Δt, $C = C_0$

at t = Δt, C change from C_0 to 0

at t > Δt, C = 0

where C_0 is the sample concentration on the membrane surface, and Δt is the duration of sample pulse. The mathematical solution for above boundary conditions is [44, 46]:

$$F(t) = F_{ss}[f(u)-\gamma f(u-(D(\Delta t)/l^2))] \quad (1\text{-}18)$$

where F(t) is the permeation rate at time t, D is diffusivity, F_{ss} is the permeation at steady state and equals to DC_0A/l, A is the membrane surface area, l is membrane thickness, $u = Dt/l^2$, and $C_0 = KC_w$, where C_w is the sample concentration in water, K is partition coefficient between membrane and water; $\gamma = 0$, for $u < D(\Delta t)/l^2$, and represents the ascending part of the curve; $\gamma = 1$, for $u > D(\Delta t)/l^2$, represents the descending part of curve.

$$f(u) = 1+2\sum_{n=1}^{\infty} (-1)^n \exp.\{-n^2(\pi)^2 u\} \quad (1\text{-}19)$$

therefore the permeation rate can be derived as:

$$F = F_{ss}\left\{\frac{2}{\sqrt{(Dt/l^2)\pi}}\sum_{n=1}^{\infty} \exp\left\{-\frac{(n-0.5)}{Dt/l^2}\right\}\right\} \quad \text{when } t < \Delta t \quad (1\text{-}20)$$

$$F = F_{ss}\left\{\frac{2}{\sqrt{(Dt/l^2)\pi}}\sum_{n=1}^{\infty} \exp\left\{-\frac{(n-0.5)}{Dt/l^2}\right\} - \frac{2}{\sqrt{(Dt/l^2 - D\Delta t/l^2))\pi}}\sum_{n=1}^{\infty} \exp\left\{-\frac{(n-0.5)}{Dt/l^2 - D\Delta t/l^2}\right\}\right\}$$

when $t > \Delta t$ (1-21)

1.2.2.5 Pervaporation: Pervaporation is the terminology used for membrane separation of solutes from a liquid to a gas phase. The first major research effort in pervaporation was undertaken in the late 50's by Binning and coworkers [51, 52]. Since then, more studies have focused on separation of anhydrous organic mixtures commonly encountered in petrochemical processing. The commercial pervaporation process was successful implemented in late 80's using composite membrane.

In the pervaporation process, in addition to the permeability of the analytes in the membrane, the interaction of analytes with water plays an important role. Polar compounds, especially the compounds which can form hydrogen bonds with water have low extraction efficiency. The low enrichment factors and high detection limits have been reported and are listed in Table 1-1 [23, 53].

Selectivity

In a pervaporation process, the selectivity is a product of the membrane's intrinsic separation factor and the relative volatility of permeant [43]:

$$\alpha_{pervap} = \alpha_{evap}\alpha_{mem} \tag{1-22}$$

where α_{pervap}, α_{evap}, α_{mem} are selectivity of pervaporation, evaporation and membrane respectively. This approach is demonstrated Fig. 1.3a and 1.3b. A typical vapor-liquid equilibrium is defined in the Fig 1.3a for a two-phase gas-liquid system. As it shows, separation is determined by volatility difference with resulting composition of the two phases defined in the vapor-liquid equilibrium diagram. When a pervaporation membrane is imposed, the selectivity is demonstrated in Fig. 1.3b. Intrinsic membrane selectivity greater than 1 enhance the selectivity, whereas those smaller than 1 decrease separation.

Table 1.1 Enrichment factor and detection limits for some VOCs using silicone membrane extraction

Compounds	Detection limits (ppb)	Enrichment factor
Toluene[a]	0.042	65.1
Trichloroethane[a]	0.28	61.8
Acetone[a]	61.1	7.5
Ethanol[a]	212	4.1
Benzene[b]	NA	11,000
Styrene[b]	NA	13,000
Ethanol[b]	NA	7
Acetone[b]	NA	50
Acetic Acid[b]	NA	70
Vinyl chloride[b]	NA	9,000

a. From reference 23. b. From reference 53.

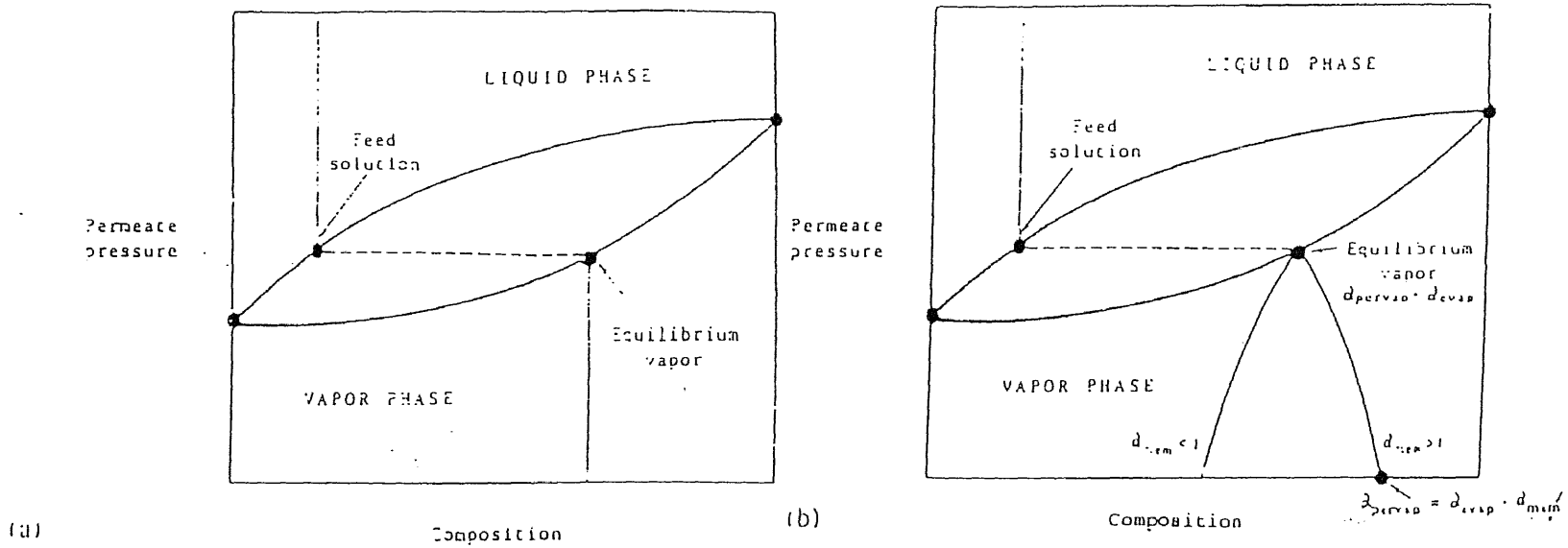


Fig. 1.3a and 1.3b Conventional versus membrane-imposed vapor-liquid equilibria.
(from reference 43)

Boundary Layer

In a pervaporation process, flowing liquid phase containing VOCs contacts one side of membrane, and a stagnant layer is formed at the membrane surface due to the poor mixing of the liquid phase with the membrane surface. This is shown in Fig. 1.4. The degree of mixing is determined by the physical properties of the liquid and the flow conditions that can be represented by the Reynolds number (Re) [54]:

$$Re = d\rho v/\mu \tag{1-23}$$

where d is fiber diameter, ρ is density, v is velocity and μ is viscosity. The higher the Re number, the better the mixing is. For a thorough mixing, a Re in the range of 20,000 - 30,000 is needed to eliminate the boundary layer. However due to the limitation in allowable flow rate, only a very small Re number can be obtained thus a thick boundary layer is formed which impedes mass transfer across the membrane.

In general, the mass transfer resistances in series are in (1) liquid phase boundary layer (I_b), (2) membrane matrix (I_m) and (3) between membrane surface and gas phase (I_v). Because of the good mass transfer property of gas and the high stripping rate of gas at the outer side of membrane, the I_3 is negligible. The extraction rate of organic molecules from a gas sample has been reported to be much faster compared to that from an aqueous sample [33].

The mass transfer rates in both phases can be expressed as the chemical potential gradient:

$$J_i = - k\, d\mu/dx \tag{1-24}$$

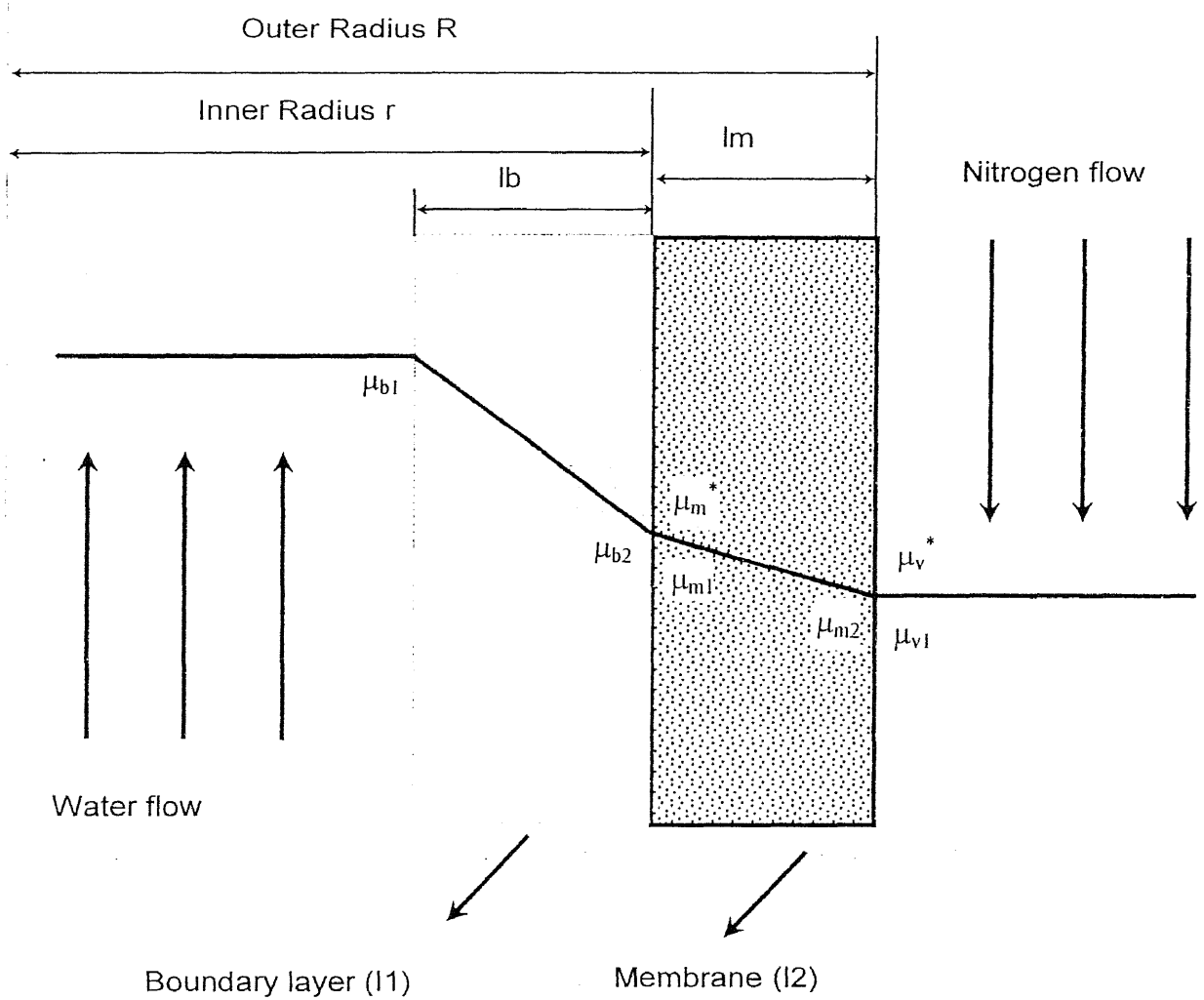


Fig. 1.4 Pervaporation diagram showing boundary layer resistance

where k is the proportional coefficient based on chemical potential gradient and μ is chemical potential.

By assuming the linear distribution of the chemical gradient in both media, the following can be obtained:

In membrane matrix: $J_i = -k_m/l_m\ (\mu_{m2}-\mu_{m1})$ (1-25)

In boundary layer: $J_i = -K_b(\mu_{b2}-\mu_{b1})$ (1-26)

where the k_m is proportional coefficient in membrane and K_b is mass transfer coefficient in boundary layer based on chemical potential. l_m is the thickness of membrane. The subscript m and b stand for membrane and boundary layer respectively and 1 and 2 stand for incoming and outgoing in that phase respectively.

The overall mass transfer rate can be illustrated as:

$$J_i = k\ (\mu_{v1}-\mu_{b1})/l_m \quad (1\text{-}27)$$

where the k is propotional coefficient for the overall process. Subscript v stands for vapor phase.

When the equilibrium conditions are applied to the interfaces of liquid layer and membrane, and membrane and vapor phase:

$$\mu_{m1} = \mu_{b2} = \mu_m^* \quad \mu_{m2} = \mu_{v1} = \mu_v^* \quad (1\text{-}28)$$

The * stands for equilibrium state. Then the overall resistance is derived as [55]:

$$l_m/k = 1/K_b + l_m/k_m \quad (1\text{-}29)$$

or $$(I) = (I_b) + (I_m) \quad (1\text{-}30)$$

I is mass transfer resistance. The equation (1-29) or (1-30) shows the mass transfer resistance is the sum of the resistance in both of water boundary layer and membrane matrix.

The boundary layer acts as a barrier to mass transfer from water to the membrane. The importance of the boundary layer depends on the nature of analytes, membrane thickness and Re. For membrane separation, the primary mass transfer resistance is often assumed in the membrane. However for the solutes having large diffusivity and selectivity and when thin membranes are used, the mass transfer resistance at the liquid boundary layer contributes significantly to the overall transport resistance, and often becomes the primary resistance. Psaume [56] found that for trichloroethylene when Re below 60, the membrane resistance was relatively unimportant and the primary mass transfer resistance was in the boundary layer. Reghunath [55] demonstrated that in a gently agitated system, almost the entire resistance lay in the liquid boundary layer. However, at high stirring speed, both resistance in membrane and in boundary layer were found to be important. Resistance in the membrane primarily determines mass transfer when a thick membrane is used and become insignificant when membrane thickness is reduced. Tsai [57] reported that resistance in aqueous layer is important only for thin membrane extraction process, especially when thickness is less than 0.005 cm. Based on theoretical calculation, the membrane flux doubled when liquid resistance was reduced 10 times. Raghunath's [55] results showed when the membrane thickness reduced to 0.04 cm, the liquid phase resistance accounted for 90 % of total mass transfer resistance for toluene using polyester-block-polyamide membrane.

Permeation of analytes having high solubility and diffusivity in membrane is limited by the aqueous phase resistance. It was reported [55] that solutes having high Henry's law constants, which is true for most volatile compounds, were likely to have their permeation through hydrophobic membranes determined primarily by the boundary layer resistance. While the higher Henry's constant of an analyte usually results in its higher membrane selectivity. The VOCs have large solubility in the membrane thus a concentration depletion zone will be formed, which largely impedes the mass transfer across membrane.

Extraction Efficiency

By studying the influence of flow rate on membrane response, Psaume [56] observed the pervaporation of VOCs was limited by the solute depleted boundary layer at the membrane-liquid interface. Extraction efficiency (EE) was then derived based on film theory.

The solute flux through the membrane wall is given as following based on mass balance on the membrane system:

$$J_i = ((Q_e \rho)/A) (w'_{i,e} - w'_{i,s}) \quad (1\text{-}31)$$

where the Q_e is the water flow rate, ρ is density, A is the internal surface area, $w'_{i,e}$ and $w'_{i,s}$ are weight fraction of analyte at inlet and outlet respectively.

A concentration depletion zone is formed due to the presence of a boundary layer as shown in Fig. 1.5. Several assumptions were made in order to derive the mass balance. The assumptions included steady state, a stagnant polarization layer and negligible connective flow. Then the flux was derived as:

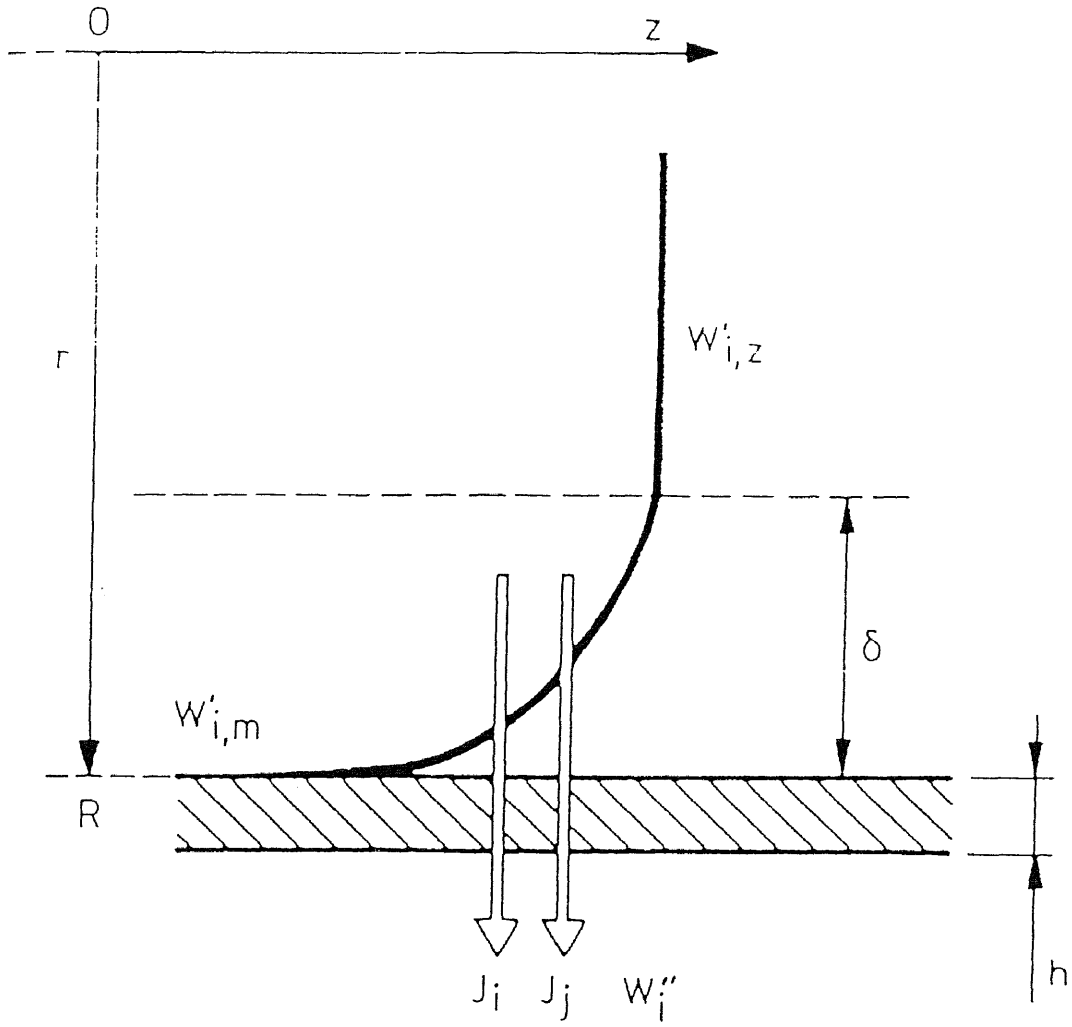


Fig. 1.5 Schematic representation of the polarization phenomenon in the neighborhood of a pervaporation membrane.

$$J_{r,z}\, dr = D_i\, \rho dw'_{i,z} \tag{1-32}$$

Integration across the boundary layer gives

$$J_{r,z} = K_i,\ \rho\ (w'_{i,z} - w'_{i,z,m}) \tag{1-33}$$

where the mass transfer coefficient $K_i = D_i / \sigma$ and the $w'_{i,z}$ and $w'_{i,z,m}$ are the concentration at both sides of the boundary layer. The assumption of the $w'_{i,z,m}$ of zero gives

$$J_{r,z} = K_i,\ \rho\ w'_{i,z} \tag{1-34}$$

Local mass balance gives $Q'_e\ \rho dw'_{i,z} = 2\pi R J_{ri,z} dz$ (1-35)

where R is radius of the fiber and the combination of equation (1-34) and (1-35) gives:

$$\ln\ (\ w'_{i,e}/w'_{i,\,s}) = K_i\ A/Q'_e \tag{1-36}$$

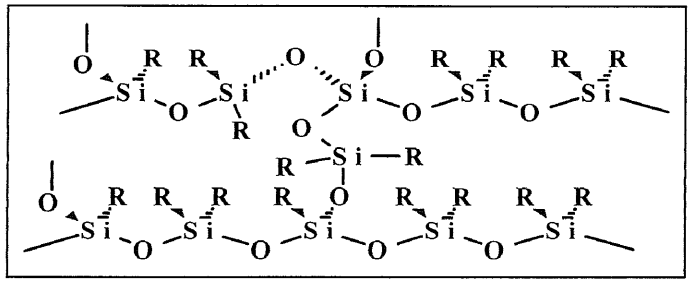
The K_i was estimated using the Leveque correction [58]:

$$(K_i\ 2R/D_i) = 1.62\ (d^2 \nu / L D_i) \tag{1-37}$$

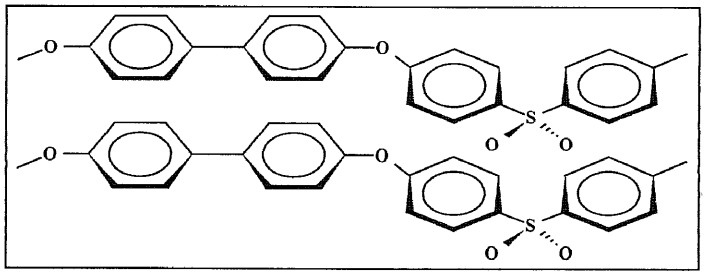
ν is velocity and L is membrane length.

The extraction efficiency was thus derived as:

$$EE = (w'_{i,e} - w'_{i,s})/w'_{i,e} = 1 - \exp.\left(-6.48\ \frac{D_a^{\frac{2}{3}}\ L^{\frac{2}{3}}}{d^{\frac{1}{3}}\ \nu^{\frac{2}{3}}}\right) \tag{1-38}$$



Polysiloxanes



Polymers with aromatic backbones

Fig. 1.6 Two major categories of polymeric membrane

1.3 Membrane Material

The polymeric membrane can be made from different materials, such as, polycarbonates, polyamides, polysiloxane, etc.. Two common classes are aromatic backbones and polysiloxane as shown in Fig. 1.6. The polymer structure affects the solute diffusivity and solubility. The polymers with aromatic backbones have less free volume and the conjugated π bonds restrict the polymer segment rotation. These membranes have small diffusivities. They are mostly used in gas separation. The polysiloxane membrane have large free volume and the σ bonds among the atoms enable the free rotation of atoms thus the diffusivity is large for most molecules.

CHAPTER 2

RESEARCH OBJECTIVES

The objectives of the research were six fold:

- To develop the system of pulse injection membrane extraction (PIME) based on non-steady state pervaporation for continuous monitoring of VOCs in water stream;
- To investigate the analytical performance of PIME;
- To investigate the reduction of boundary layer and membrane response characteristics thus enhance the analytical performance of the PIME system;
- To investigate alternative membrane module design to increase membrane extraction efficiency;
- To use PIME for on-line monitoring and compare with OLMEM which was based on steady state permeation;
- To explore membrane extraction on on-line monitoring of SVOCs in water using HPLC analysis.

CHAPTER 3

NON-STEADY STATE, PULSE INTRODUCTION MEMBRANE EXTRACTION OF VOLATILE ORGANIC COMPOUNDS FROM AQUEOUS MATRIX

3.1 Introduction

Analytical methods for the measurement of volatile organic compounds (VOCs) in water include purge and trap, head space analysis, solid phase microextraction and solid phase extraction. All these techniques involve a separation/extraction step for the isolation of analytes from the aqueous matrix prior to GC or GC/MS analysis. Although these methods have some excellent merits, none are designed for continuous real time extraction, which is desirable for the development of automated, on-line instrumentation.

Use of polymeric membrane for the extraction of organic compounds from an aqueous matrix have received much attention [12-39], where the analysis can be carried out on-line using a GC, or a mass spectrometer (MS) as the detection device. A variety of porous (involving pore flow) and nonporous membrane materials have been evaluated [23, 36-39]. A high extraction selectivity and permeation rate can be achieved for organic analytes by choosing the appropriate membrane and optimum operating condition. Polydimethyl siloxane silicone membranes which provide high diffusivity for different molecules due to the large free volume inside the polymer matrix have been most widely used. Organic compounds have higher solubility in silicone than inorganic molecules such as water, therefore high selectivity is achieved by the membrane. In such nonporous structures, organic molecules first dissolve in the membrane and then diffuse under a concentration gradient. The rate of diffusion depends upon the size and the chemical

nature of the molecule. Steady state permeation flux is described by Fick's first law:

$$J = -D(\delta c/\delta x) \quad (3\text{-}1)$$

where the D is the diffusivity and $\delta c/\delta x$ is the concentration gradient.

Analytical application of membrane sampling was first published by Hoch and Kok [12] in 1963. Since then different approaches have been reported, the majority of them focusing on membrane interface for mass spectrometry (MIMS) [13-22]. In MIMS, the sample is contacted on one side of the membrane and the other side is directly exposed to the ion source of a mass spectrometer. Thus the diffused organics are directly introduced into the mass spectrometer. Interface of membrane extraction with GC has also been studied, where sorbent or cryogenic traps have been used for sample concentration prior to GC analysis [23, 35-39]. In both GC and MS applications, the advantage of membrane extraction is that the sample can be extracted continuously by the membrane for automated on-line analysis [20, 21, 23, 36-39]. These techniques have demonstrated high selectivity, large linear dynamic range, sensitive response and the capability of real time measurement [23].

In most reported membrane applications, the samples were continuously introduced into a membrane module, and the permeates were removed continuously. In this approach, measurements are made after permeation reaches steady state. It can take a fairly long time to reach steady state since the diffusion through the membrane and the boundary layer on the membrane surface are slow processes. When the sample concentration changes, the system does not instantly reach steady state, but slowly reaches equilibrium over a period of time. Any measurement during this transition period

does not truly reflect the analyte concentration. The time taken to reach equilibrium is referred to as lag time and results in slow instrument response. The lag time is much longer in a GC interface than in a MIMS where the vacuum provides a large partial pressure gradient for rapid mass transfer. In a GC, a positive pressure needs to be maintained at the permeate side to facilitate the flow of carrier gas. Consequently, the lag time is the limiting factor in on-line membrane extraction coupled with gas chromatography. In addition, continuous sample introduction onto membrane is not suitable for analyzing discrete, individual samples of small volume. A relatively large volume needs to flow through the membrane before steady state is reached. Not only does it take a long time, but it is functionally more complex and is not easily amenable to automation.

Recently, flow injection type membrane introduction techniques have been reported for MIMS [40, 57, 59, 60]. In this study, an alternate, non-steady state, pulse introduction membrane extraction method which is suitable for the analysis of small volume individual samples, as well as for continuous on-line monitoring was explored [34, 39]. The elimination of the steady state requirement eliminates the lag time associated with equilibration leading to a faster instrumentation response. Instead of continuous sample introduction, the sample is injected as a pulse, and sample volumes as small as a few microliters can be used. This approach can also be used in continuous monitoring applications by introducing a series of pulses from a flowing aqueous stream. Each injection truly represents the sample concentration when carryover from the previous

injection is eliminated. A non-steady state model is presented here to describe this system.

3.2 Experimental Section

The pulse introduction technique which can be used for any membrane extraction application is presented here for a GC interface. The schematic diagram of the experimental system is shown in Fig. 3.1. The aqueous sample is to be introduced as a pulse into the membrane. An eluent stream is used for transporting the sample to the membrane module. The analytes that permeate through are stripped by a countercurrent gas stream. The GC interface is accomplished using a micro-sorbent trap (referred to as a microtrap) which concentrates the organics before injecting them into the GC.

The sample size used was anywhere from 100 microliter to 10 ml depending upon the analysis requirements. The injection was accomplished by a pneumatically controlled 6 port valve (Valco Instruments Co. Inc., Houston, TX). The eluent was HPLC grade high purity water. A HPLC pump was used as the eluent pump. Typical operation consisted of injecting a sample into the eluent stream. A few minutes were allowed for the permeation to complete. The permeated analytes were pneumatically transported to the microtrap by a flow of nitrogen. The analytes were concentrated and then desorbed into the GC for analysis. During continuous on-line monitoring [39], the aqueous stream continuously flowed through the sample loop of the valve, and periodically injections were made into the membrane module. Corresponding to each injection, a chromatogram was obtained.

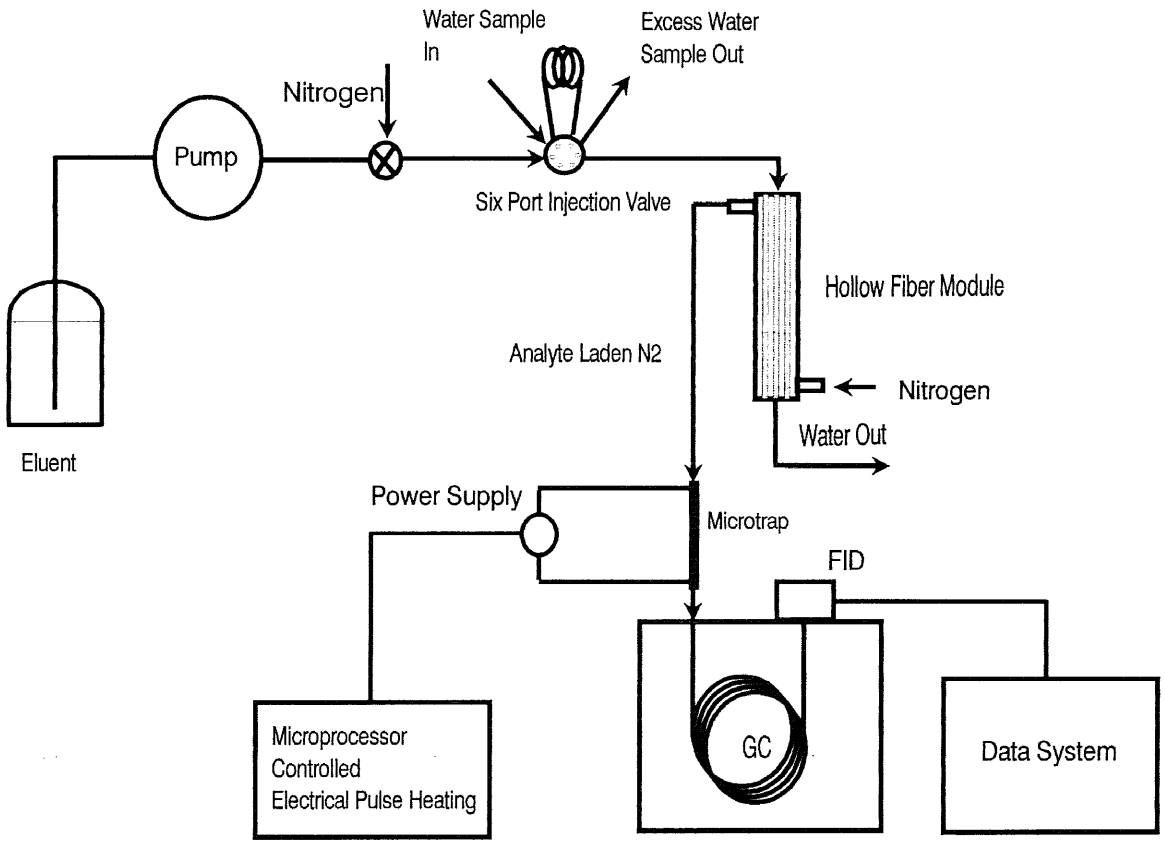


Fig. 3.1 Schematic diagram of the pulse introduction membrane extraction GC system.

The membrane contractor was a standard shell-and -tube design. The membrane module was made of 12, 8.5 cm long composite membranes of dimension 0.260 mm OD×0.206 mm ID (Applied membrane Technology, Minnetonka, MN). The composite structure comprised of 1 μm thick homogenous siloxane film as the active layer supported on a layer of microporous polypropylene. The membrane module was constructed by inserting 12 fibers into a 1/4'' OD tubing. At each end of the tubing, a "T" unit (Components & Controls Inc., Carlstadt, NJ) was used to connect the inlet and the outlet for both the nitrogen and the aqueous stream. The connection points of membrane and "T" units were sealed with epoxy to separate nitrogen from the aqueous phase.

The microtrap was a small diameter silica lined tube packed with a small amount of adsorbent. It had low thermal mass and could be heated and cooled rapidly. When nitrogen carrying organics flowed through the microtrap, the analytes were trapped and concentrated. An electrical current heated the microtrap resistibly and the desorption pulse served as an injection for GC analysis. The details of the microtrap and its working principle have been studied in our research group [61, 62]. A 15 cm long, 0.53 mm ID silica lined tubing (Restek Corp., Bellefonte, PA) packed with Carbotrap C (Supelco, Supelco Park, PA) served as the microtrap. A 7-10 amp current was supplied from a 40 V AC power source to heat the microtrap. The duration and the interval between the heat pulses were controlled using a microprocessor based controller fabricated in-house. A HP 5890 series II GC (Hewlett Packard Company, Avondale, PA) equipped with a Flame Ion Detector and a 30 m long , 0.53 mm OD ×0.21 mm ID SE-54 megabore column with

2.4 μm thick stationary phase was used for GC separation. HP Chemstation 3365 software was used for data acquisition and analysis.

3.3 Results and Discussion

3.3.1 Theory of Non-steady State Pulse Introduction

In this approach, the membrane receives a sample pulse of certain duration. The ideal pulse input is an impulse function as shown in Fig. 3.2. Experimentally, this was achieved by injecting the sample onto an eluent stream that transported it to the membrane. This was similar to flow injection type of introduction, except that, after the sample permeates through the membrane a flow of nitrogen could be used to purge/clean the membrane. There was axial mixing between the eluent and the sample at the front and back end of the pulse. Consequently, the ideal pulse was distorted and underwent band broadening. The input concentration profile was experimentally determined and is also shown in Fig. 3.2. This was obtained injecting a 2 ml sample containing toluene and monitoring its exit concentration using a UV detector connected at the outlet of the membrane module. The input profile showed some tailing that increased the duration of the pulse. The permeation profile is also shown in Fig. 3.2. This was measured by monitoring the permeate concentration every 30 seconds by making microtrap injection at that interval. Slow permeation through the boundary layer, and the membrane further broadened the response profile resulting in a skewed bell shaped curve with sample tailing. From Fig. 3.2 it is seen that a 2.5 minutes impulse broadened to 5 minutes due to the axial mixing, and the permeation profile further broadened to 13 minutes due to slow permeation.

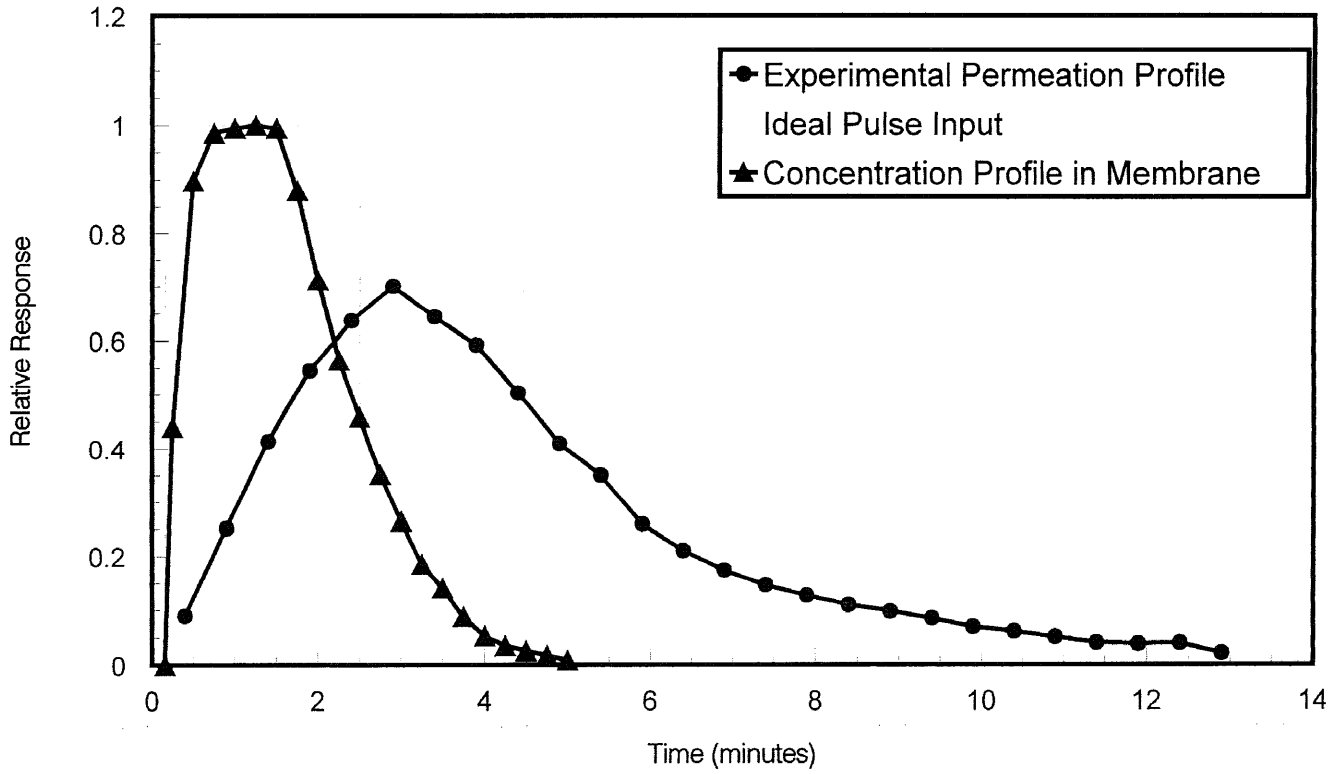


Fig. 3.2 Input and permeation profiles in pulse introduction membrane extraction. Membrane response was obtained using 2 ml 31.5 ppb toluene solution at flow rate of 1 ml/min. Input profile was obtained using 2 ml 4.4 ppm toluene solution.

For the pulse input described above, membrane permeation never reached equilibrium. Non-steady state permeation can be described by Fick's second law as:

$$\delta C(x, t)/\delta t = -D(\delta^2 C(x, t)/(\delta x^2) \quad (3\text{-}2)$$

where C(x, t) is the concentration at position x at time t. The boundary conditions are as follows:

When x = 0, at t = 0, concentration C changes from 0 to C_0

at t = 0 to Δt, $C = C_0$

at t = Δt, C change from C_0 to 0

at t > Δt, C = 0

where C_0 is the sample concentration on the membrane surface, and Δt is duration of sample pulse. The mathematical solution of equation (3-2) for the above boundary conditions is [44, 46]:

$$F(t) = F_{ss}[f(u)-\gamma f(u-(D(\Delta t)/l^2))] \quad (3\text{-}3)$$

where F is the permeation rate at time t, D is diffusivity, F_{ss} is the permeation at steady state and equals DC_0A/l, A is the membrane surface area, l is membrane thickness, $u = Dt/l^2$, and $C_0 = KC_w$, where C_w is the sample concentration in water, K is partition coefficient between membrane and water; $\gamma = 0$, for $u < D(\Delta t)/l^2$, and represents the ascending part of the curve; $\gamma = 1$, for $u > D(\Delta t)/l^2$, represents the descending part of curve.

$$f(u) = 1+2\sum_{n=1}^{\infty} (-1)^n \exp.\{-n^2(\pi)^2 u\} \quad (3\text{-}4)$$

Reduced permeation rate F_r is defined as $F(t)/F_{ss}$ thus the equation (3-4) is reduced to

$$F_r = 1+2 \sum_{n=1}^{\infty} (-1)^n \exp. \{ -n^2(\pi)^2 Dt/l^2 \} \quad \text{when } t < \Delta t \tag{3-5}$$

$$F_r = 2 \sum_{n=1}^{\infty} (-1)^n \exp. \{ -n^2(\pi)^2 Dt/l^2 \} - 2 \sum_{n=1}^{\infty} (-1)^n \exp. \{ -n^2(\pi)^2 D(t-\Delta t)/l^2 \}$$

$$\text{when } t > \Delta t \tag{3-6}$$

It's seen that the reduced permeation rate is a function of diffusivity, pulse duration (Δt) and membrane thickness. It has been reported that a thick membrane reduces permeation and prolongs lag time [38], and is consistent with the above equation.

The diffusion coefficient is an important parameter for application of the above equation. Most reported diffusion coefficients in the literature [63] have been obtained by measuring the permeation of pure vapors across a membrane. These high concentrations tend to swell the polymeric membranes which enhances the diffusion. Consequently, diffusion coefficients tend to be much lower for trace concentration samples commonly encountered in analytical application [64]. Furthermore, in a pervaporation process where analyte diffuses from the liquid phase and across the membrane, an aqueous boundary layer is formed on the membrane surface. The organics usually have high solubility in the membrane material resulting in a concentration depletion zone. This boundary layer impedes mass transfer from water to the membrane. It's considered to be the major contributor to mass transfer resistance in thin membrane extraction processes [55, 56].

In order to include the boundary layer resistance and calculate an overall diffusion coefficient for this system, the following approach was taken. From equation (3-5) and (3-6), it can be seen that the maximum value in the reduced permeation profile is a function of Δt. When applied to the maximum value, equation (3-3) can be rewritten as:

$$F_{max} = F_{ss} \{2 \sum_{n=1}^{\infty} (-1)^n \exp. \{ -n^2(\pi)^2 D t_{max}/l^2\} - 2 \sum_{n=1}^{\infty} (-1)^n \exp. \{ -n^2(\pi)^2 D(t_{max}-\Delta t)/l^2\}\} \quad (3\text{-}7)$$

where F_{max} is the maximum value in the response profile, and t_{max} is the corresponding time when it occurs. These two parameters were determined experimentally. It was observed that the first two terms in the above equation accounted for more than 99% of the total response. By changing the sample size while keeping other conditions the same, Δt was varied. Corresponding to different Δt, different t_{max} and F_{max} were obtained. The overall diffusion coefficient was computed from equation (3-7) using two sets of measurements at two different sample volumes. Overall diffusion coefficient for benzene was found to be 9.04×10^{-9} cm^2/sec. Such a low value indicates the presence of a well formed boundary layer which significantly reduces the permeation rate [55, 56].

The permeation profile was computed according to equation (3-5) and (3-6) using the overall diffusion coefficient and the first 10 terms in the series expansion. The computed and the experimental results for benzene permeation presented in Fig. 3.3 show reasonably good agreement. The observed differences are attributed to the distortion of input profile due to axial mixing.

3.3.2 Effect of Process Parameters

The sample introduction rate affects the system response by changing Δt in equation (3-5) and (3-6). According to equation (3-3), the maximum response in the response profile increases with Δt till it reaches F_{ss}. A slower flow rate represents a longer Δt, the

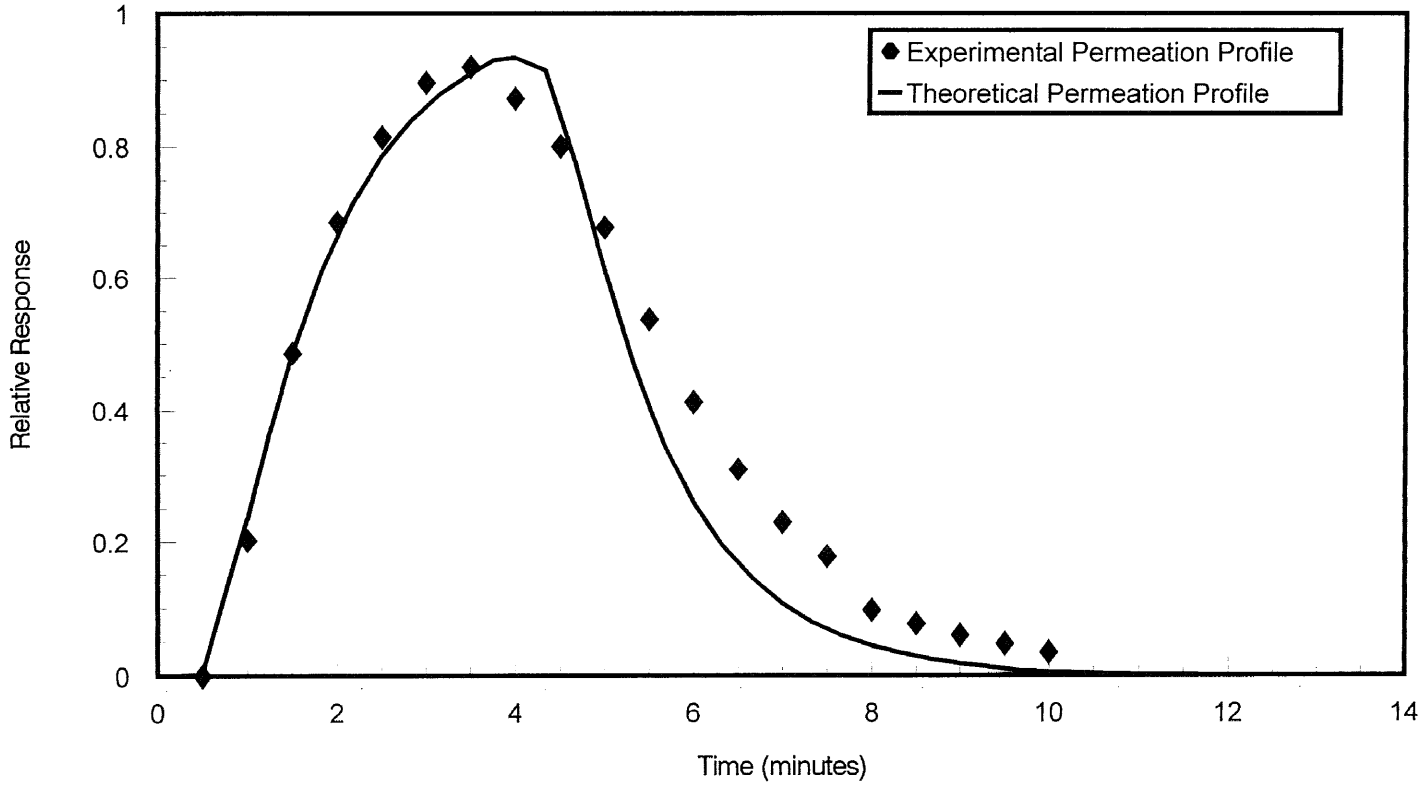


Fig. 3.3 Experimental and computed permeation profiles for benzene. A 3 ml 50 ppb benzene sample at eluent flow rate of 0.8 ml/min was used in this analysis.

corresponding profile takes a longer time to reach its maximum, and a higher maximum response can be obtained. A series of sample input, and permeation profiles at different flow rates are shown in Fig. 3.4. It was seen that, the maximum response and the time at which it occurred both increased with decreased flow rate or increased Δt.

A faster flow rate also increased mixing of sample with the eluent resulting in a more dispersed sample introduction. The dispersed volume is defined as the total volume into which the analytes are dispersed, and is calculated as the product of flow rate and the duration of input profile in Fig. 3.4. For example, for a 2 ml injection at eluent flow rates of 1 and 4 ml/min (corresponding to Δt of 2 and 0.5 minutes), the dispersed volume were found to be 9 and 11 ml respectively. A more dispersed sample introduction at higher flow rates reduces the analyte concentration on the membrane surface and effectively the concentration gradient for mass transfer. In order to reduce sample dispersions, low instrument void volume and low flow rates are preferred.

The lag time in pulse introduction is proportional to the duration of the permeation profile, and is defined as $t_{10\text{-}10\%}$, which is the time interval between the points corresponding to 10% of maximum response in the ascending and descending parts in the permeation profile. Faster the flow rates, shorter are the Δt, and lag time. Fig. 3.5 is a plot of lag time as a function of Δt. As the flow rate increased, residence time decreased along with lag time. Lower flow rates provided higher response, but increased lag time. One may notice that being a larger molecule, ethylbenzene exhibited longer lag time due to its lower diffusion coefficient.

When flow rate was high, the residence time in the membrane module was low.

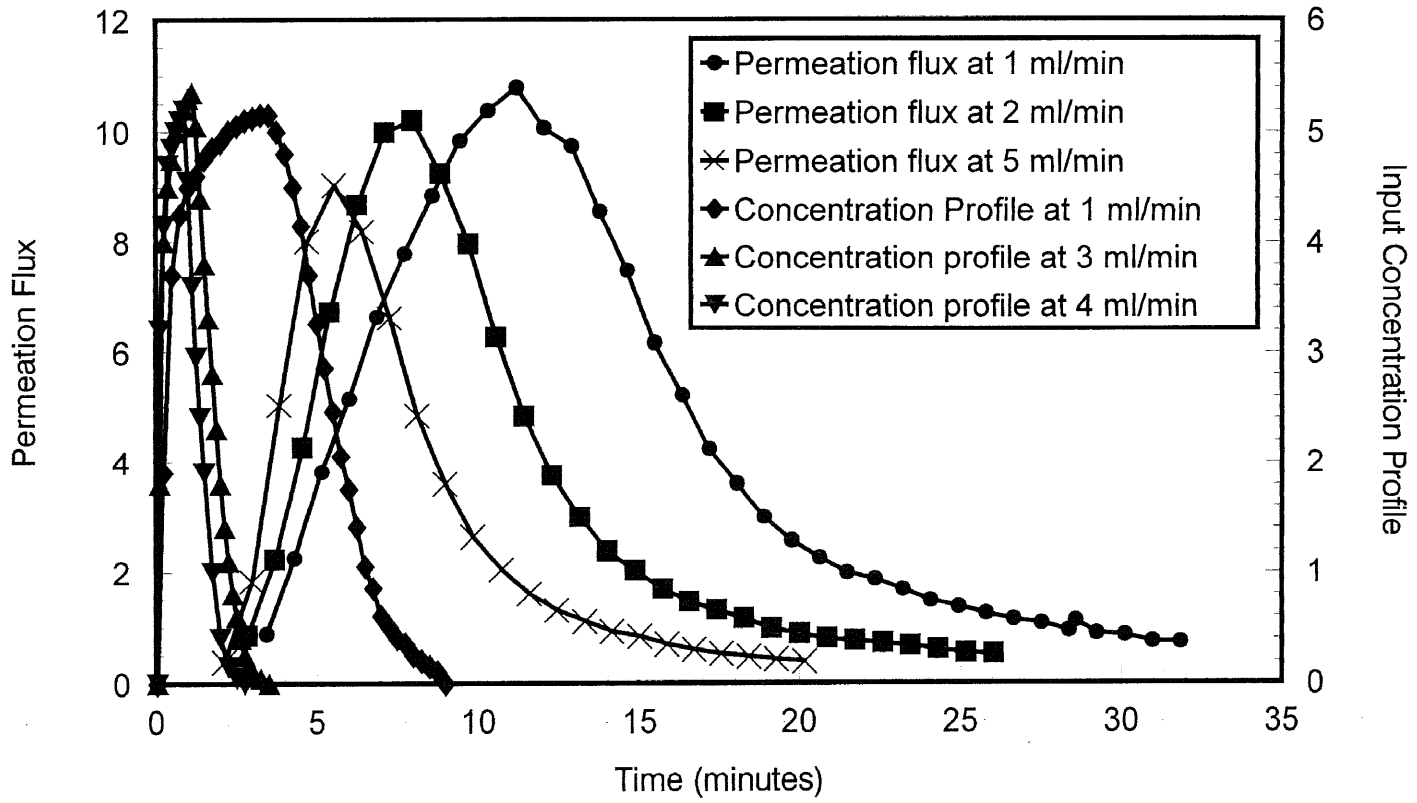


Fig. 3.4 Permeation and input concentration profiles at different flow rates. Permeation profiles were obtained using a 8 ml sample containing 75 ppb toluene. Input profiles were obtained using 5 ml sample containing 4.4 ppm toluene.

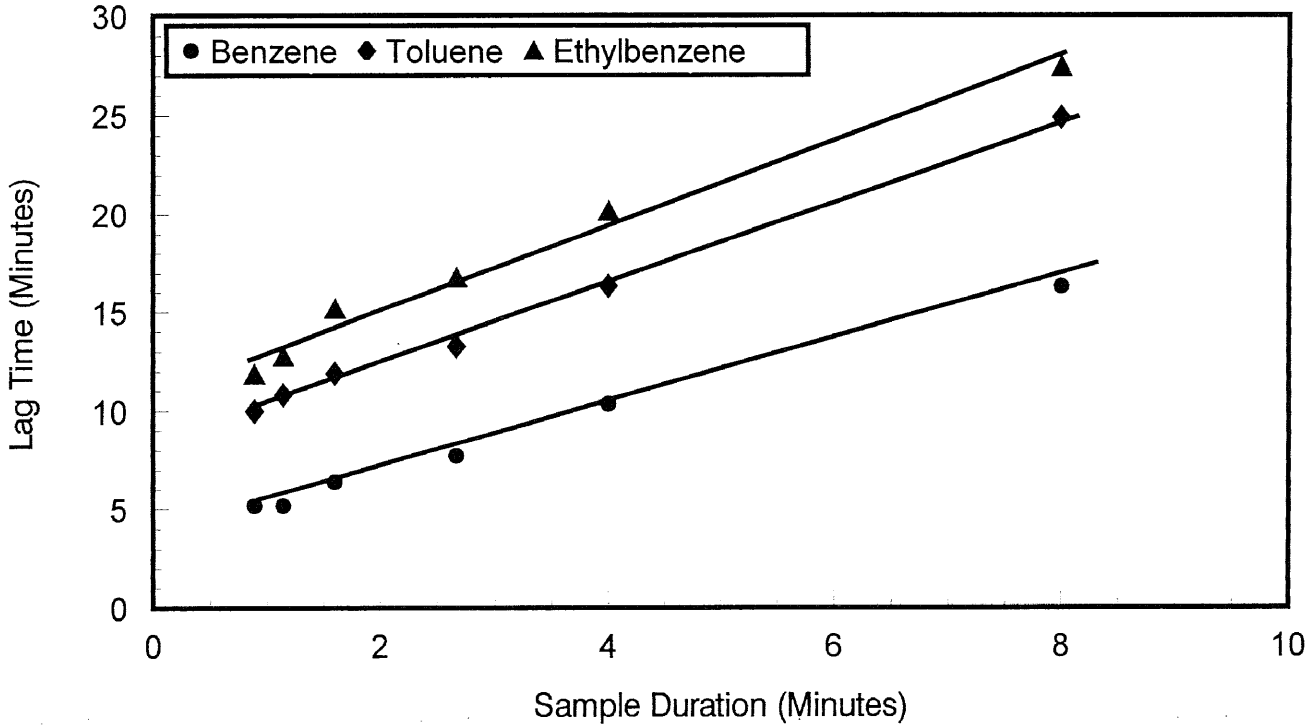


Fig. 3.5 Lag time as a function of sample duration on membrane module at room temperature. Sample duration was varied by varying eluent flow rates. Experiments were done with 8 ml injection volume using 75 ppb toluene, 67.5 ppb benzene and 60 ppb ethylbenzene.

Consequently, there was less time for permeation which resulted in lower extraction efficiency as shown in Fig. 3.6. At low flow rates, extraction efficiencies as high as 90% were achieved. The partition coefficient of the analytes in the membrane is the determining factor for extraction efficiency. The extraction efficiency for acetone was significantly lower than that of nonpolar benzene and toluene, because acetone has strong affinity for water and consequently low partition coefficient on the membrane. In general, the extraction efficiency can be increased by increasing the residence time either by having low flow rate, or by having a membrane module of longer length.

Sample size was an important variable since the introduction of a larger sample quantity resulted in higher detector response and sensitivity. However, at a given flow rate, a larger size sample increased the Δt, resulting in a broadened permeation profiles that increased lag time. Typical response profiles from different injection volumes are shown in Fig. 3.7. For low concentration samples, a large volume is necessary to achieve low detection limits. For high concentration samples, a small sample volume is preferred to obtain short lag time.

In general, in the pulse introduction approach there is a trade off between sensitivity and lag time that needs to be optimized. The factors such as larger sample volume, and lower flow rate that enhance sensitivity tend to increase the lag time. These parameters need to be adjusted based on the analysis requisite. If concentrations are very low, one will have to live with long lag time. Much of the work in this study was performed with low concentration samples, and injection volumes were between 100 μl to 10 ml. For high concentration samples, smaller sample volumes can be used to obtain lower lag time.

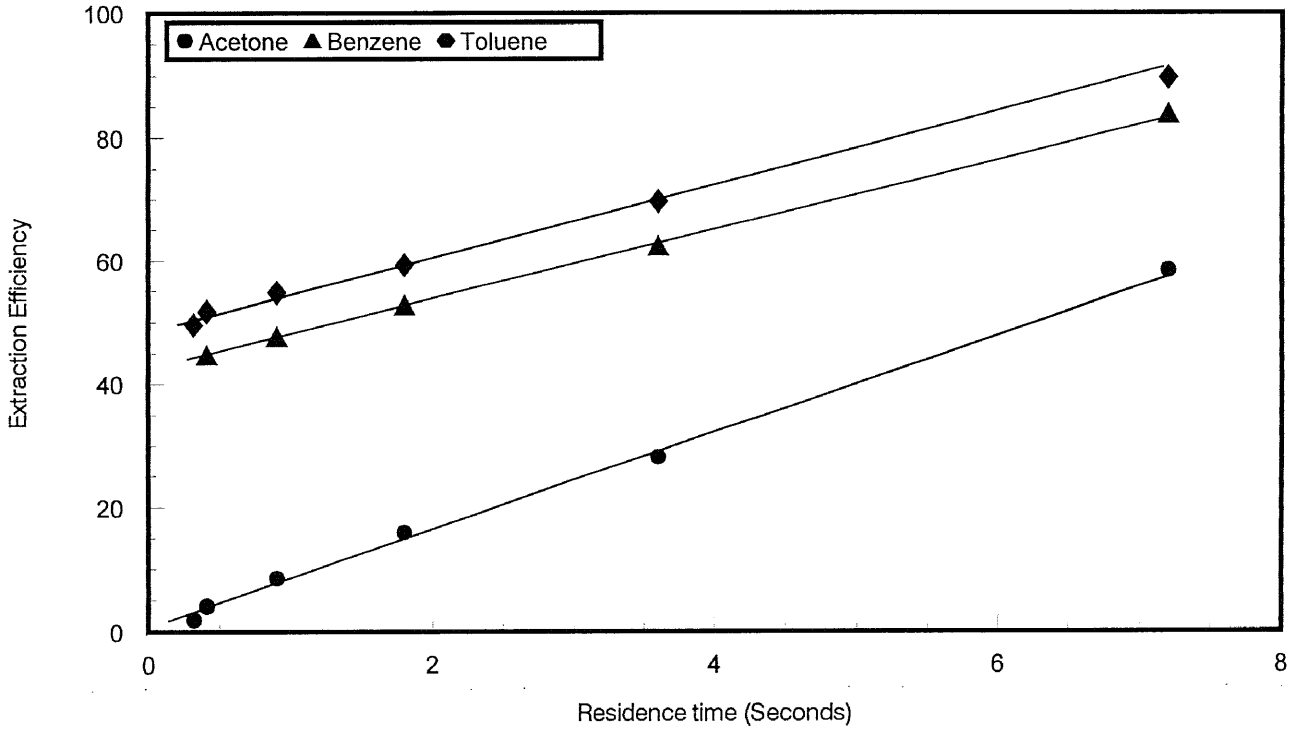


Fig. 3.6 Extraction efficiency as a function of residence time. A 5 ml sample containing 48 ppm acetone, 54 ppm benzene and 56 ppm toluene was used in this analysis. Membrane temperature was 48 C.

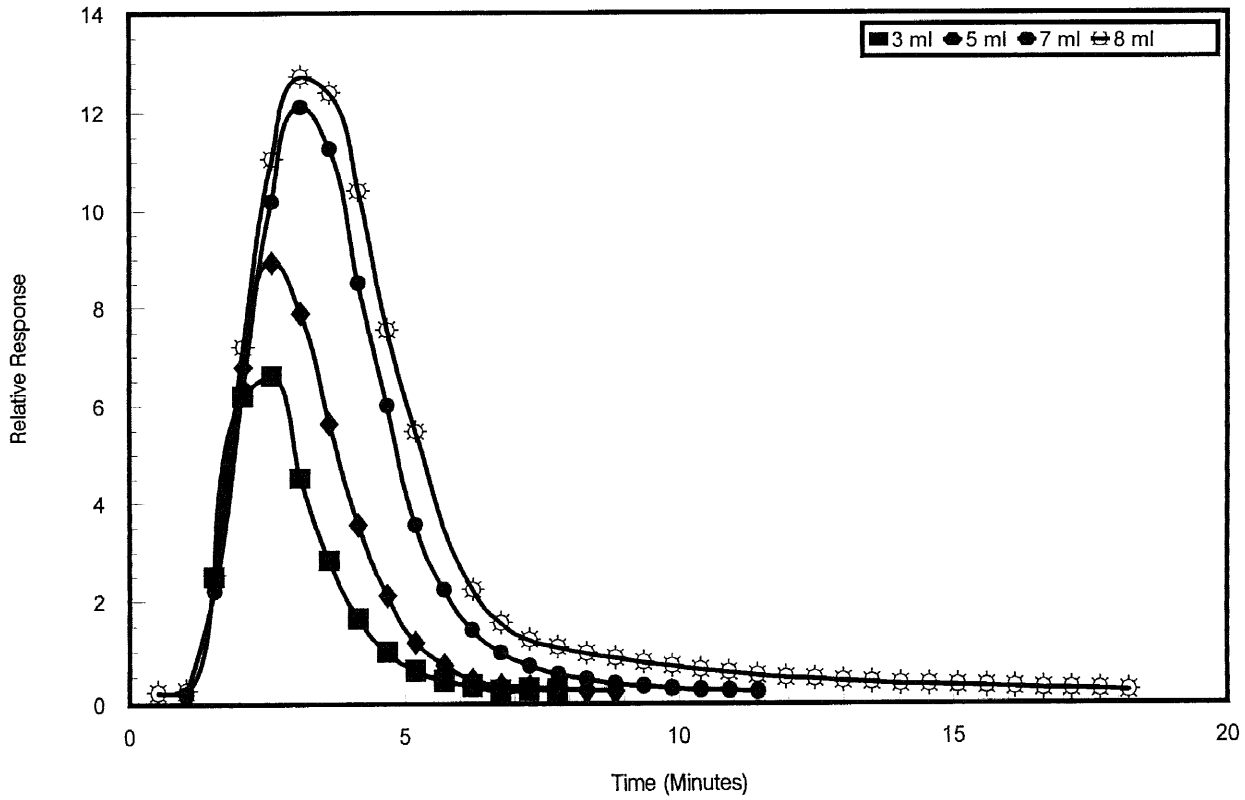


Fig. 3.7 Permeation profiles of 1 ppm toluene as a function of injection volume. Membrane temperature was 50 C and sample flow rate was 3.5 ml/min.

3.3.3 Advantages of Non-steady State Pulse Introduction

As mentioned before, most membrane extraction studies have relied on steady state diffusion, where an equilibrium is reached between concentration of organics in the aqueous and the permeated vapor phase. Since the boundary layer and membrane provide barriers to mass transfer, equilibrium is not reached instantly. The time required to reach equilibrium was determined as follows. A sample containing 53 ppb toluene was continuously introduced into membrane at flow rate of 1 ml/min. For a period of 10 minutes, the concentration was dropped to 27 ppb, after which the concentration was changed back to the original 53 ppb. The system response is presented in Fig. 3.8. The response lagged behind, so that even fifty minutes after the sample concentration came back up to 53 ppb, the response had not reached its original value. Part of this lag time may be attributed to internal volume of tubing and fittings and axial mixing with the eluent. An estimated 10 minutes is attributed to these factors, but the equilibration time was still 40 minutes or more. The objective of this experiment was not to determine the exact equilibration time which is a function of flow rate, but to demonstrate the long time required to reach equilibrium. These results are in line with other published data on time required to reach steady state in pervaporation processes [65, 66]. In a continuous introduction technique, any measurement made when the steady state is not reached does not represent the actual concentration. On the other hand, in PIME, no steady state assumption is made. Each injection truly represents the sample concentration. The only requirement here is the elimination of carryover from the previous sample. This is

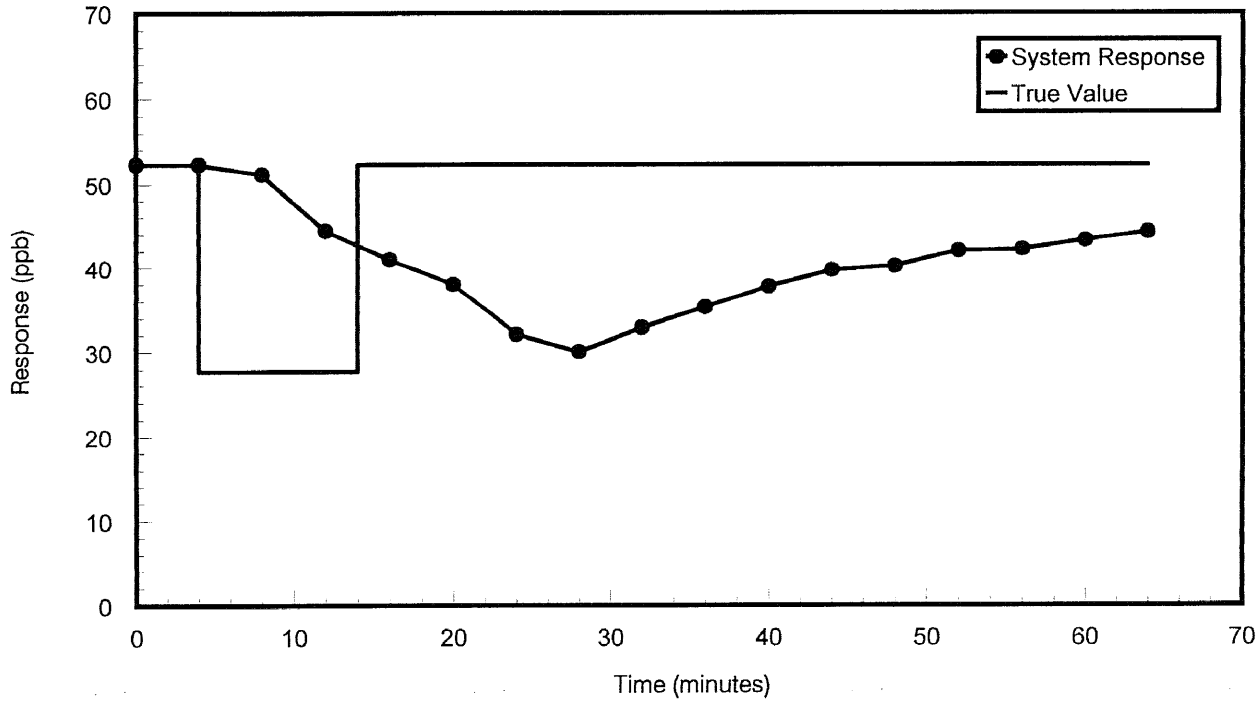


Fig. 3.8 System response during continuous sample introduction. A 52.3 ppb toluene solution flowed continuously through the membrane module at 1 ml/min rate. Then the sample concentration was dropped to 27.7 ppb for 10 minutes before being changed back to 52.3 ppb.

equivalent to reducing the lag time, and can be achieved by injecting a smaller sample volume to, and/or by gas purging the membrane after sample has passed through [34, 39].

Another disadvantage of continuous sample introduction is that it is not appropriate for analysis of discrete individual samples. In the pulse introduction approach, individual samples are injected one at a time. Continuous monitoring is easily done by making a series of injection from an automated injection valve [39]. Combination of pulse introduction with a micro-sorbent trap results in a simple instrumentation for on-line extraction/analysis of organics in aqueous matrix.

The system was used to analyze different samples. A typical chromatogram for water sample is shown in Fig. 3.9. The relative standard deviation (RSD) obtained by 7 replicated analysis of 5 ml spiked aqueous sample were 1.3%, 1.6%, and 1.6% for benzene, toluene, and 1,1,-trichlororethane respectively which shows good precision of the pulse introduction technique. A linear relationship between system response and concentration were observed at different flow rates and sample sizes. Fig. 3.10 shows typical calibration curves for several common organics. The method detection limits for 8 ml sample were 0.0012 ppb, 0.0063 ppb, and 0.010 ppb for benzene, toluene, and 1,1,1-trichloroethane respectively at an eluent flow rate of 2.5 ml/min and 0.045 ppb for ethylbenzene at flow rate of 1.2 ml/min. The MDLs were computed based on the standard EPA procedure [67]. One should note that the method detection limit depends upon operating parameters such as membrane module design, residence time and sample volume.

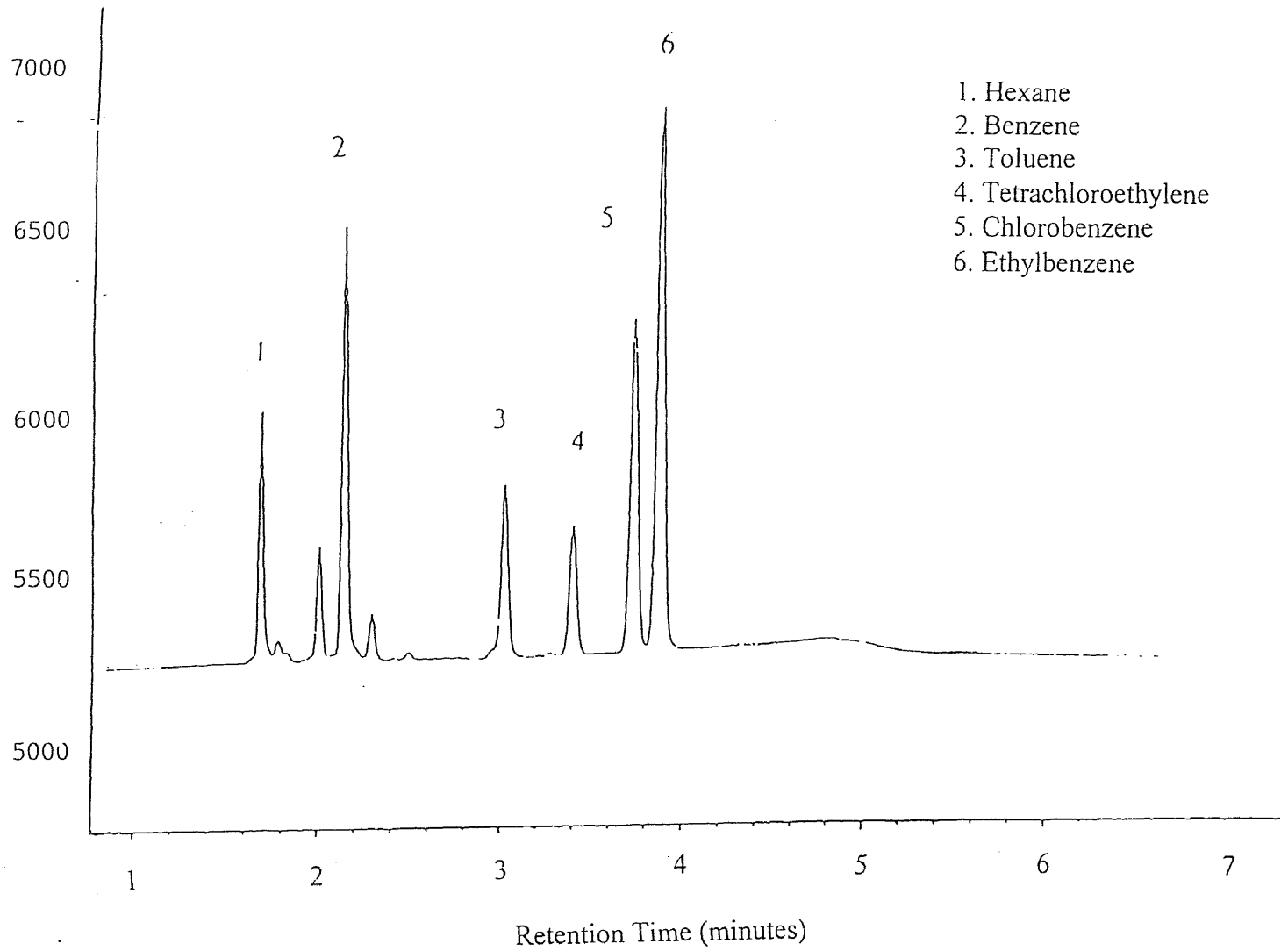


Fig. 3.9 Chromatogram of PIME system

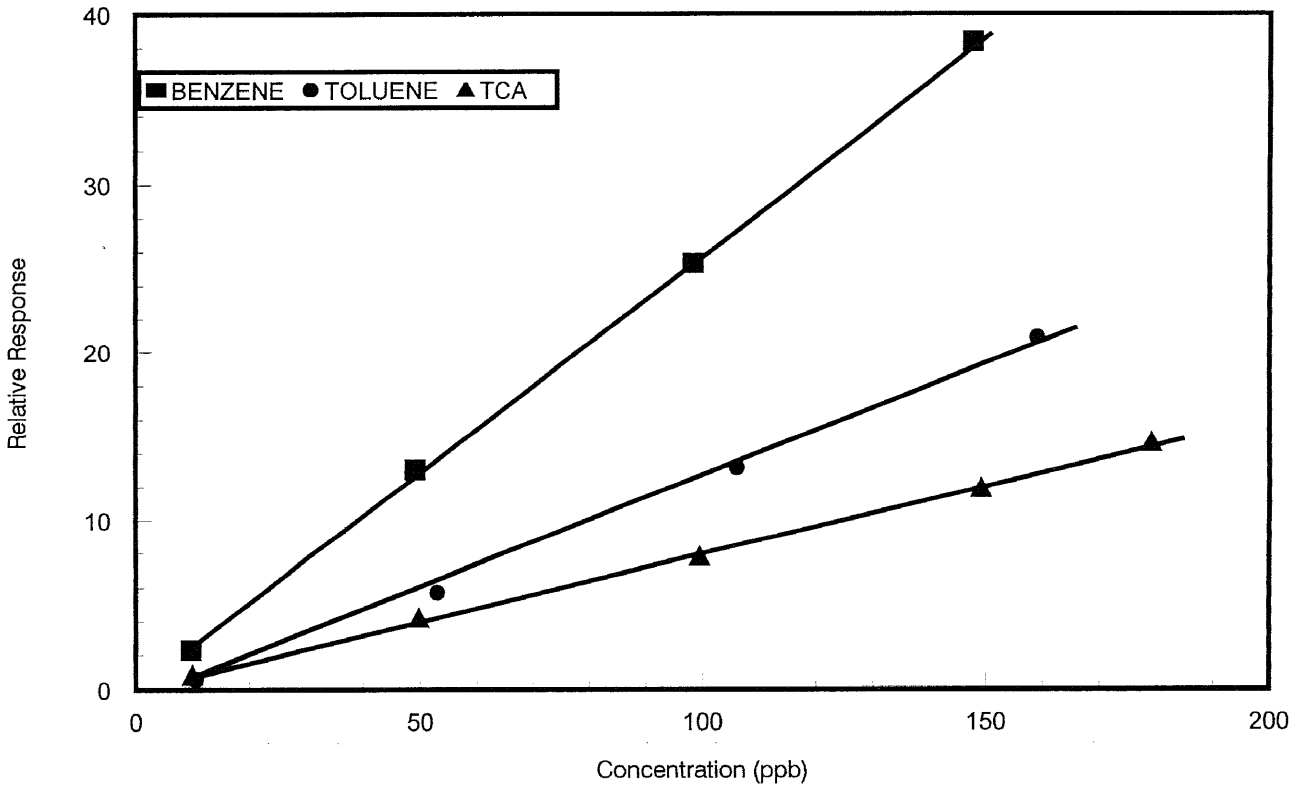


Fig. 3.10 Calibration curves of several organic compounds. Sample volume was 5 ml at eluent flow rate of 1 ml/min. The membrane module temperature was 42 C.

3.4 Conclusion

A pulse introduction method for on-line membrane extraction was explored. A mathematical model was developed for predicting the permeation process. A major advantage here was that it could be used for analysis of individual, small volume samples. The system demonstrated short lag time, low detection limits and high precision.

CHAPTER 4

ENHANCING PERFORMANCE OF PULSE INTRODUCTION MEMBRANE EXTRACTION AND REDUCING BOUNDARY LAYER EFFECTS

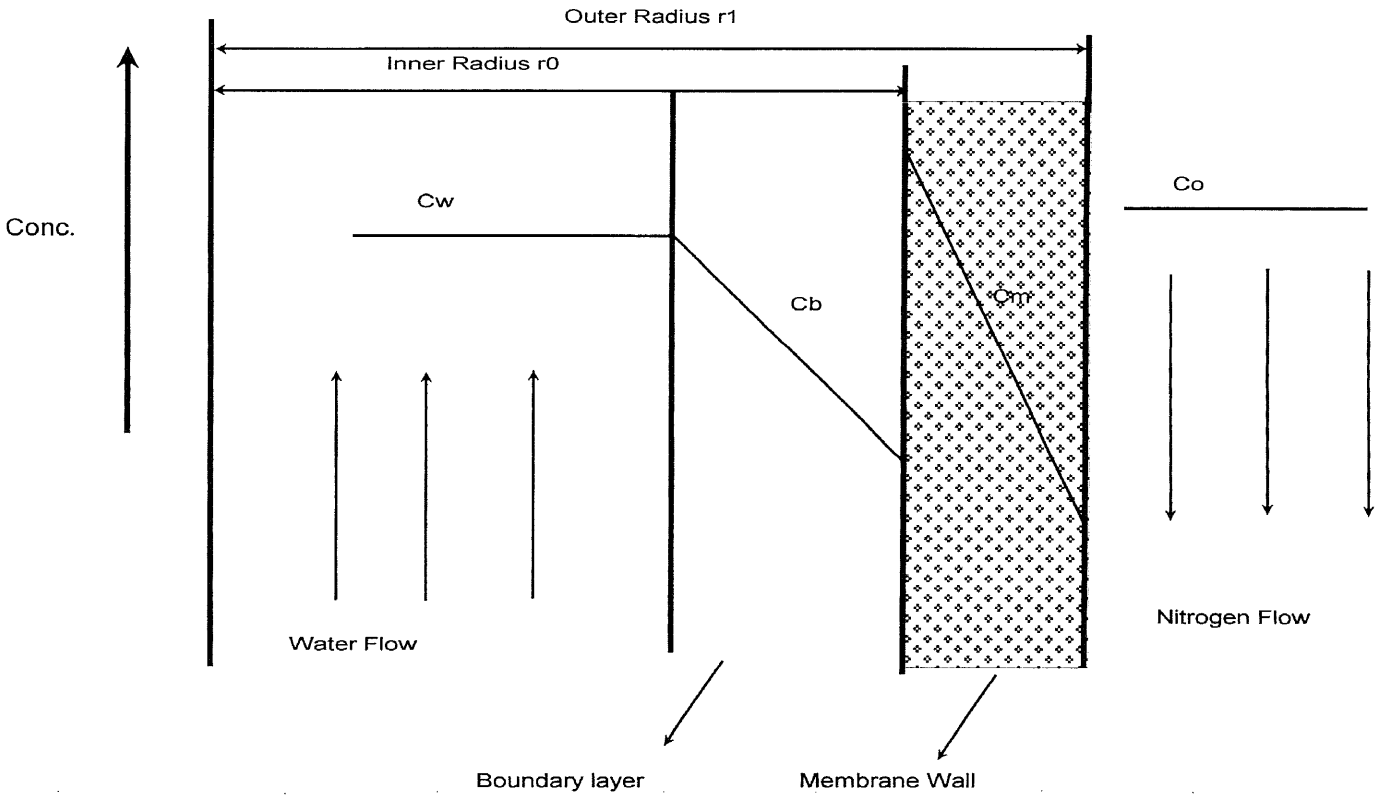
4.1 Introduction

When water is contacted with the membrane, a static boundary layer is formed at the membrane surface due to the poor mixing of the aqueous phase with the membrane. The boundary layer serves as an additional diffusional barrier to the permeation process. The degree of mixing depends upon the Reynolds number (Re) which is a function of the flow conditions:

$$Re = \rho \nu d / \mu \qquad (4\text{-}1)$$

where ρ is density, ν is velocity, μ is viscosity and d is the diameter of the tubing.

The higher the Re, the better is the mixing and less are the boundary layer effects. For turbulent condition which eliminates the boundary layer, a Re of 20,000-30,000 is required. Such high Re numbers require very high flow rates where the pressure drop is enough to rupture the membrane. High flow rates also reduce extraction efficiency thus lowering sensitivity. In a typical analytical-type membrane extraction, Re is less than 300 and a thick boundary layer is encountered. Since the organics have high solubility in the membrane material, a concentration depletion zone is formed in the boundary layer which impedes the mass transfer from water to membrane as shown in Fig. 4.1. In general, the three barriers to mass transfer are the aqueous boundary layer, the membrane and the boundary layer in the gas phase. The overall mass transfer resistance, 1/K is following by considering the individual resistance to be in series [33]:



Cw --- Concentration in water, Cb --- Concentration in boundary layer
Cm --- Concentration in membrane surface, Co --- Concentration in gas phase

Fig. 4.1 Concentration profile in aqueous boundary layer and membrane

$$1/K = 1/K_{wb} + 1/K_m + 1/K_{vb} \quad (4\text{-}2)$$

where the K, K_{wb}, K_m and K_{vb} is the mass transfer coefficient for the overall mass transfer, in the aqueous boundary layer, membrane and the gas boundary layer respectively. Extraction rates of organic molecules from a gas sample have been reported to be much faster compared to that from an aqueous sample [33]. This demonstrates that the aqueous boundary layer is the major impediment to permeation in the extraction of aqueous samples.

The relative importance of the boundary layer resistance depends upon hydrodynamic conditions, and membrane thickness, as well as the nature of analytes. For the analytes having high diffusivity and partition coefficient in the membrane, and when thin membranes are used, boundary layer is the major resistance to permeation [55-57]. For example, it has been reported [56] that the liquid phase resistance accounted for 90 % of total mass transfer resistance for toluene permeation using polyester-block-polyamide membrane when the membrane thickness was less than to 0.4 mm. It has also been reported [56] that the permeation of compounds having high Henry's constant through a hydrophobic membrane is limited by the boundary layer resistance.

In most previous membrane extraction applications in analytical chemistry, the sample was continuously introduced into the membrane. The water sample continuously contacted one side of membrane, and the organic compounds were continuously removed from the permeate side. Here a well formed boundary layer impeded mass transfer, and slowed instrumentation response. In this approach, the measurement was made after the permeation reached steady state, which could take a fairly long time [39]. The transition

period during which equilibrium was being reached did not truly represent the analyte concentration, and no measurement could be made at this time. Another limitation of continuous extraction is that it can not analyze discrete individual samples of small amount, since a large sample amount is needed to reach steady state.

In the previous chapter, we have discussed the non-steady state permeation and the development of PIME system based on non-steady state permeation, pulse introduction membrane extraction. The schematic diagram of the system with modified membrane module is shown in Fig. 4.2. The membrane receives a pulse of sample in an eluent which transports it to the membrane. The permeation takes place over a period of several minutes resulting in a permeation profile with large tailing as shown in Fig. 4.3. In this chapter, the study was aimed at enhancing the performance of PIME, such as, eliminating the permeation tailing, increasing extraction efficiency, by optimizing operating conditions, modifying membrane module design, and developing a process that minimizes boundary layer resistance.

4.2 Experimental Section

The schematic diagram of the experimental system is shown in Fig. 4.2. The aqueous sample is to be introduced as a pulse into the membrane. An eluent stream is used for transporting the sample to the membrane module. The sample size used was anywhere from 100 microliter to 10 ml depending upon analysis requirements. The injection was accomplished by a pneumatically controlled 6 port valve (Valco Instruments Co. Inc., Houston, TX). The eluent was HPLC grade high purity water. A HPLC pump was used as

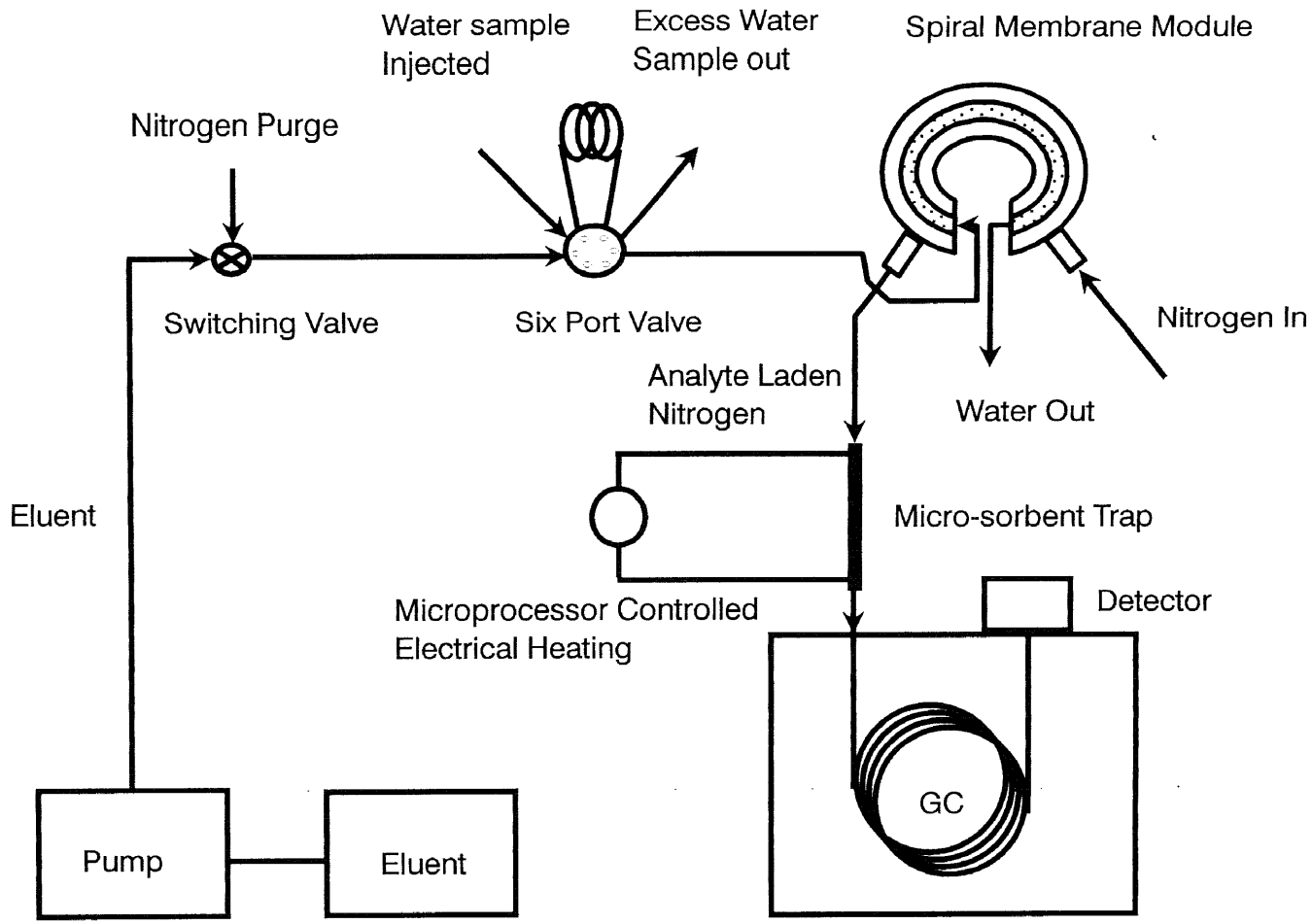


Fig. 4.2 Schematic diagram of PIME system with spiral membrane module

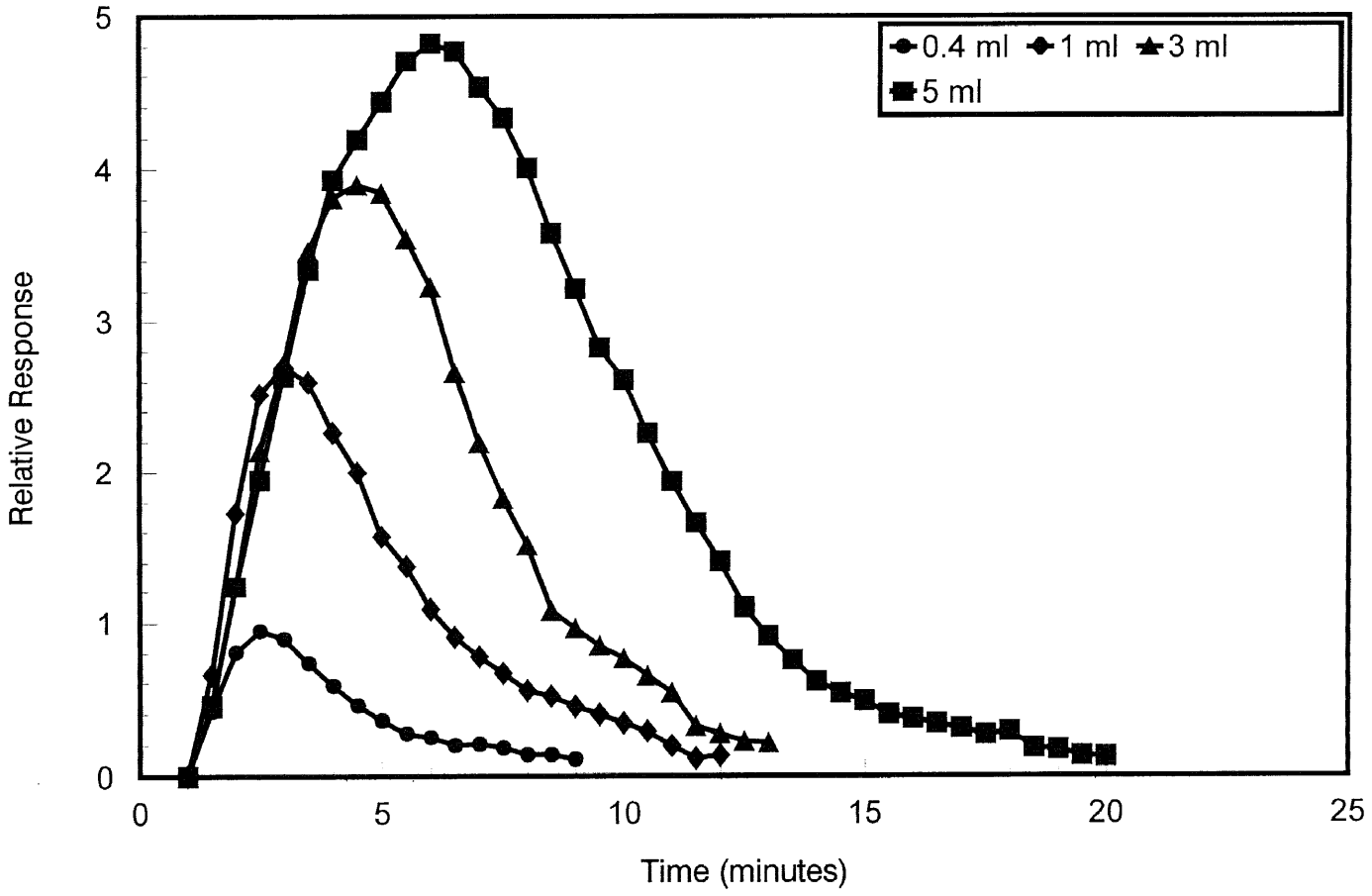


Fig. 4.3 System response profiles. 48.4 ppb toluene solution at flow rate of 0.8 ml/min was used.

the eluent pump. A three way valve was used for introducing a nitrogen stream into the membrane module. For each injection, a nitrogen could be introduced into the system prior to and/or after sample elution to clean the membrane.

Membrane module was made of composite hollow fiber membranes of dimension 0.260 mm OD×0.206 mm ID (Applied membrane Technology, Minnetonka, MN). The length was anywhere from 10 to 60 cm. The composite structure comprised of 1 μm thick homogenous siloxane film as the active layer supported on a layer of microporous polypropylene. The membrane module was either straight or spiraled. The later was made by bending the straight module into 3 circles with ID of 6 cm.

The microtrap was a small diameter silica lined tube packed with a small amount of adsorbent. It had low thermal mass and could be heated and cooled rapidly. When nitrogen carrying organics flowed through the microtrap, the organics were trapped and concentrated. An electrical current heated the microtrap resistibly and the desorption pulse served as an injection for GC analysis. The details of the microtrap and its working principle have been studied in our research group [61, 62]. A 15 cm long, 0.53 mm ID silica lined tubing (Restek Corp., Bellefonte, PA) packed with Carbotrap C (Supelco, Supelco Park, PA) served as the microtrap. A 7-10 amp current was supplied from a 40 V AC power source to heat the microtrap. The duration and the interval between the heat pulses were controlled using a microprocessor based controller fabricated in-house. A HP 5890 series II GC (Hewlett Packard Company, Avondale, PA) equipped with a Flame Ion Detector and a 30 m long , 0.53 mm OD ×0.21 mm ID SE-54 megabore column with

2.4 μm thick stationary phase was used for GC separation. HP Chemstation 3365 software was used for data acquisition and analysis.

4.3 Results and Discussion

By studying the influence of flow rate on membrane permeation, Psaume et al [55] observed that the pervaporation rate of organics is limited by the solute depleted boundary layer at the membrane-liquid interface. Thereafter, based on mass balance on the membrane system, the solute flux through the membrane wall was given as:

$$J_i = ((Q_e \rho)/A)\ (w'_{i,e} - w'_{i,s}) \qquad (4\text{-}3)$$

where the Q_e is the water flow rate, ρ is density, A is the internal surface area, $w'_{i,e}$ and $w'_{i,s}$ are weight fraction of analyte at inlet and outlet respectively. Assuming steady state, stagnant polarization layer and negligible convective flow. Then the flux was given as

$$J_{r,z} = K_{i,}\ \rho\ (w'_{i,z} - w'_{i,z,m}) \qquad (4\text{-}4)$$

where the mass transfer coefficient $K_i = D_i / \sigma$ (σ is the boundary layer thickness) and the $w'_{i,z}$ and $w'_{i,z,m}$ are the concentration at both sides of the boundary layer.

Local mass balance gives $Q'_e\ \rho dw'_{i,z} = 2\pi R J_{ri,z} dz$ (4-5)

The assumption of the $w'_{i,z,m}$ of zero and the integration of equation (4-5) with boundary conditions:

$z = 0,\ w'_{i,0} = w'_{i,e}$

$z = L,\ w'_{i,L} = w'_{i,s}$

gave:

$$\ln\ (w'_{i,e}/w'_{i,s}) = K_i\ A/Q'_e \qquad (4\text{-}6)$$

The K_i was estimated using the Leveque correction [58]:

$$(K_i\, 2R/D_i) = 1.62\ (d^2\, v/Ld_i) \tag{4-7}$$

where R and d are the radius and diameter of the fiber respectively, v is the fluid velocity.

The extraction efficiency was thus derived as:

$$EE = (w'_{i,e} - w'_{i,s})/w'_{i,e} = 1 - \exp.\left(-6.48\ \frac{D_a^{\frac{2}{3}} L^{\frac{2}{3}}}{d^{\frac{4}{3}} v^{\frac{2}{3}}}\right) \tag{4-8}$$

Similar equations have also been obtained in other study [36] for porous membrane by assuming the mass transfer is limited by liquid phase.

Since the mass transfer mechanism of "solution and diffusion" are the same whether steady state is reached or not, the equation can be adopted for non-steady state permeation. To confirm that, we investigated the system response for steady state permeation and non-steady state permeation. The results showed that for the same amount of sample (3 ml), both system response differences were less than 2% which is in the range of analysis deviation which is shown in Fig. 4.4. For small amount samples (0.4 ml), "clean membrane effect" which increases extraction efficiency reported [39] will be discussed in the next chapter. In this case, a factor of K_1 can account for the extraction increasing. Therefore the system response in pulse introduction can be given as:

$$M = K_1 \times K_2 \times C \times V \times (EE) = K \times C \times V \times \left[1 - \exp.\left(-6.48\ \frac{D_a^{\frac{2}{3}} L^{\frac{2}{3}}}{d^{\frac{4}{3}} v^{\frac{2}{3}}}\right)\right] \tag{4-9}$$

where M is the system response, K_2 is a response factor for the analyte, C is the analyte concentration in water sample and V is the sample volume.

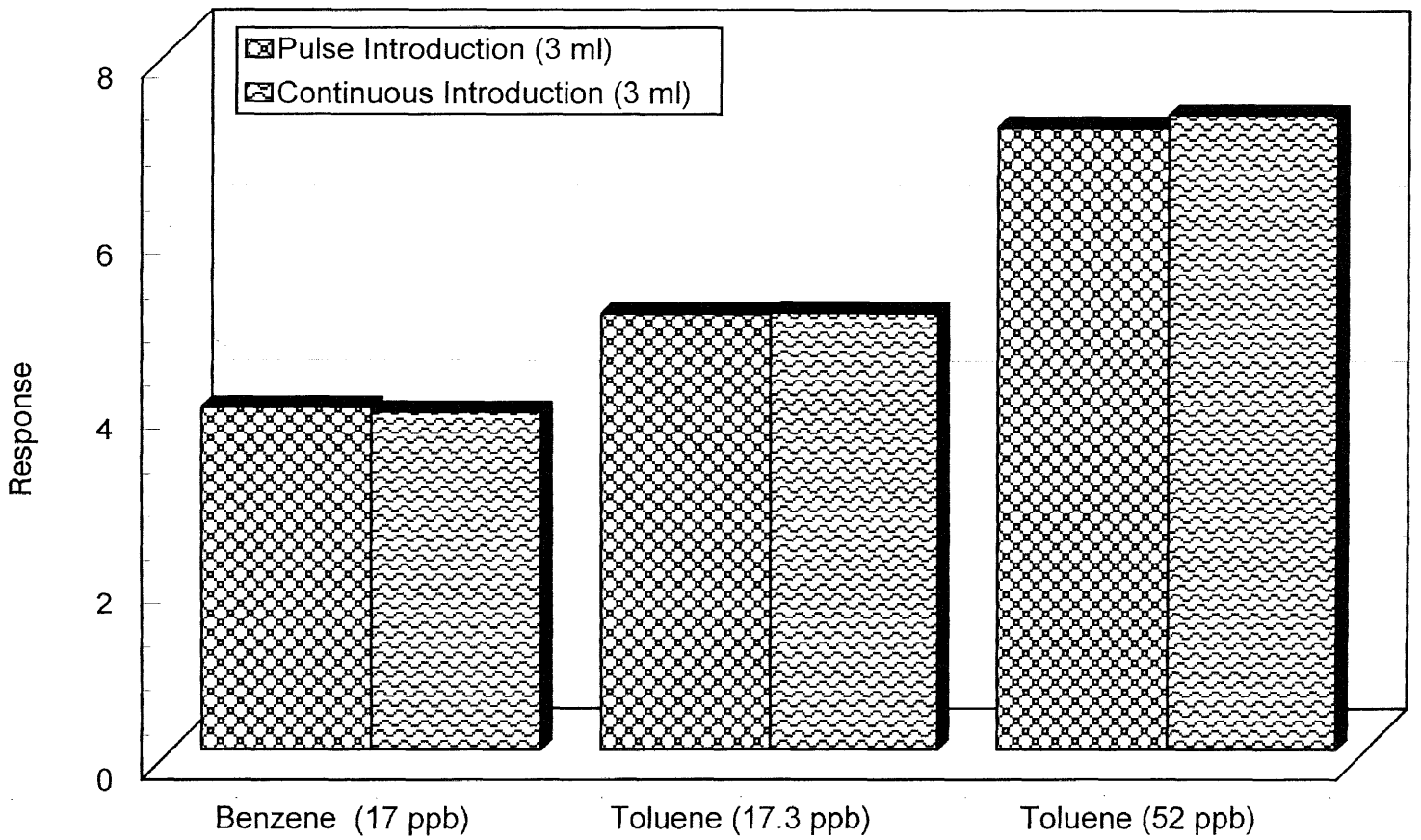


Fig. 4.4 Comparison of system response for sample pulse injection and continuous introduction. Water sample flow rate of 2 ml/min was used.

In order to see if the above equation was applicable for the PIME system, the system response was plotted as a function of $\{1\text{-exp.}[-6.48\ (\frac{D_a^{\frac{2}{3}} L^{\frac{2}{3}}}{d^{\frac{4}{3}} v^{\frac{2}{3}}})]\}$ as shown in Fig. 4.5. Diffusivities of benzene and toluene in water were calculated from Wilke-Chang equation [68] and the molar volumes of benzene and toluene used for the calculations were obtained from the literature [69]. The experiments were done with a 8 ml sample containing 67.5 ppb benzene and 75 ppb toluene. Water velocity was varied while fiber diameter and length were fixed. A linear fit with r^2 of 0.993 and 0.996 were obtained for benzene and toluene respectively. This demonstrated the applicability of the above equation to the PIME system. Since the equation (4-9) was obtained by assuming that the permeation across the boundary layer is the rate determining step, this fit further confirms the importance of the boundary layer.

Flow rate is an important parameter according to above equation. As flow rate increased, the residence time decreased and there was less time for permeation. Consequently a large fraction of the analytes went through unextracted. In continuous membrane extraction, it has been reported [23] that the system response increased as the flow rate increased because more sample was brought into the membrane. However, as flow rate increased further, the response stabilized because extraction efficiency decreased resulting in no additional permeation flux. In the PIME, the sample amount is fixed, so a reduction in extraction efficiency reduces system response. Fig. 4.6 is a plot of system response vs. flow rate. Both calculated response using equation (4-9) and experimental response were presented here. The constants in equation (4-9) were obtained from the regression line in Fig. 4.5. Both figures showed good fit between the

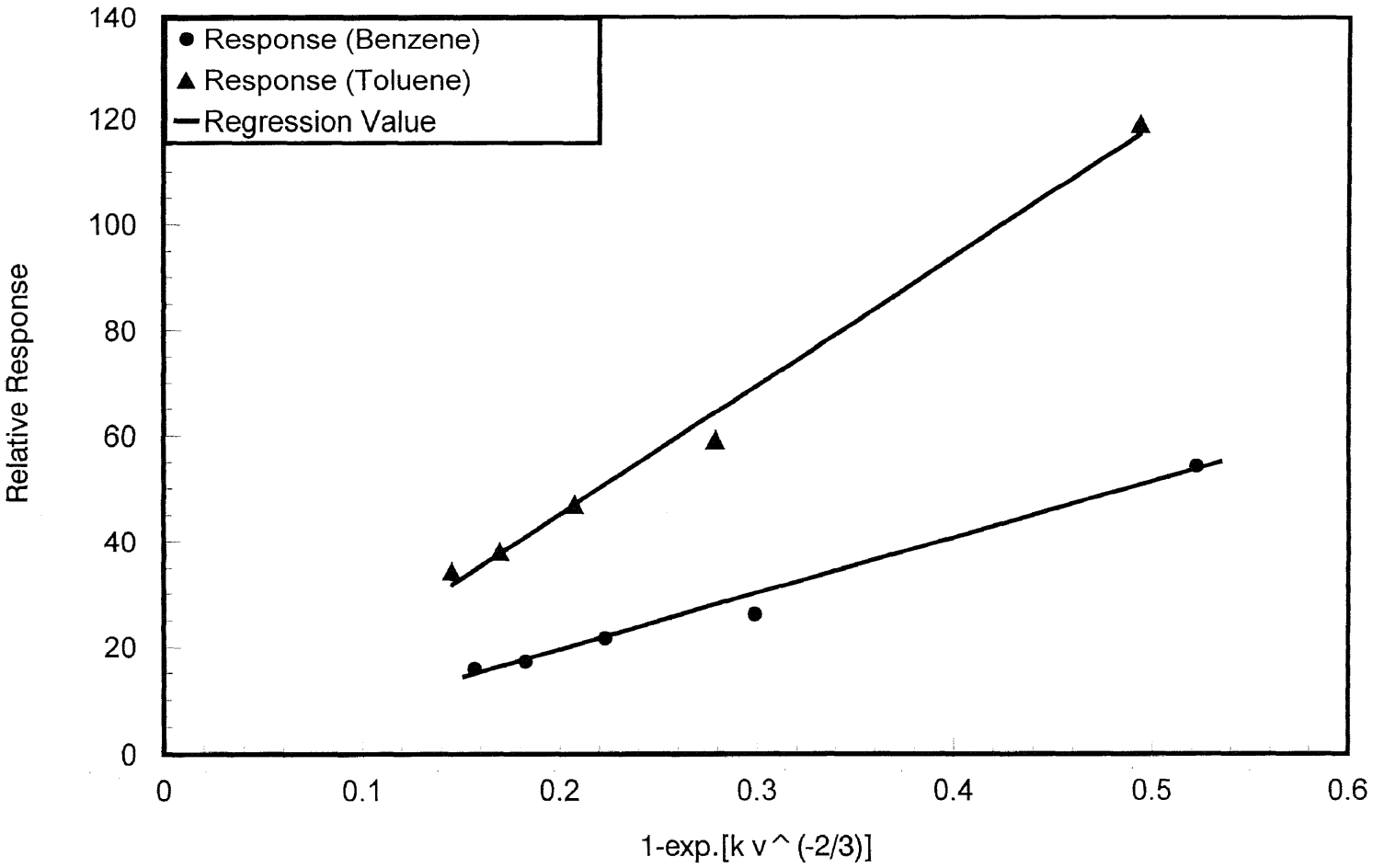


Fig. 4.5 System response as a function of {1-exp. [k/v^(2/3)]}. A 8 ml sample containing 67.5 ppb benzene and 75 ppb toluene was used in these experiments.

equation and experimental results and it demonstrated the importance of flow rate in the pulse introduction system.

Lag time in PIME is defined as the time interval between 10% of the maximum response in the ascending and the descending part in the response profile as shown in Fig. 4.3. It is a measure of the duration over which the permeation process takes place. Lag time is an important parameter in membrane extraction, because it is directly related to frequency of analysis. A sample can be injected only after the permeation from previous sample has reached completion. A slow flow rate is preferred for high extraction efficiency. However slow flow rate also reduces Re and results in slower mass transfer due to the formation of thick boundary layer. The combination of longer residence time and slower mass transfer results in longer lag time. Thus flow rate provides a trade off between sensitivity and lag time.

Sample volume also affects the system response and lag time. At the same flow rate, system response is proportional to sample size as shown in Fig. 4.7. A large sample contains a larger mass of analytes resulting in a larger detector response. However, a large sample also stays longer in the membrane increasing the lag time and this is shown in Fig. 4.3. Therefore, increasing sample size is not necessarily an ideal approach for increasing system response.

4.3.1 Membrane Module Design

From a practical point of view, the lag time is the limiting factor that prevents the use of very large sample volume or very low flow rates. To enhance the performance of PIME,

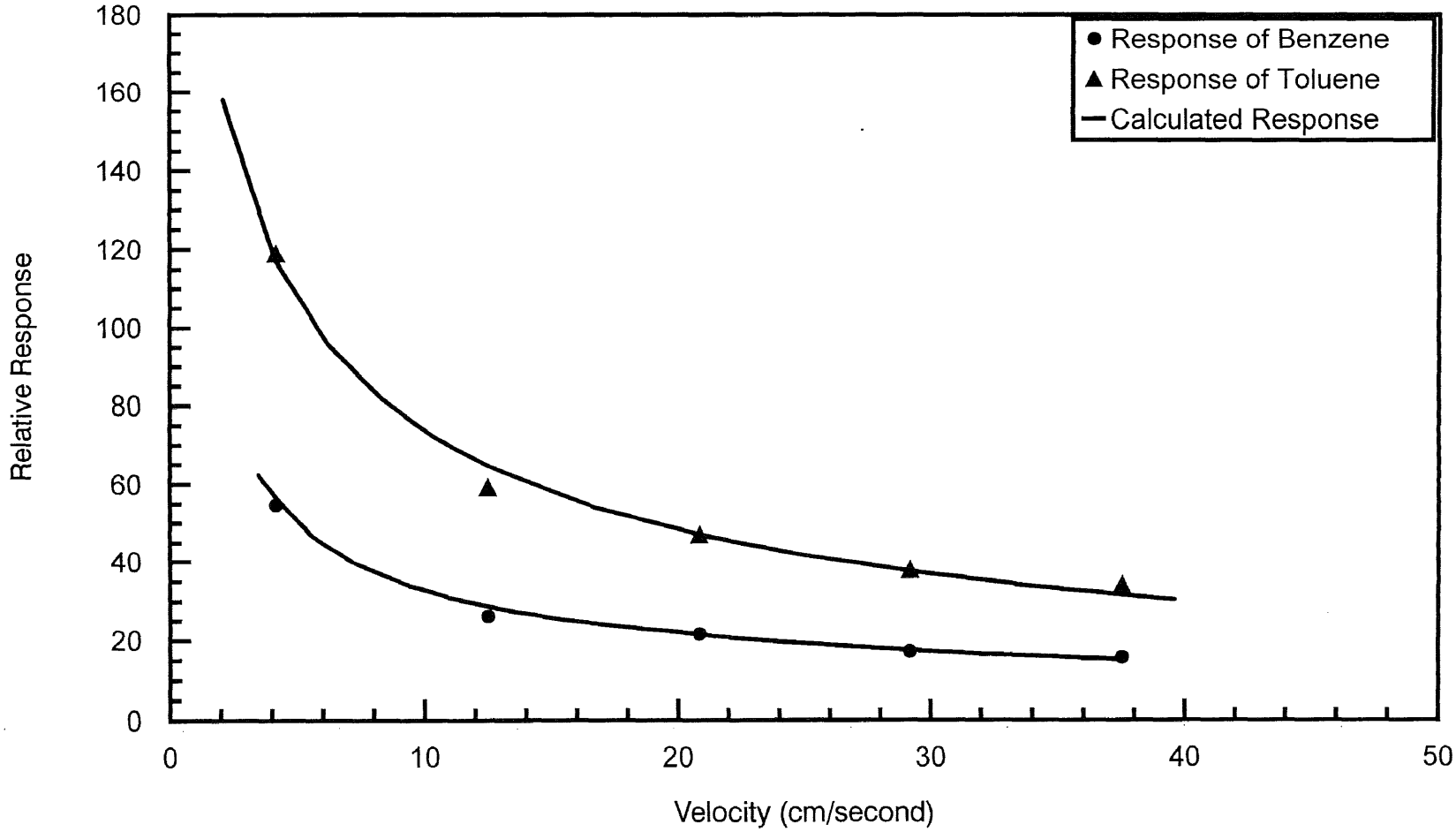


Fig. 4.6 Response as a function of sample velocity. A 8 ml sample containing 67.5 ppb benzene and 75 ppb toluene was used in these experiments.

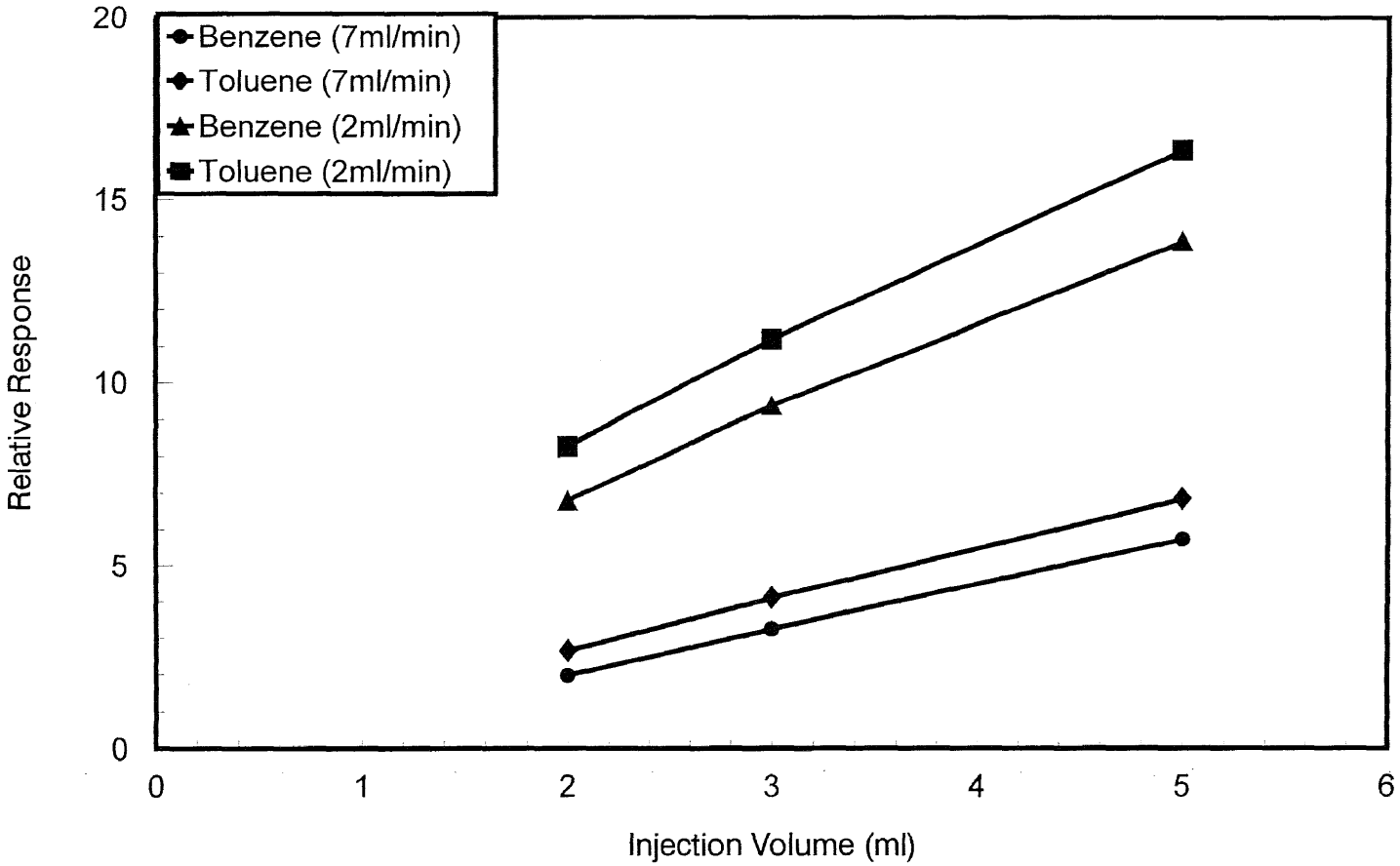


Fig. 4.7 Response as a function of injection volume for a sample containing 87.4 ppb benzene and 173.4 ppb toluene.

alternative approaches need to be studied to obtain high extraction efficiency and short lag time. Extraction efficiency can be increased by increasing membrane active surface area. Multiple hollow fibers packed into module has been used to increase active surface area and consequently system response [33].

For a fixed sample amount injected during pulse introduction, system response increases with extraction efficiency. According to equation (4-8), extraction efficiency will increase with the length of the membrane module as long as the membrane length is shorter than that required for exhaustive quantitative extraction. PIME response and the calculated response using equation (4-9) as a function of membrane length (other conditions remaining constant) are both presented in Fig. 4.8 for a 0.7 ml sample containing 30 ppb benzene and 40 ppb chlorobenzene. The constants in equation (4-9) were obtained from the regression of system response to $\{[1\text{-exp.}[-6.48\ (\frac{D_a^{\frac{2}{3}} L^{\frac{2}{3}}}{d^{\frac{4}{3}} v^{\frac{2}{3}}})]\}$ where the length was varied and the other variables were kept constant. The diffusivity of benzene and chlorobenzene were calculated as mentioned before. A good fit between the experimental results and the equation is seen. It also shows that increasing membrane length is an effective approach of increasing efficiency and thus sensitivity.

When a small sample is used, a short lag time can be obtained. For 0.7 ml sample containing 40 ppb of benzene and toluene, lag times were 2.6 and 3.3 minutes for benzene and toluene respectively in a 10 cm module. The lag time increased to 2.8 minutes for benzene and 4.1 minutes for toluene on a 40 cm fiber module. Therefore, a long fiber does not significantly affect lag time.

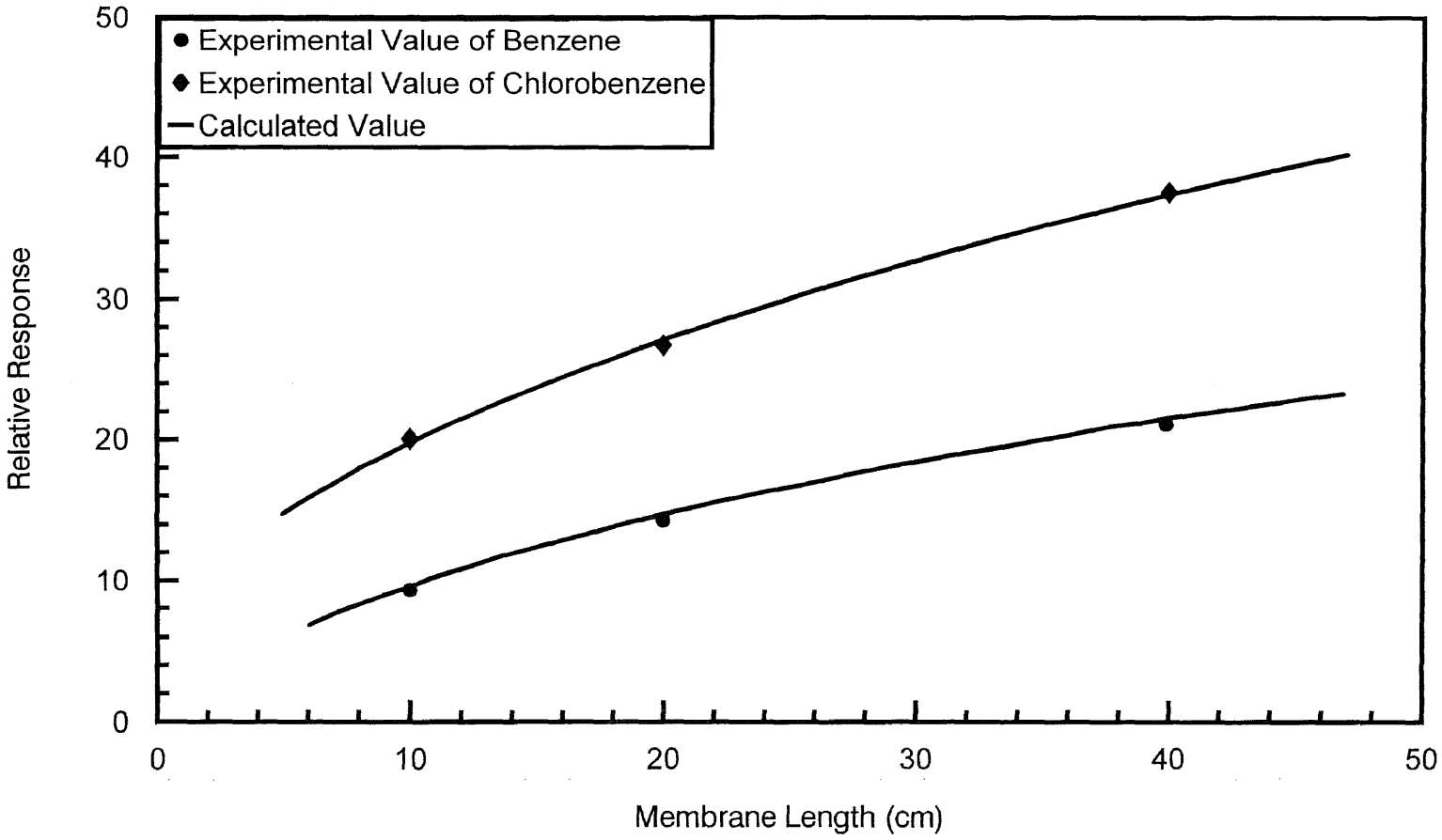


Fig. 4.8 System response as a function of membrane length. A 0.7 ml sample containing 30 ppb benzene at an eluent flow rate of 1 ml/min was used.

A comparison of sensitivity for 10 cm and 40 cm long membrane fiber is presented in Fig. 4.9. The figure shows that longer membrane fibers, the higher is the sensitivity due to its higher extraction efficiency. The ratio of the slope of calibration curves of the 40 cm hollow fiber to that of the 10 cm is 2.02, and it shows that increasing the membrane length is a simple and efficient method to increase analytical sensitivity. For an efficient analysis, a long membrane module with multiple fibers appeared to be more practical than reducing sample flow rate and/or increasing sample size.

Extraction efficiency of benzene as calculated from equation (4-8) is presented in Fig. 4.10 for different conditions, e.g. sample flow rate, membrane module length and number of hollow fibers. Based on equation (4-8), using a module with 7 pieces of the hollow fiber with length of 70 cm at an eluent flow rate of 1 ml/min (or similar combinations, for example, 12 pieces of hollow fiber with length of 19 cm at flow rate of 0.5 ml/min), extraction efficiency of benzene would be 90%.

Previous studies have shown that the boundary layer resistance can be reduced by increasing Re [55-56]. But as mentioned before, the increased flow rate reduces sample residence time on membrane thus lower system response. More turbulence can also be brought about by having a flow pattern that changes direction. This would reduce the thickness of the boundary layer and introduce more mixing of the sample on the membrane surface. A spiral membrane module was fabricated. The spiral configuration allows the sample to flow in a circular path inside the membrane thus disrupting the boundary layer as shown in Fig. 4.11. This geometry also provides a practical way of reducing the physical length of the membrane module. For example, a 70 cm long module

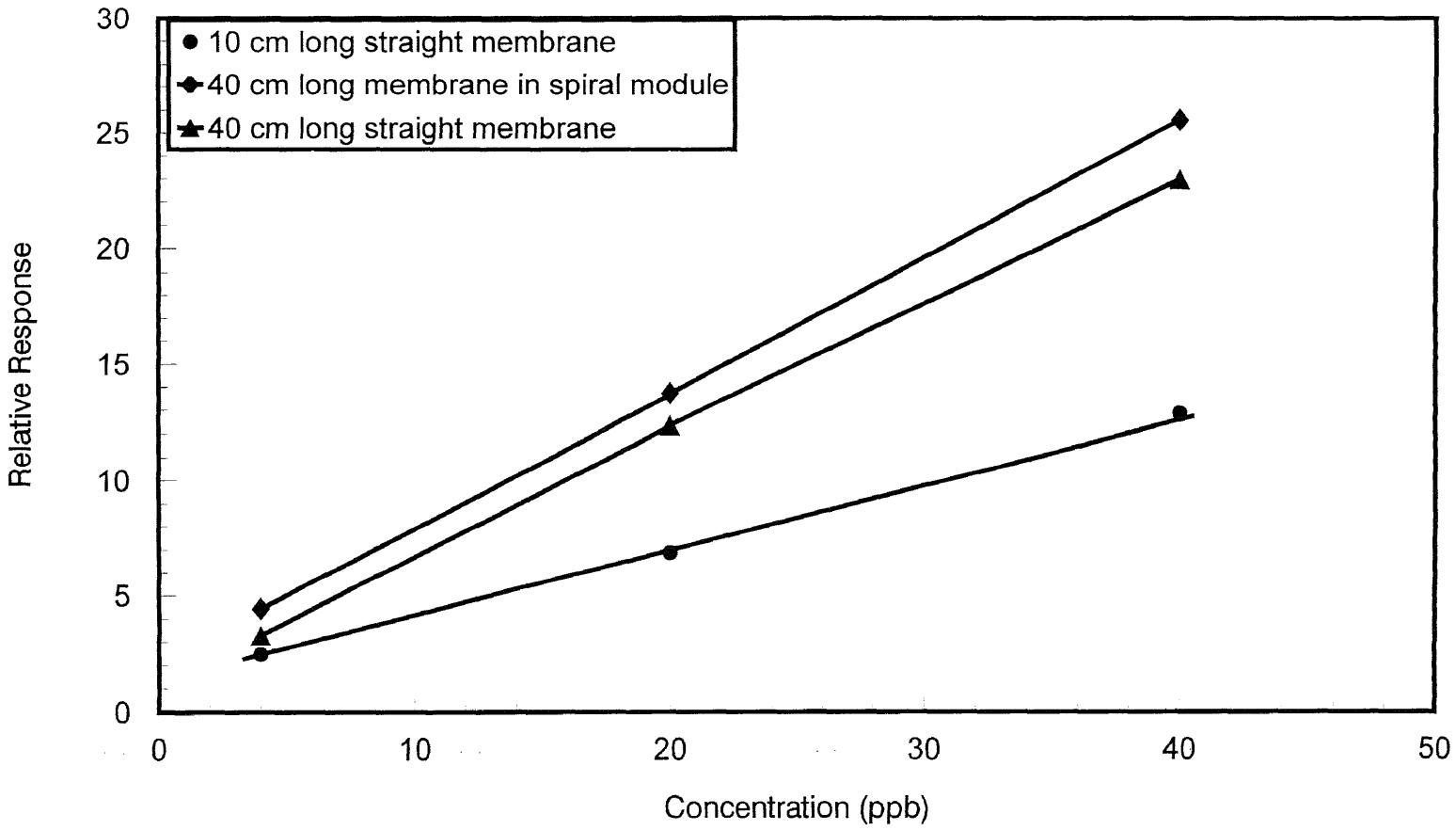


Fig. 4.9 Comparison of sensitivity for different membrane module design. A 0.7 ml sample at an eluent flow rate of 1 ml/min was used.

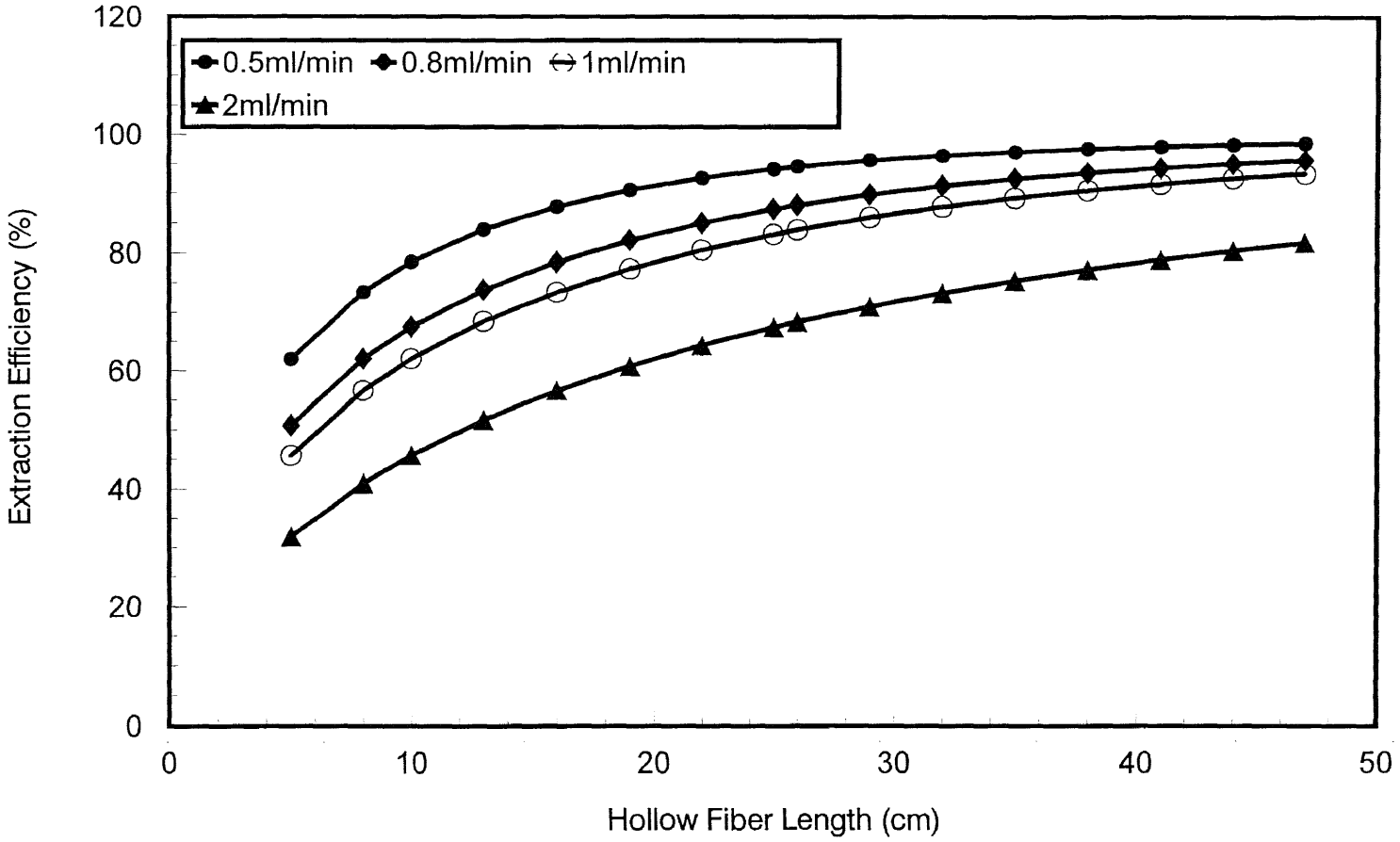
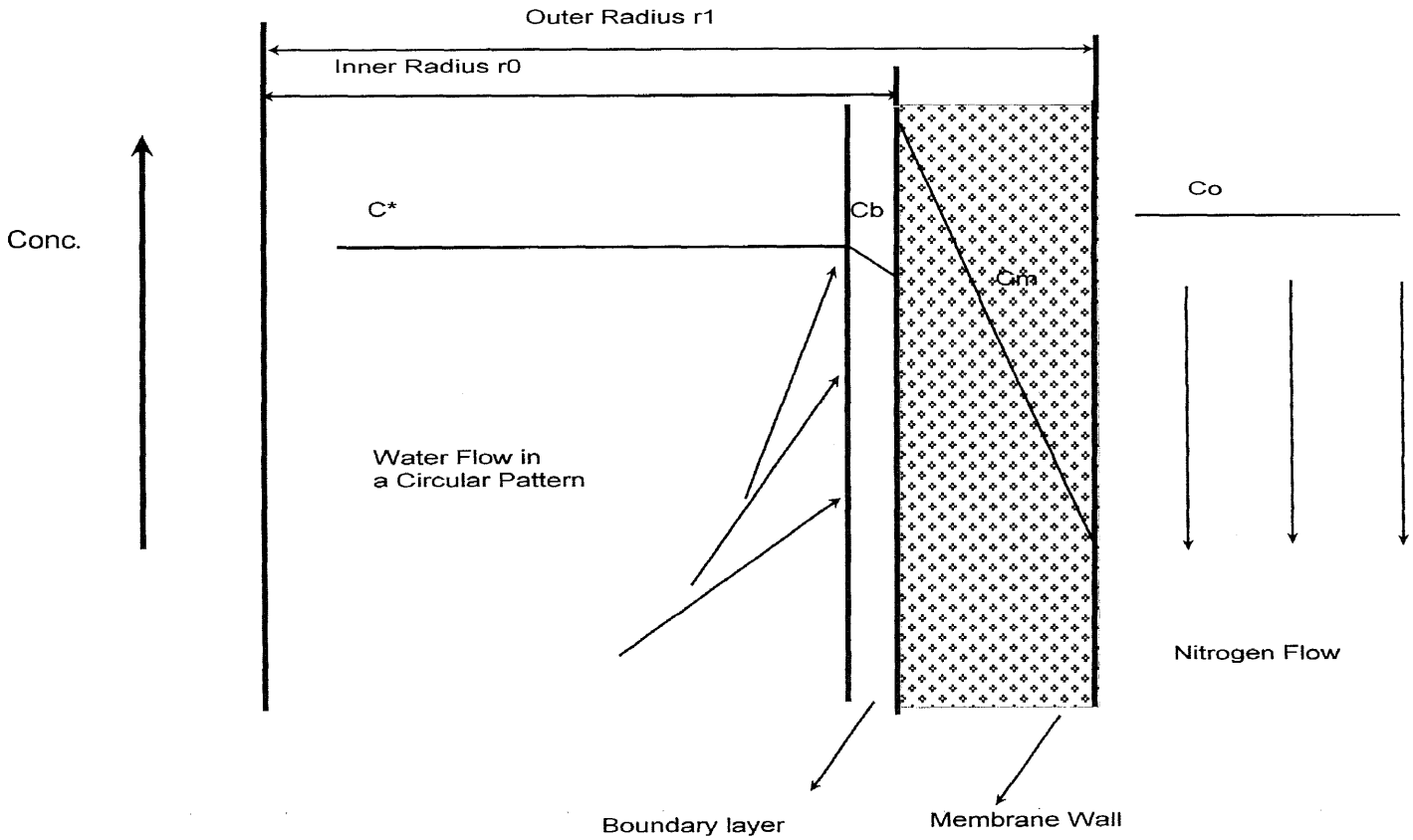


Fig. 4.10 Calculated extraction efficiency of benzene as a function of membrane fiber length. The membrane module contained 12 pieces of hollow fibers.



C* --- Concentration in water, Cb --- Concentration in boundary layer
Cm --- Concentration in membrane surface, Co --- Concentration in gas phase

Fig. 4.11 Reduced boundary layer thickness by changing flow direction of fluid

mentioned above was made into spiral of 8 cm diameter. A comparison of sensitivity between straight and spiral module of same length is also presented in Fig. 4.9. The spiral configuration consistently generated higher response than the straight module. The signal enhancement of the spiral membrane module confirms the presence of a concentration depletion zone and demonstrates that the mass transfer is limited by the boundary layer.

4.3.2 Elimination of Boundary Layer by Nitrogen Purge

In PIME, either a gas or a liquid can be used as the eluent. The main difference between gas and liquid is their transport properties, i.e. diffusivity, viscosity, and density. Reynolds number can be used to normalize the difference between gases and liquids [33]. Membrane extraction from gases and aqueous media follow the same pattern. As diffusion coefficients are significantly higher in gases, the boundary layer resistance is practically negligible compared to the aqueous layer or the membrane. Consequently, the lag time in gas extraction is significantly shorter compared to that in water. However, the problem with gas elution of the water sample is that a high pressure is required for sample elution which results in a high flow rate thus reduce the residence time and consequently the extraction efficiency.

A short lag time is required to eliminate memory effects so that samples can be analyzed frequently. It is also an important factor in continuous on-line analysis. In PIME, a sample pulse is introduced into the membrane and an eluent serves as a carrier fluid. The axial mixing of the sample with the eluent broadens the input pulse. We have discussed the slow permeation through the boundary layer and the membrane broadened

the permeation profile in the previous chapter. The tailing part of the sample input profile makes little contribution to the system response but significantly increases the lag time.

In the PIME system presented here, water was used for eluting the sample for a predetermined period of time. Then a flow of inert gas, such as nitrogen was used to purge the membrane to eliminate the tailing part of sample input and the boundary layer. A three way valve shown as in Fig. 4.2 was used to introduce the nitrogen purge. The purge was turned on depending upon the performance requirements. The effect of the purge interval (interval between sample input and nitrogen purge) is seen in Fig. 4.12. If no nitrogen purge was used, the response continues for nearly 25 minutes. If the purge was turned on after 1 minute, the response duration was only 5 minutes. However some sensitivity was lost because much of the sample passes unextracted. In general, the longer the purge interval, closer is the response to the maximum possible sensitivity, but longer is the lag time. If the purge is turned on where the profile tailing is seen, relatively less sensitivity is lost but lag time is significantly reduced. For example, it can be seen from Table 4.1, that when the purge is turned on 6 minutes after sample elution, the lag time reduced by almost 50%, with only 16.8% loss in sensitivity. In general, the trade off between lag time and sensitivity depends upon what point the nitrogen purge is turned on as shown in Table 4.1. By starting nitrogen purging, the lag time can be reduced but sensitivity will also decrease. For high concentration samples, an early nitrogen purge is recommended, where as for low concentration samples, the purge should be initiated later.

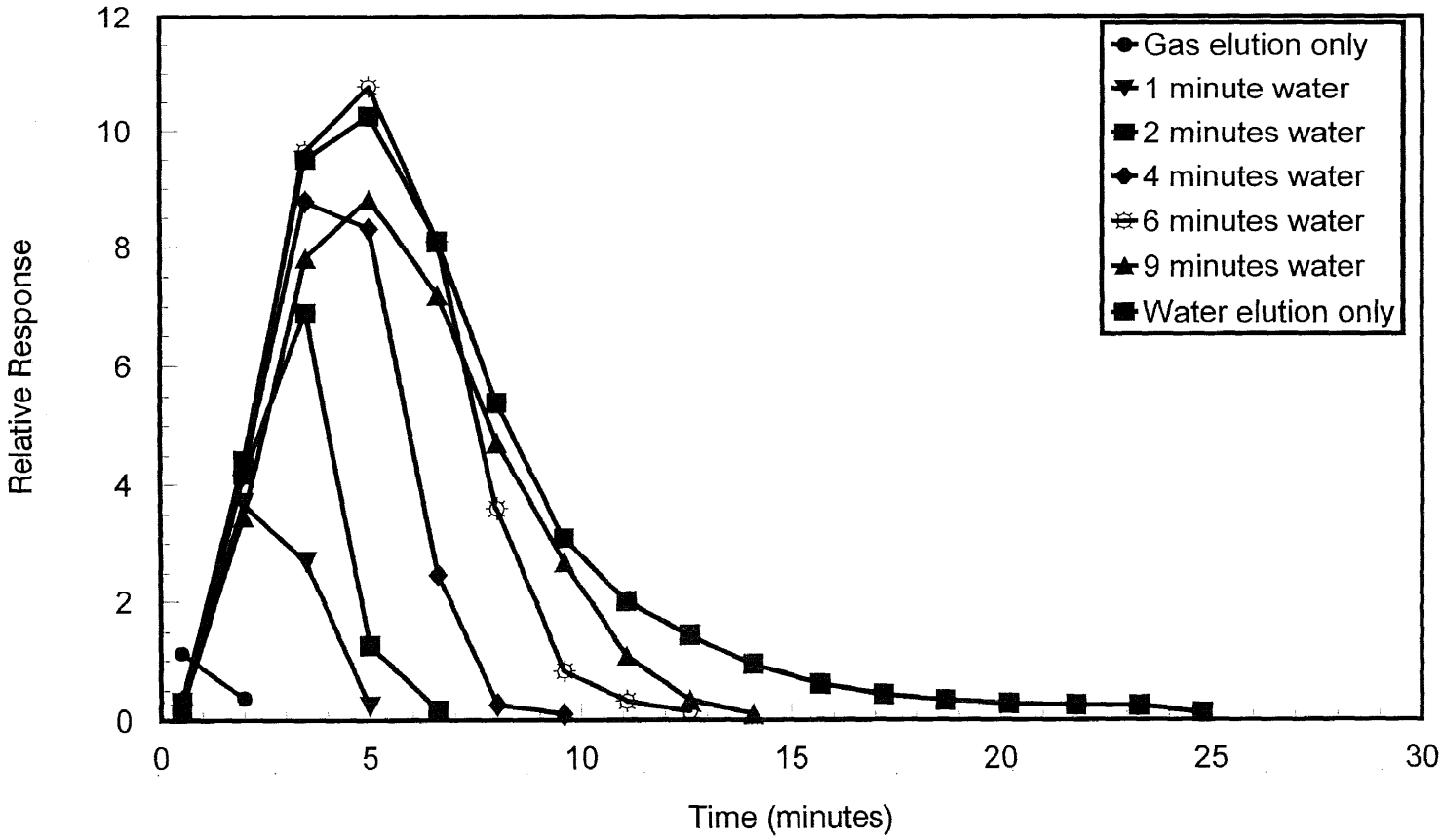


Fig. 4.12 The effect of nitrogen purge on system response and lag time. The nitrogen was turned on after a predetermined period of water elution. The experiments were done with 37.5 ppb toluene, injection volume was 3 ml at an eluent flow rate of 1 ml/min.

Table 4.1 Reduction in Lag Time and Loss in Sensitivity in Nitrogen Purged Elution

	Lag Time for Benzene (min)	Lag Time for Toluene (min)	Lag Time for Chlorobenzene (min)	Reduction in System Response for Toluene (%)
Water elution	23	24.5	24.5	0
9 minutes water elution followed by nitrogen purging	14	14	15.5	19.8
6 minutes water elution followed by nitrogen purging	12.5	12.5	12.5	16.8
5 minutes water elution followed by nitrogen purging	11	9.5	9.5	32.9
4 minutes water elution followed by nitrogen purging	9.5	9.5	8	46.2
3.6 minutes water elution followed by nitrogen purging	9.5	8	8	56.3
2 minutes water elution followed by nitrogen purging	8	6.5	8	72.1
1 minute water elution followed by nitrogen purging	6.5	5	6.5	84.8
Nitrogen elution only	3.5	2	5	96.7

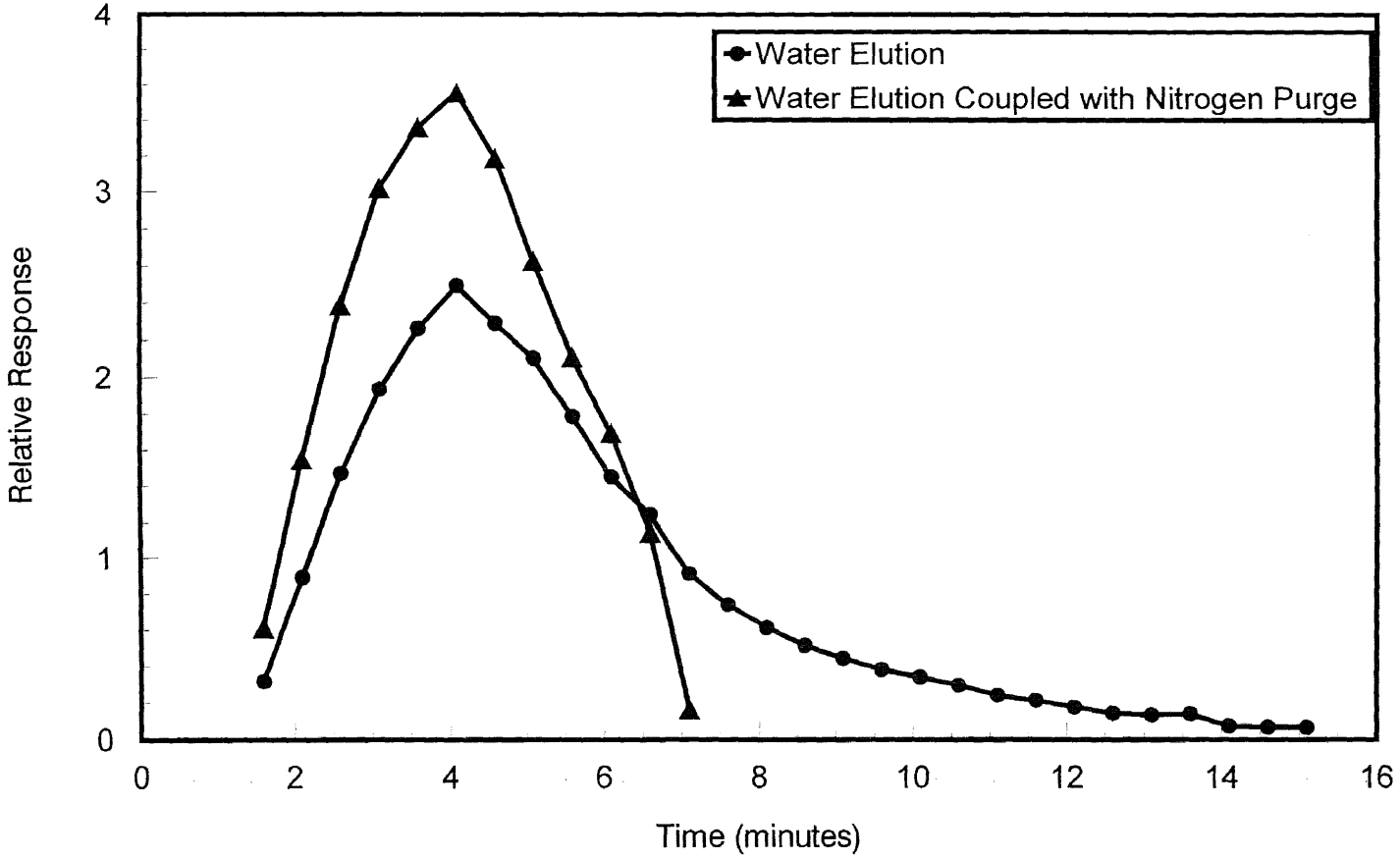


Fig. 4.13 Permeation profiles in nitrogen purged and unpurged membranes. Nitrogen was turned on 6 minutes after sample injection. A 2 ml sample containing 27.3 ppb toluene, at an eluent flow rate of 0.8 ml/min was used.

Another advantage of the nitrogen purge is that the nitrogen purge cleans the membrane by eliminating the aqueous boundary layer that formed at the surface. As a result, when the next sample is injected, it encounters no boundary layer and a high permeation rate is obtained. Eventually, as the sample is eluted, the boundary layer is re-established. Consequently, a higher overall extraction efficiency is expected in the gas purged PIME. A comparison between nitrogen purged membrane with only water elution is presented in Fig. 4.13. It is clearly seen that along with a shorter lag time, the response is significantly higher in the nitrogen purged membrane. In this experiment with toluene, the response was 33% higher in the purged membrane as compared to the one with aqueous elution only. The sample initially encountered a "clean" membrane with no boundary layer and since the contact period with the membrane was only 6 minutes, a fully developed boundary layer was never formed. However, in case of water elution where an aqueous solution continuously flowed through the membrane, a fully developed boundary layer was always encountered.

4.4 Conclusion

The system performances in terms of lag time and sensitivity were studied. Sensitivity was increased by increasing the extraction efficiency, and reducing the thickness of boundary layer. Eluent flow rate and sample size were important factors for a high response and a short lag time. A spiral membrane module with a long hollow fiber provided enhanced sensitivity; and nitrogen purge was effective in reducing lag time and enhancing sensitivity.

CHAPTER 5

CONTINUOUS MONITORING OF VOLATILE ORGANIC COMPOUNDS IN WATER USING PULSE INTRODUCTION MEMBRANE EXTRACTION (PIME)

5.1 Introduction

Conventional analytical techniques for measurement of volatile organic compounds (VOCs) in water are purge and trap, and head space analysis. These processes usually involve distinctive steps, such as, sampling at site, transportation, storage, and sample preparation before GC analysis. Sample loss and cross contamination during any of these steps can introduce errors in the measurements. These techniques are designed for laboratory analysis of discrete samples and are not suitable for continuous, on-line monitoring. Laboratory analysis is also expensive and limits the number of samples that can be analyzed. In these techniques each sample represents concentration of the sample at a given point in time or space and information on temporal variations in a sample stream is not obtained. At present, there is a real need for instrumentation for continuous monitoring of trace level organic compounds in waste water discharge and process streams. This is especially true as clean fresh water becomes scarce and water recycling becomes more prevalent. Continuous monitoring of high purity water in semi-conductor manufacturing is another important application. For a continuous monitoring technique, the separation of organics from water matrix has to be carried out on-line in a continuous fashion prior to analysis by an instrument. On the whole, the advantage of continuous monitoring is high quality data at a lower analytical cost.

Membranes offer the advantage of continuous on-line extraction of analytes, because the sample can be introduced continuously on the feed side, while the analytes permeate selectively to the permeate side where they are removed. Membrane have been used in a variety of applications such as gas separation, dehumidification, dialysis, osmosis and reverse osmosis[43]. Although industrial scale membrane process have been around for many years, the analytical applications are limited. Most common analytical applications of membrane extraction have been the development of membrane interface with mass spectrometer (MIMS) [14-21], where the sample continuously flow at the feed side of the membrane and the permeated organics are led directly into the ion source of the mass spectrometer. Membrane interface with mass spectrometer has been used in continuous monitoring of water and air streams [15-19]. Continuous in vivo mass spectrometric determination of select organics in blood with a membrane probe has also been reported [20]. However, real world environmental samples usually contain numerous species which results in a complex mass spectrum that is difficult to interpret. In some cases, gentle ionization techniques are used to avoid extensive fragmentation to obtain a simple spectrum. In MIMS, the vacuum in the mass spectrometer provides a large partial pressure gradient required for mass transfer across the membrane. In gas chromatography, the driving force for mass transfer is significantly less because a positive pressure has to be maintained for the flow of carrier gas. Over the past few years, we have reported the development of On-line Membrane Extraction Microtrap Gas Chromatography (OLMEM-GC) [23, 33, 37] for continuous monitoring of organics in water and air. In OLMEM-GC, water or air sample continuously flowed into membrane module and

nitrogen flowed countercurrently at the permeate side to strip the permeated organic compounds into a vapor phase. The organics were transported to and concentrated in a micro-sorbent trap (referred to as the microtrap). The microtrap is a silica lined tube packed with sorbent. The concentrated organics were injected onto a GC column by rapid thermal desorption of the microtrap using a 1.2 seconds pulse of electrical current. Continuous monitoring of water stream was performed by running the water continuously though the membrane and periodically making microtrap injections. Corresponding to each injection, a chromatogram was obtained. This method demonstrated high precision, large linear dynamic range, low detection limits and the ability to monitor a variety of organic compounds in water.

In general, most analytical applications of membrane extraction have involved continuous introduction of the sample into the membrane. In these studies, the measurements were made after membrane permeation reached a steady state. Since the diffusion of analytes in the aqueous matrix, and through the membrane is a slow process, it takes a certain amount of time to reach steady state. Any measurement made during the unsteady state period does not represent the true concentration of the sample stream. Furthermore, a relatively large sample volume is needed for the analysis because the sample has to be introduced continuously. This is especially true when steady state is not reached instantly. Another limitation of this approach is that the sample could only be introduced as a flowing stream. There was no way to inject discrete samples. So, these techniques are limited to continuous monitoring application.

In the previous chapters, we have discussed the development of an alternative approach for continuous on-line membrane extraction referred to as pulse introduction membrane extraction (PIME). Here a pulse of sample is injected into the membrane for extraction. This concept can be used in gas chromatography, mass spectrometry, as well as other analytical techniques. In this study, the GC application (PIME-GC) is presented. The permeated organics are stripped by a flow of nitrogen, concentrated and injected into the GC using a microtrap. The system does not need to reach steady state, thus the errors associated with steady state requirement are eliminated. The lag time in PIME-GC is an important parameter since it determines the frequency at which the analysis can be carried out. It has been reported [55-57] that the mass transfer resistance in stagnant aqueous boundary layer formed on the membrane surface due to poor mixing of water with the membrane significantly reduces the permeation flux. In PIME-GC system, a pulse of nitrogen is used before and after the sample injection to eliminate the boundary layer and reduce the response time. The nitrogen purge of the membrane before the sample elution eliminates the existing boundary layer and increases permeation flux. Nitrogen purge membrane after the sample has passed through eliminates the sample tailing. This reduces response time and eliminates the boundary layer that is formed as sample passes membrane module.

In this study, the application of PIME-GC for continuous analysis of VOCs in a water stream is reported. A sample valve is used for injecting samples onto an eluent stream which carries it to the membrane. Continuous monitoring is done by injecting water sample into the membrane at predetermined intervals. Corresponding to each

sample loading, a chromatogram is obtained. A short lag time is required for continuous monitoring. In this study, conditions for short lag time are presented. A comparison of PIME with steady state, continuous sample introduction is also presented.

5.2 Experimental Section

The PIME-GC system is shown on Fig. 5.1. The water sample was injected using an automatic 6 port valve. Membrane module was made of 20 pieces of 0.290 mm OD×0.240 mm ID composite membrane (Applied membrane Technology, Minnetonka, MN). The membrane is comprised of 1 μm thick film of homogenous siloxane supported on microporous polypropylene fiber. The membrane module was constructed by inserting hollow fiber membranes into a 1/8'' OD stainless tubing.

The microtrap was made from 15 cm long, 0.5 mm ID silcosteel tube (Restek Corp.) packed with carbotrap C (Supelco, Supelco Park, PA). The microtrap was heated with a 1.2 second pulse of 10 amperes current supplied by a Variac. Mili Q water was used as the eluent and was pumped through the system using an HPLC pump. A HP 5890 series II GC (Hewlett Packard Company, Avondale, PA) equipped with a Flame Ion Detector and a 30 m long , 0.53 mm OD × 0.21 mm ID SE-54 column with 2.4 μm thick stationary phase were used for analysis. A HP chemstation 3365 software package was used for data acquisition.

The sample stream flowed continuously through the sample loop of the injection valve. Periodically injections were made, and the eluent transported the sample to the membrane. Each injection sent a pulse of sample into the membrane module. Flow

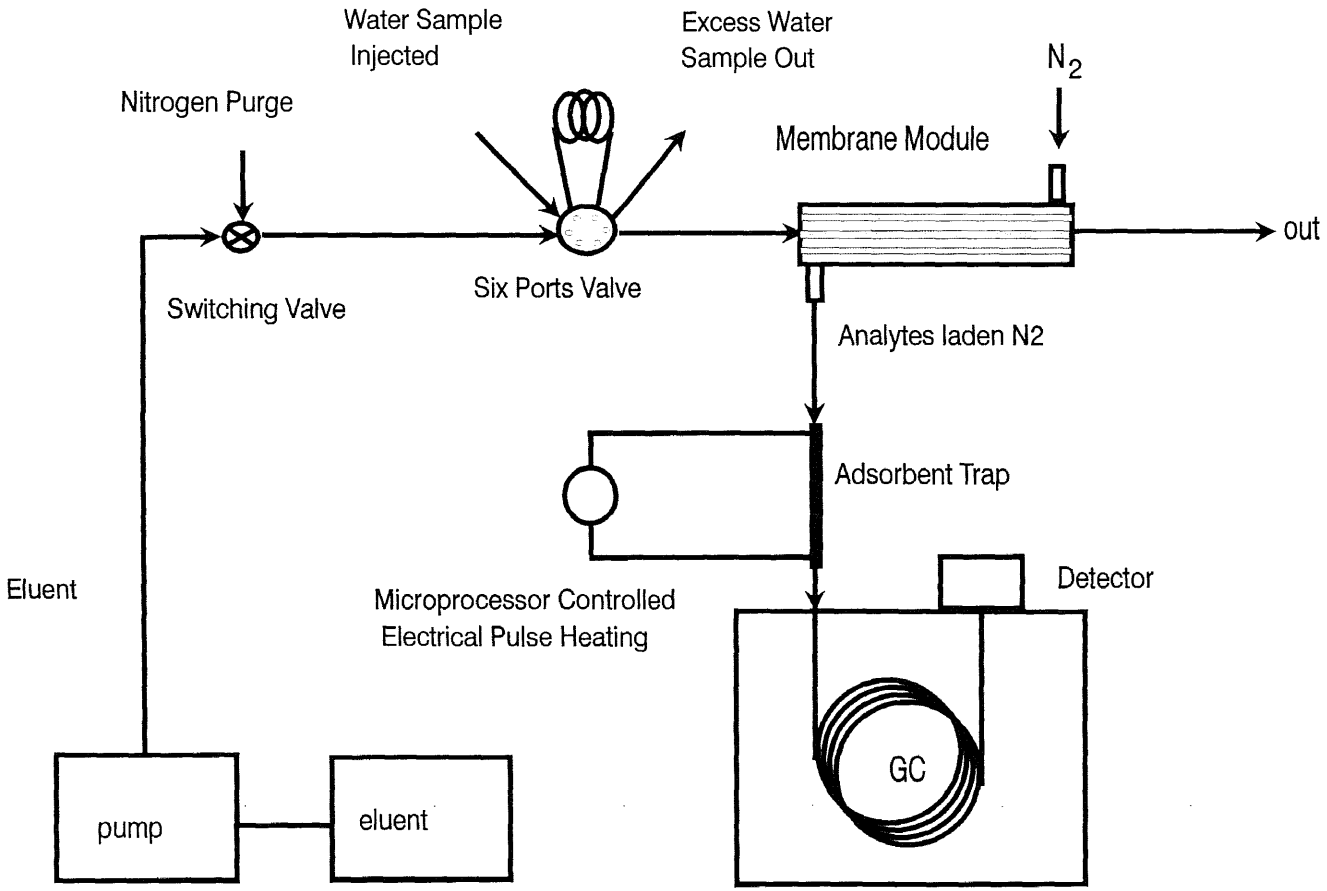


Fig. 5.1 Schematic diagram of the pulse introduction membrane extraction GC system.

through configuration was used, i, e, water sample passed the inside of membrane while nitrogen stream passed on the outside of membrane contercurrent to water flow. The nitrogen served as a stripping gas as well as a carrier gas for GC. Analytes from water permeated through the membrane to the outside of the membrane, were stripped by nitrogen gas and concentrated by the microtrap. After the sample passed through the membrane and the permeation was complete, the microtrap was thermally desorbed to inject the sample into the GC. For large sample volumes, for which the response time is large, a flow of nitrogen was used to clean the membrane after sample passed through it. A three way valve was used to introduce the nitrogen purge. The interval between the sample injection and the nitrogen purge was optimized.

The continuous monitoring was done by injecting the sample at regular intervals and corresponding to each injection, a microtrap pulse generated a chromatogram. The membrane module was maintained at 50°c to accelerate the diffusion. All transfer lines between the membrane module and the microtrap were heated to 70°c to prevent condensation of organics.

5.3 Results and Discussion

5.3.1 Continuous Monitoring of Water with PIME-GC

Continuous, on-line monitoring involves making a series of injections. An important consideration in membrane extraction is the slow permeation rate of the analytes through the boundary layer and the membrane. For each sample injected, the permeation of analyte must be complete before the next sample can be injected. To determine the time

required for extraction, a sample was injected and the microtrap was pulsed every 30 seconds to monitor the permeate concentration. Permeation profiles as shown in Fig. 5.2 were obtained. The response time which is the duration of the permeation profile increased with sample size, and can be reduced by nitrogen purge as mentioned before.

In this study two different approaches were taken to carry out continuous monitoring at relatively high frequency (every few minutes), while having the sensitivity to analyze at ppb levels. The first approach was to inject a small sample volume (0.4 ml) to ensure short response time of 5 minutes. A small volume sample passes rapidly through the membrane resulting in a reduced response time. A long membrane module was used to ensure high extraction efficiency. The other approach was to use a relative larger volume sample (2 ml), and then to use a nitrogen purge to reduce the response time. For the 2 ml sample, the response time was 12.5 minutes. However, by initiating nitrogen purge 4 minutes after sample injection, the response time decreased to 5 minutes. From the response profiles shown in Fig. 5.2 it can be seen that response time was limited to 5 minutes in either case, and continuous monitoring of water at that interval was possible.

A series of chromatograms from repeated injections of 0.4 ml sample without nitrogen purge is shown in Fig. 5.3. Here the water sample containing 30 ppb of benzene, 30 ppb of toluene and 40 ppb of chlorobenzene was analyzed. For the sake of brevity, a similar series of chromatograms from 2 ml sample injection with nitrogen purge of the membrane is not presented here. Here the analysis frequency was limited by the separation time on GC column rather than the response time of membrane permeation. Each injection represented concentration of the sample stream at a point in time. Since

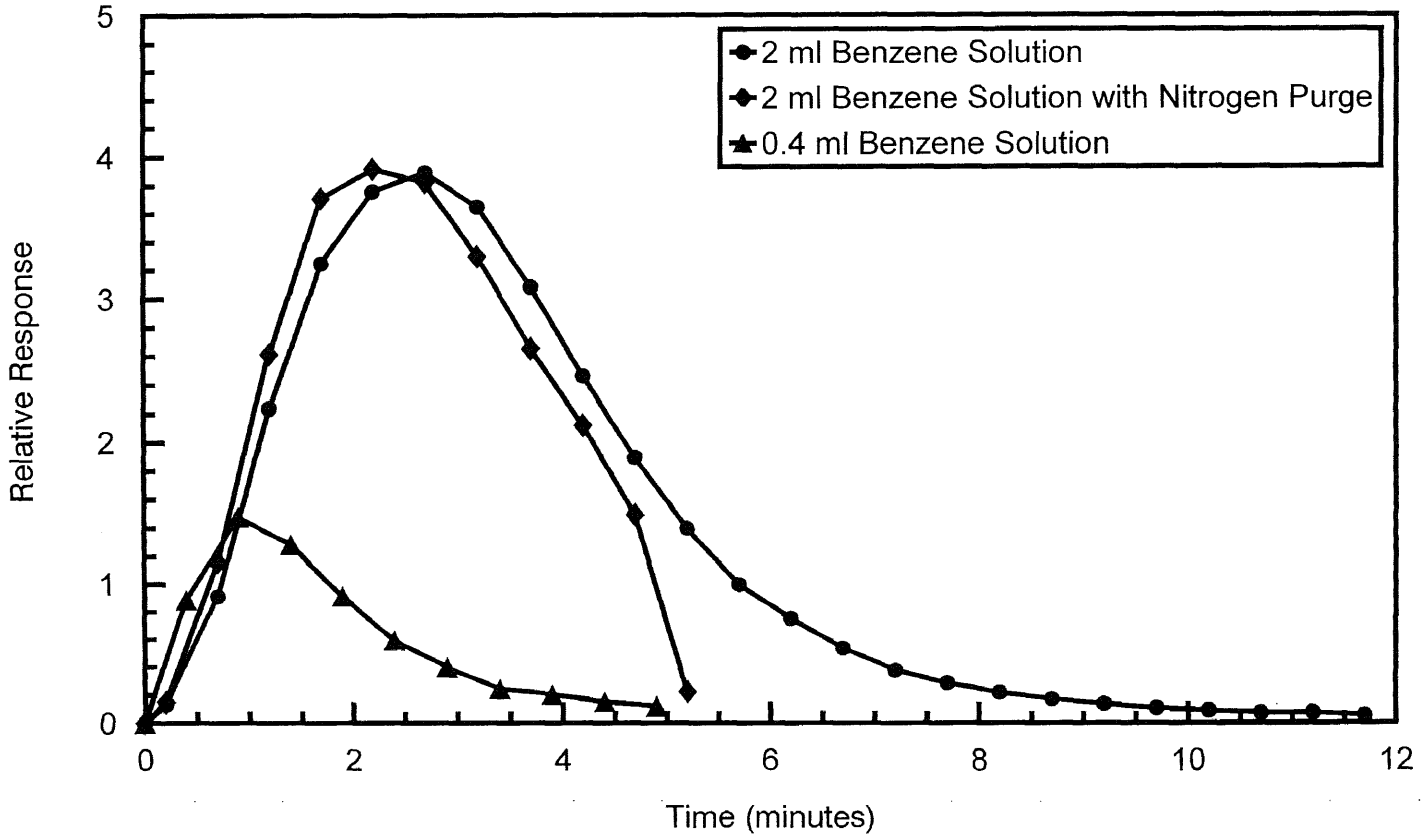


Fig. 5.2 Permeation profiles of benzene. A sample containing 48 .7 ppb benzene at an eluent flow rate of 0.8 ml/min was used.

any carryover from a previous injection would introduce error, it was important that the response in Fig. 5.2 came down to zero before the next injection was made.

Figure 5.3 shows good reproducibilities of retention time, peak shape as well as peak area and demonstrated the applicability of PIME in continuous monitoring. Relative standard deviations based on five replicate injections of benzene, toluene and chlorobenzene were 3.5%, 2.6% and 3.3 % respectively for 0.4 ml sample injection and 5.3%, 5.6% and 5.7% for 2 ml sample injection with nitrogen purge membrane. This shows the good precision of the analytical system. Typical calibration curves for different organics are shown in Fig. 5.4. The data presented here is for 1 ml sample injection followed by nitrogen purge of the membrane. The system demonstrated linear response in the low ppb levels studied here.

Short response times could be obtained by both approaches mentioned above and both are suitable for continuous monitoring. The advantage of large sample loop with nitrogen purge is that a larger amount of sample is injected resulting in a larger detector response thus higher sensitivity. The advantage of using a small injection volume without nitrogen purge is that the instrumentation and the operation is simpler. The method detection limits (MDLs) for 0.4 ml injection were 0.0031 ppb, 0.0068 ppb and 0.0035 ppb for benzene, toluene and chlorobenzene respectively. The MDLs were evaluated by 7 replicates and calculated according to EPA standard method [67]. Lower detection limits are expected with 2 ml sample with nitrogen purge since more sample can be injected.

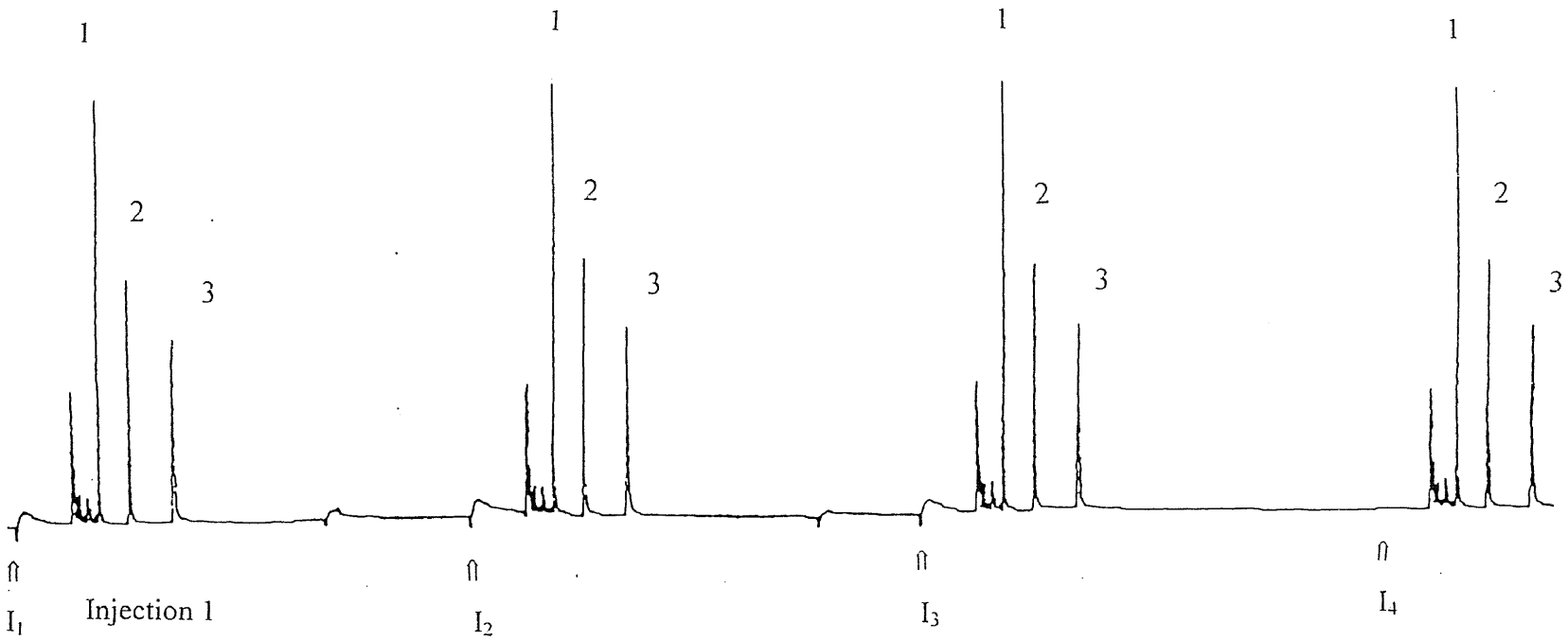


Fig. 5.3 Series of chromatograms of continuous monitoring a water stream

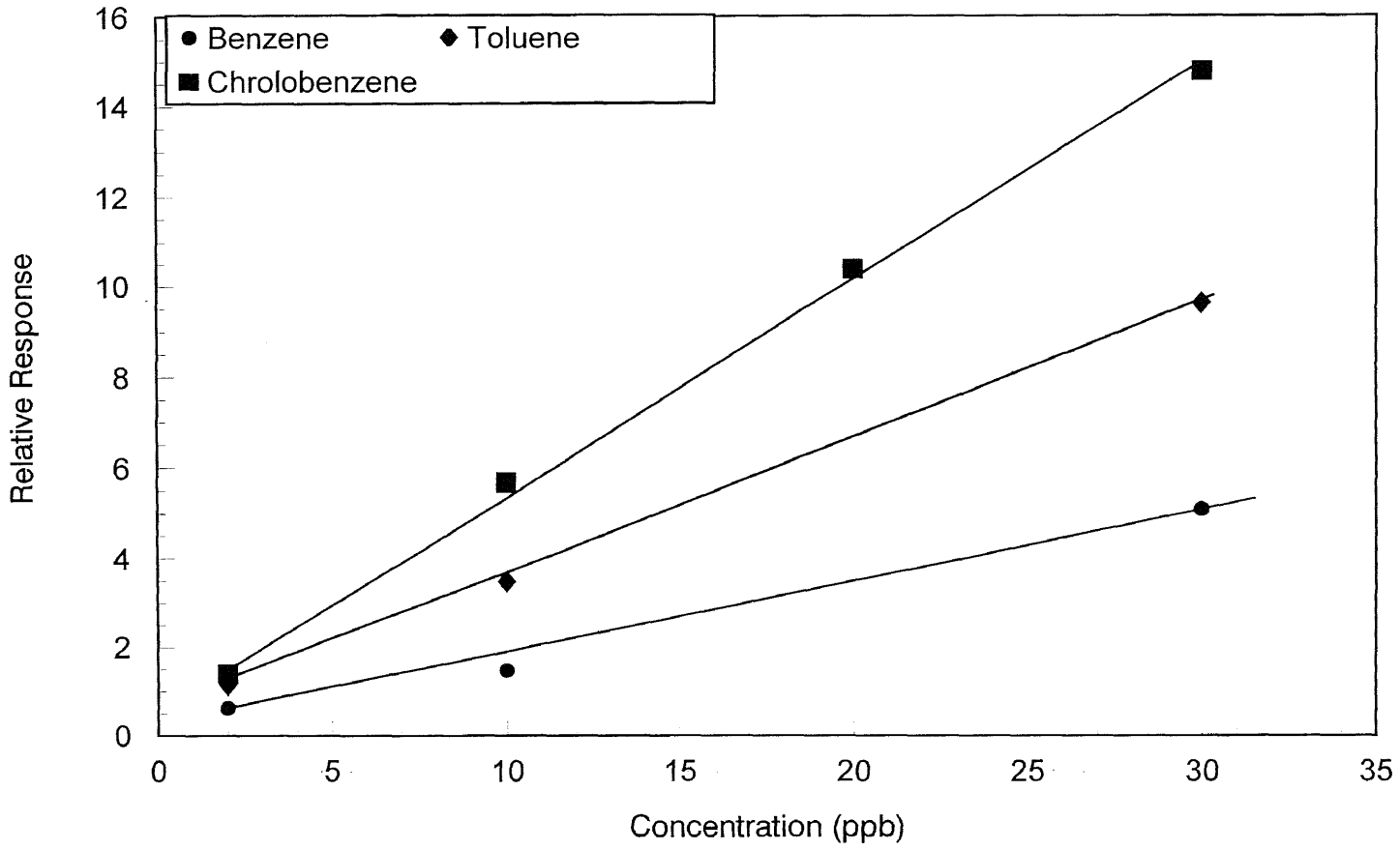


Fig. 5.4 Calibration curves for different VOCs in PIME. A 1 ml sample at flow rate of 0.8 ml/min was used. Nitrogen was turned on 5 minutes after sample injection.

5.3.2 Comparison with Continuous Sample Introduction

The pulse sample introduction approach of PIME was compared with continuous sample introduction of OLMEM. Different from PIME, in OLMEM, the water sample continuously flowed through the feed side of the membrane and the contercurrent gas stream continuously stripped the permeated organics. The organics were concentrated and injected by the microtrap at regular intervals into the GC. Since the sample flows continuously, nitrogen purge of membrane can not be used to break the boundary layer. There is also no way of injecting individual samples in this approach and it can only be used for on-line analysis. PIME is a versatile system where individual sample can also be analyzed by manually injecting the samples. The differences between the two systems can be understood by studying the permeation process.

The flux across the membrane according to Fick's laws is:

$$J = -D(\partial C/\partial x) \tag{5-1}$$

where the J is the flux, D is the diffusivity of the compound in the membrane, C is the analyte concentration in membrane, and x is the position along membrane thickness. Fick's second law describes the analyte concentration as a function of membrane thickness and time:

$$\partial C/\partial t = -D_{AB}(\partial^2 C/\partial x^2) \tag{5-2}$$

In OLMEM, the water sample continuously flows through the membrane and the measurements are made when the permeation reaches steady state. Therefore the left side of equation (5-2) is zero, and the concentration distribution in membrane is linear ($\partial C/\partial x$ is a constant). Assuming the concentration at the permeate side to be zero due to the high

nitrogen stripping rate, integration of equation (5-1) along the membrane thickness results in a steady state permeation flux J_{ss}:

$$J_{ss} = D(C/L) \tag{5-3}$$

where L is membrane thickness. The steady state permeation flux is constant for a certain sample concentration C at fixed operating conditions.

On the other hand, in PIME, the membrane receives a sample pulse of certain duration (Δt) and the permeation does not reach steady state. For a pulse sample input, the boundary conditions are as follows:

At the feed side, at time $t = 0$, $C = 0$, changes to $C = kC^*$

at $0 < t < \Delta t$, $C = kC^*$

at $t = \Delta t$, $C = kC^*$, change to $C = 0$

at $t > \Delta t$, $C = 0$

C is the analyte concentration at membrane surface, C* is concentration in water and k is the distribution coefficient of the organic between water and membrane. The mathematical solution for equation (6-1) and (6-2) for the PIME system is [44, 46]

$$J_{ns.} = J_{ss}(1+2\sum_{n=1}^{\infty}(-1)^n \exp.\{-n^2(\pi)^2(D(t)/l^2)\}) \quad \text{when } t < \Delta t \tag{5-4}$$

$$J_{ns.} = J_{ss}(2\sum_{n=1}^{\infty}(-1)^n \exp.\{-n^2(\pi)^2(D(t)/l^2)\} - 2\sum_{n=1}^{\infty}(-1)^n \exp.\{-n^2(\pi)^2((D/l^2)(t-\Delta t))\})$$

when $t > \Delta t$ (5-5)

So, along with the sample concentration, the permeation flux is also a function of time in the PIME system. The permeation profile is similar to Gaussian distribution shown in Figure 5.2. The Δt which is determined by the sample size and flow rate is an

important parameter for system response (i. e. sensitivity) and response time. The analysis time is limited by the response time for a complete permeation. According to equation (5-4), if the Δt is very long, the system approaches steady state.

Analyte diffusion through boundary layer and the membrane matrix are the major resistance to mass transfer and are the rate limiting steps. The system also has a certain internal volume. Thus it takes a certain amount of time to reach steady state. In this study, the time required to reach steady state was experimentally determined. Fig. 5.5 shows the response of the analytical system to a step change in concentration. As the concentration changed from 45 ppb to 14.5 ppb at a flow rate of 1 ml/min, the system response lagged behind and it took more than 40 minutes to reach the 14.5 ppb level. This demonstrated that the time required for equilibrium is fairly long. In continuous sample introduction methods, where steady state is a prerequisite, a measurement in the non-equilibrium region does not represent the true value. In this region, each chromatogram is an average response proportional to the permeation over that injection interval. This is only an approximation. For error-free analysis, one has to wait till steady state is reached before doing the next analysis. On the other hand, the PIME system has no steady state requirement and each injection truly represents the sample concentration. The only consideration is the elimination of carryover from the previous sample, which was taken care either by nitrogen purge or by using small sample volume.

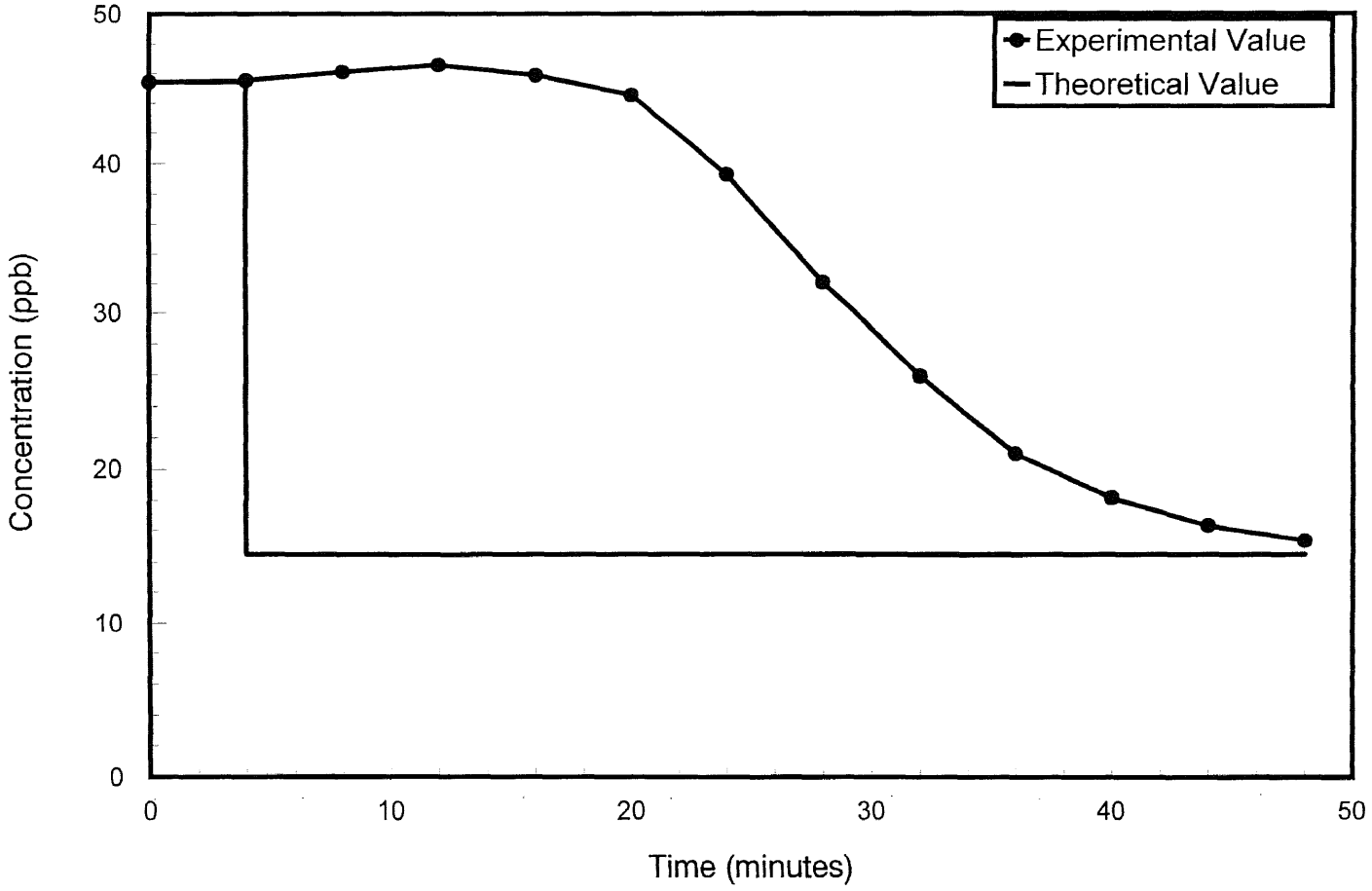


Fig. 5.5 System response of OLMEM system during sample concentration change. During the monitoring, toluene concentration changed from 45.4 ppb to 14.5 ppb. Flow rate of 1ml/min was used.

5.3.3 Advantage of "Fresh Membrane"

The theory of "sorption and diffusion" is widely used to describe permeation through nonporous membrane. The solute first partition into membrane surface and an equilibrium is established between the aqueous sample and membrane. The concentrations of organics in the membrane depends upon the partition coefficient according to:

$$C = kC_w \tag{5-7}$$

The dissolved solute rotates and translates the polymer segment utilizing the diffusion activation energy and then creates a suitable size vacancy to jump in. The diffusion direction is determined by the concentration gradient. In the membrane permeation process, the diffusion is found to be the rate limiting step. This is also consistent with our observation in Fig. 5.2, where the sample was in contact with the membrane for only 0.5 minutes, the response time was 5 minutes or more.

When sample is carried to the membrane by water, the front part of sample pulse immediately dissolves in the "fresh membrane" where the analytes concentration is zero, providing a large driving force for diffusion. The tailing part of pulse now encounters membrane that has some analytes within it. Thus the driving force is lower in this section of the sample pulse. The phenomena can be illustrated as follows. The analyte uptake ΔM at any time is the amount of analytes in the membrane minus what was already there.

$$\Delta M_f = V_m C - 0 = V_m kC_w \tag{5-8}$$

ΔM_f is the mass uptake for the front part of the pulse encountering "fresh membrane". Here the V_m is the membrane volume. The analyte uptake ΔM_l in the tailing part of the sample pulse, where original concentration in membrane is C_0:

$$\Delta M_l = V_m C - V_m C_0 = V_m (kC_w - C_0) \quad (5\text{-}9)$$

It is evident that the analytes uptake of the later part of the sample pulse is less than that of front part. Fig. 5.6 is plot of response per unit volume sample v.s. sample volumes of same concentration sample injected into membrane. No gas purge of the membrane was done here. A sample containing 100 ppb of benzene and toluene, and an eluent flow rate of 1 ml/min were used here. The Response/Volume for 5 ml sample is assumed to be 1. (this is to normalize the response of different volume and different chemicals.) As the sample volume increased, the response per unit of volume decreased because relatively lesser amount of analyte encountered the "fresh membrane". The curve is more or less flattened past 3 ml, and possibly equilibrium was reached in this region. Beyond this, the response was controlled by the rate of diffusion through membrane rather than sorption or dissolution in the membrane. This indicates that for the same amount of analytes, small sample injected on a "fresh membrane" would provide higher sensitivity than sample continuously flowing into the membrane. A sensitivity comparison of 0.4 ml sample introduced by PIME and OLMEM systems under similar operating conditions was carried out and the results are shown in Fig. 5.7. In PIME, 0.4 ml sample was injected onto the "fresh membrane" while in OLMEM, sample continuously flowed into the membrane. When reaching steady-state, the analyte in the membrane surface established an equilibrium with diffusional analytes in the membrane thus reducing the driving force

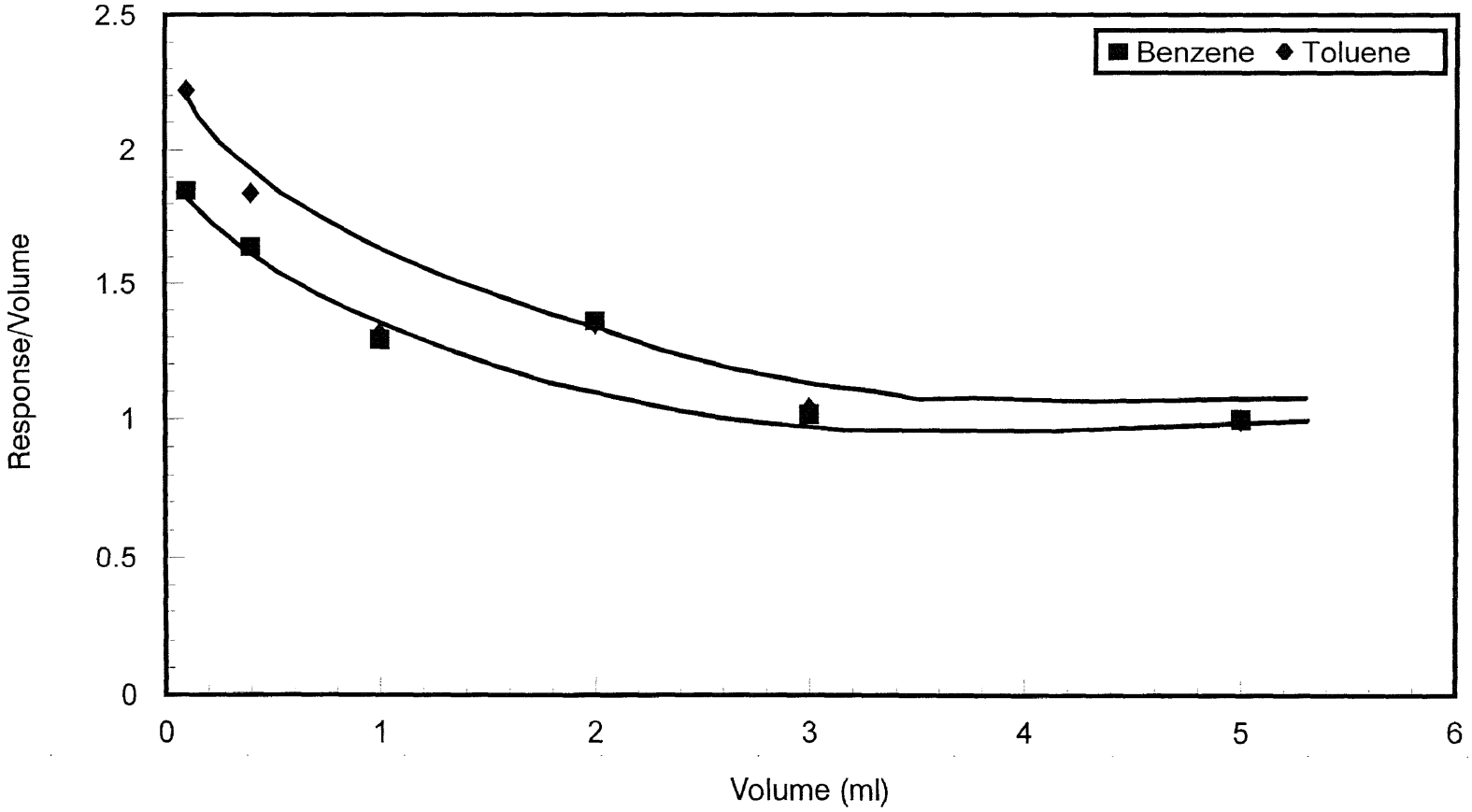


Fig. 5.6 Response per unit of sample volume as a function of sample volume. Samples containing 100 ppb benzene and toluene at flow rate of 1 ml/min were used. The response per unit of sample volume for 5 ml sample were assumed to be 1.

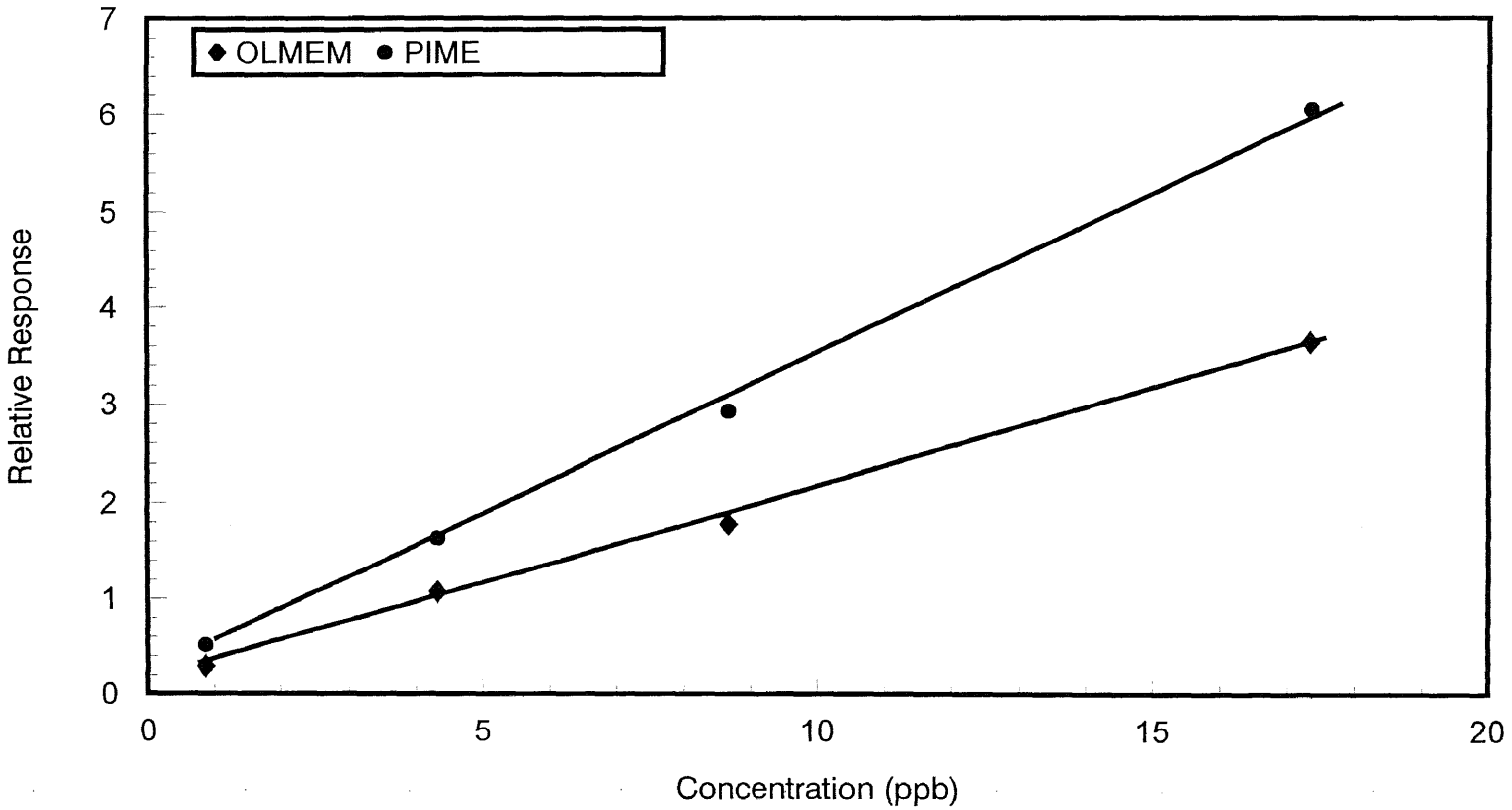


Fig. 5.7 Comparison of sensitivity for PIME and OLMEM based on fresh membrane effect. 0.4 ml toluene samples at flow rate of 0.7 ml/min were used.

for dissolution. The slope of the calibration curve for PIME was 1.67 times larger than that of the OLMEM demonstrating a higher sensitivity of this approach. Method detection limits (MDLs) for 0.4 ml sample in PIME-GC were 0.0031 ppb for benzene and 0.0068 ppb for toluene. Under the same condition, MDLs were 0.0043 ppb for benzene and 0.0086 ppb for toluene using OLMEM-GC. Both methods exhibited low detection limits, but PIME was more sensitive and had lower detection limits because of the "fresh membrane" effect.

5.3.4 Advantage of Nitrogen Purge

As water flows through the membrane at low velocity, a stagnant film (or the boundary layer) is formed at the membrane surface. The contribution of the boundary layer to overall mass transfer resistance in membrane permeation has been studied extensively [55-57]. Generally speaking, the relative contribution of the boundary layer to total mass transfer resistance across membrane depends upon the chemical nature of the analyte, flow conditions and membrane thickness. The flow conditions can be represented by Reynolds number [54]:

$$Re = (\nu\, d\, \rho)/\mu \qquad (5\text{-}10)$$

Where ν is the velocity of the water, d is the diameter of the tubing, ρ is the sample density and μ is the viscosity of the sample. At higher Re (over 20,000), turbulent condition eliminates the effects of the boundary layer. In our experiments, Re was less than 100 and membrane used was as thin as 0.025 mm. Studies [55-57] have shown that

at these conditions, the boundary layer is well formed and results in a significant resistance to mass transfer.

In PIME system, a nitrogen purge was used to break up the boundary layer and eliminate sample tailing to increase system response and reduce response time. First the membrane was purged with nitrogen so that there was no boundary layer on the membrane surface to begin with. Then water was used to elute the sample during which, the boundary layer was formed. After the sample passed through, nitrogen was used once again to "freshen" the membrane and eliminate the sample tailing. Moreover, elution of the sample only took a few minutes, and the boundary layer was not formed completely. Thus, permeation rate was still higher than that encountered in a fully developed boundary layer of the steady state system. Since nitrogen purge is not applicable in continuous sample introduction, the sample always encounters a well formed boundary layer resulting in relatively lower permeation rate. A sensitivity comparison of 1 ml sample in continuous sample introduction, and PIME with nitrogen purge membrane was carried out and the result is shown in Fig. 5.8. It is clear that at the same concentration, the response is higher in the PIME system than that of sample continuous introduction. The ratio of the slopes of the calibration curves for PIME to that of sample continuous introduction was 1.57 demonstrating higher sensitivity of PIME system. This can be attributed to "fresh membrane" effect along with the reduction in boundary layer with nitrogen purge.

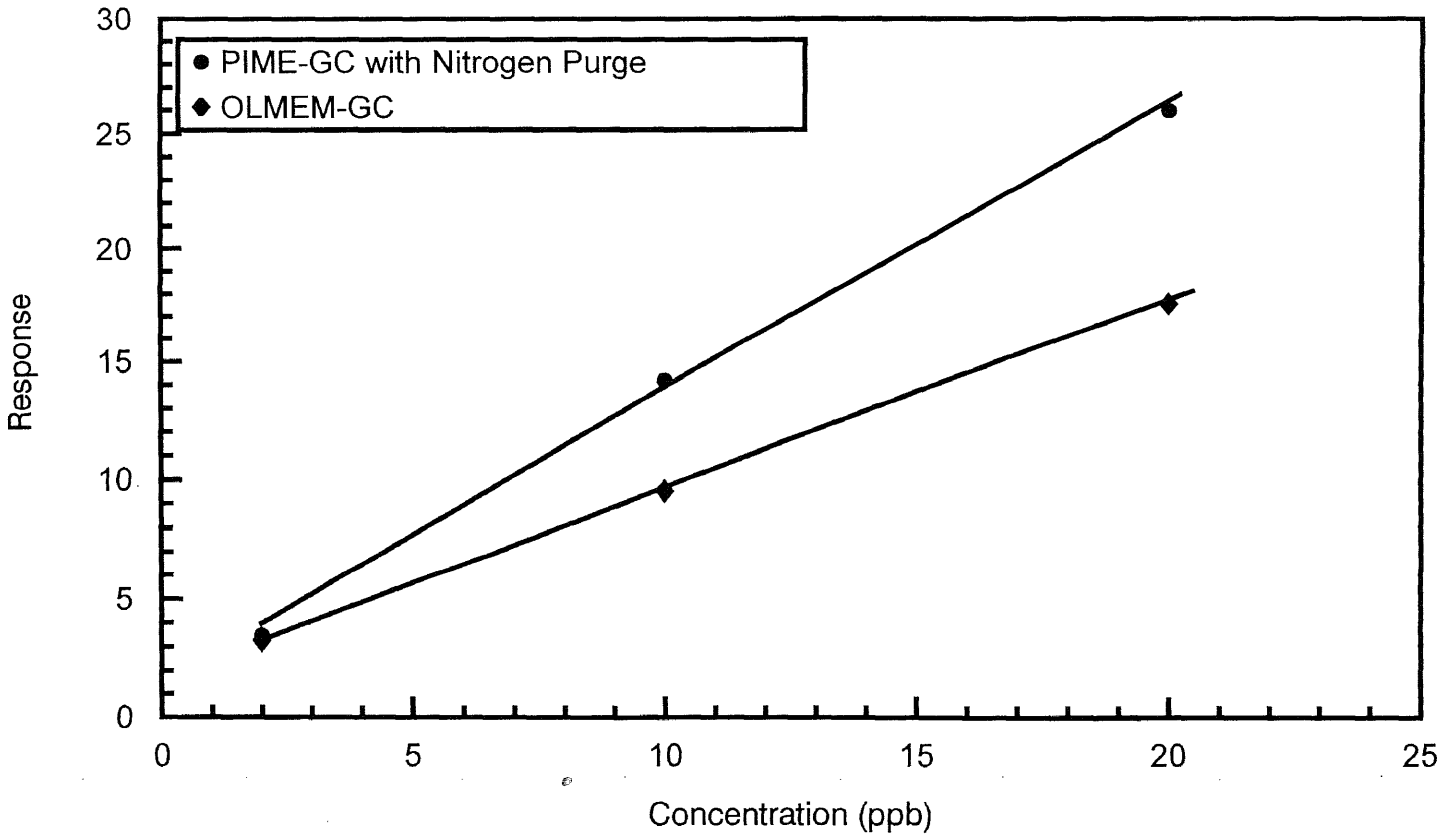


Fig. 5.8 Comparison of sensitivity for PIME and OLMEM based on nitrogen purge of membrane. 1 ml water samples containing chlorobenzene at flow rate of 0.8 ml/min were used.

5.4 Conclusions

The PIME system demonstrated capability of applications on both discrete sample analysis and continuous monitoring of organics in water. In the application of continuous monitoring, PIME showed faster response and higher sensitivity than sample continuous introduction system.

CHAPTER 6

CHARACTERISTIC STUDY OF PIME SYSTEM AND ITS APPLICATION

6.1 Introduction

In the previous chapters, the development of PIME system and the methods for enhancing its performance were studied. Good analytical performance in terms of linearity, low detection limits, high precision and extraction efficiency were obtained. The PIME was used for continuous monitoring of a water stream and compared to the previous developed continuous introduction system. The advantages of fast analysis, accurate response and the capability to analyze discrete samples were demonstrated.

Real environmental analysis is challenging since the real sample matrices are complex and contain a variety of different compounds. These require the analytical instrumentation to be rugged and be able to handle different samples. Conventional analysis methods include liquid-liquid extraction, solid phase extraction, head space analysis, and purge and trap. Among these, purge and trap is the most popular method, and several standard EPA methods are based on it. Purge and trap uses a stream of inert gas to purge a small amount of water sample. The purgable compounds are purged out and carried onto an adsorbent trap. Later, a thermal desorption is applied on the adsorbent trap and the analytes are refocused on a cryogenic trap. Another thermal desorption is needed for GC injection therefore a large cycle time is needed for purge and trap. The long travel path of analytes in the instrumentation may cause sample condensation and the moisture purged out often form ice which blocks the cryogenic trap. The

instrumentation is also bulky and expensive and is not suitable to be modified to continuously monitor water stream at site.

In this study, the performance of PIME was compared to that of purge and trap. Studies carried out here were focused on investigation of the PIME system characteristics, instrumentation design to meet the challenge of environmental analysis. Finally, the instrumentation was used to analyze real ground water sample.

6.2 Experimental Section

Membrane module was made of 12, 8.5 cm long composite membranes of dimension 0.260 mm OD×0.206 mm ID (Applied membrane Technology, Minnetonka, MN). The membrane module was heated using heating tape and a temperature controller (ACE Glass) was used to maintain a certain temperature. A HP 5890 series II GC (Hewlett Packard Company, Avondale, PA) equipped with a flame ionization detector and a 30 m long , DB-624 column with ID 0.32 mm and 1.8 μm thick stationary phase was used for GC separation. A HP Chemstation 3365 software was used for data acquisition and analysis. A purge and trap system of Tekmar LS 2000 model was used for the comparison with the performance of PIME system.

A multibed microtrap was prepared to retain VOCs of different volatility. The multibed trap contains Carbotrap C, Carbotrap B and a small amount of Carboseive S-III. The physical properties of the three adsorbents are listed in Table 6.1.

Table 6.1 General properties of the three adsorbents used in the study

Adsorbent	Carbotrap C	Carbotrap B	Carbosieve S-III
Particle Size	24/40 mesh	60/80 mesh	60/80 mesh
Surface area	10 m^2/g	100 m^2/g	820 m^2/g
Suitable application	carbon # > C_8	carbon # C_4-C_8	carbon # C_2-C_3

The schematic diagram of the multibed microtrap is shown in Fig. 6.1. The length of Carbotrap C, Carbotrap B and Carbosieve S (Superco, Superco Park, PA) in the multibed trap were 6.5 cm, 4.5 cm and 0.5 cm respectively, and the corresponding mass of sorbent were 0.0110, 0.0121 and 0.0010 g respectively. The multibed trap was attached to a 6 port injection valve (Valco Instruments Co. Inc., Houston, TX). Back-flush of the multibed was used to provide efficient desorption.

Contaminated ground water samples were obtained from several different wells in the Naval Engineering Research Center located at Toms River, NJ. They were stored in amber bottles in a refrigerator with zero head space and were analyzed within 4 days. Spiked water samples were prepared by spiking regent grade chemicals into water.

6.3 Results and Discussion

6.3.1 Microtrap Trapping Interval

In the PIME system, the permeating VOCs were accumulated onto the microtrap until the permeation is complete. Typical response as a function of pulse interval is shown in Fig. 6.2. It was observed that the responses increased linearly as the pulse interval increased

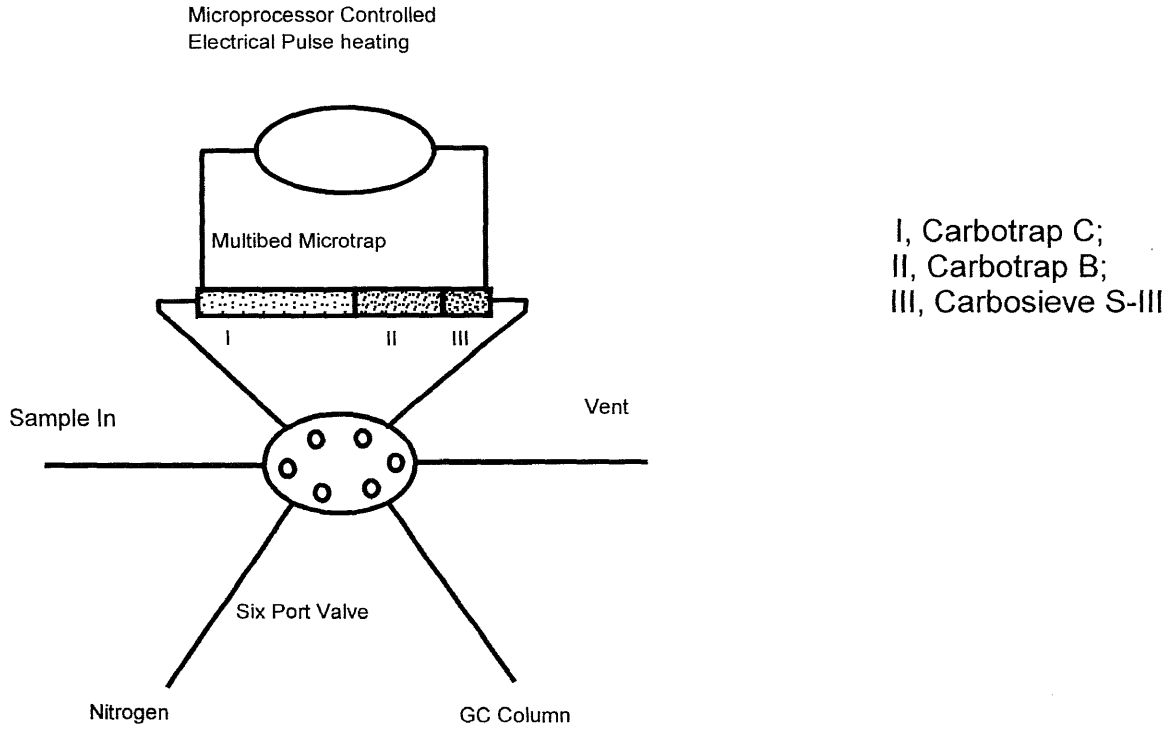


Fig. 6.1 Schematic diagram of multibed microtrap with back flush desorption

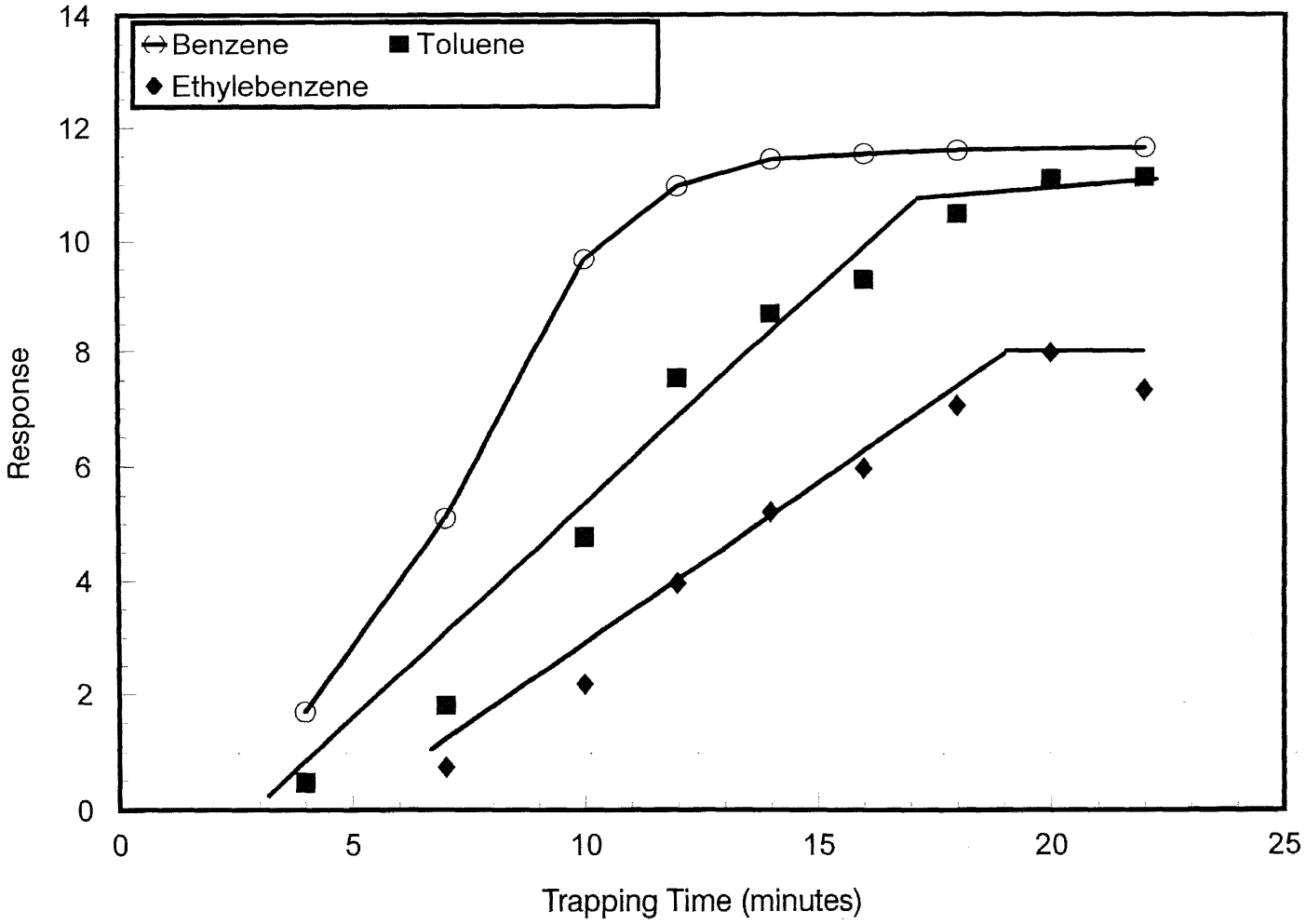


Fig. 6.2 Response a function of trapping interval

until a maximum was reached beyond which no more sample left the membrane module. GC injections can be made when the eluent concentration becomes constant. The time when the curves become flat depends on the sample volume, eluent flow rate et. al.. It is important that the sample does not breakthrough the microtrap during trapping and that will be discussed later in the study.

6.3.2 Temperature Effects

Three mass transfer mechanisms of vaporization, solvation and diffusion are involved in pervaporation. The overall resistance is the sum of resistance in aqueous phase and membrane as discussed in previous chapter. Diffusivity increases with temperature, e.g. diffusivity increased 35% in water and 45% in the membrane when temperature increased from 26-45 °C [15]. However temperature affects the membrane permeation of different compounds differently as shown in Fig. 6.3. For nonpolar compounds which can easily vaporize, temperature effects on response is limited by the temperature effects on diffusivity in aqueous phase and permeability in membrane. Solubility and diffusivity in membrane can be described by the Arrhenius-type relationship:

$$S = S_0 \exp(-\Delta E_s/RT) \tag{6-1}$$

$$D = D_0 \exp(-\Delta E_d/RT) \tag{6-2}$$

thus:

$$P = S \times D = P_0 \exp(-(\Delta E_d + \Delta E_s)/(RT)) \tag{6-3}$$

where E_s is heat of solution. For vapors the heat of solution is negative, thus solubility decreases with temperature. E_d is activation energy of diffusivity which is always positive. The solubility decreases with temperature while diffusivity increases. The

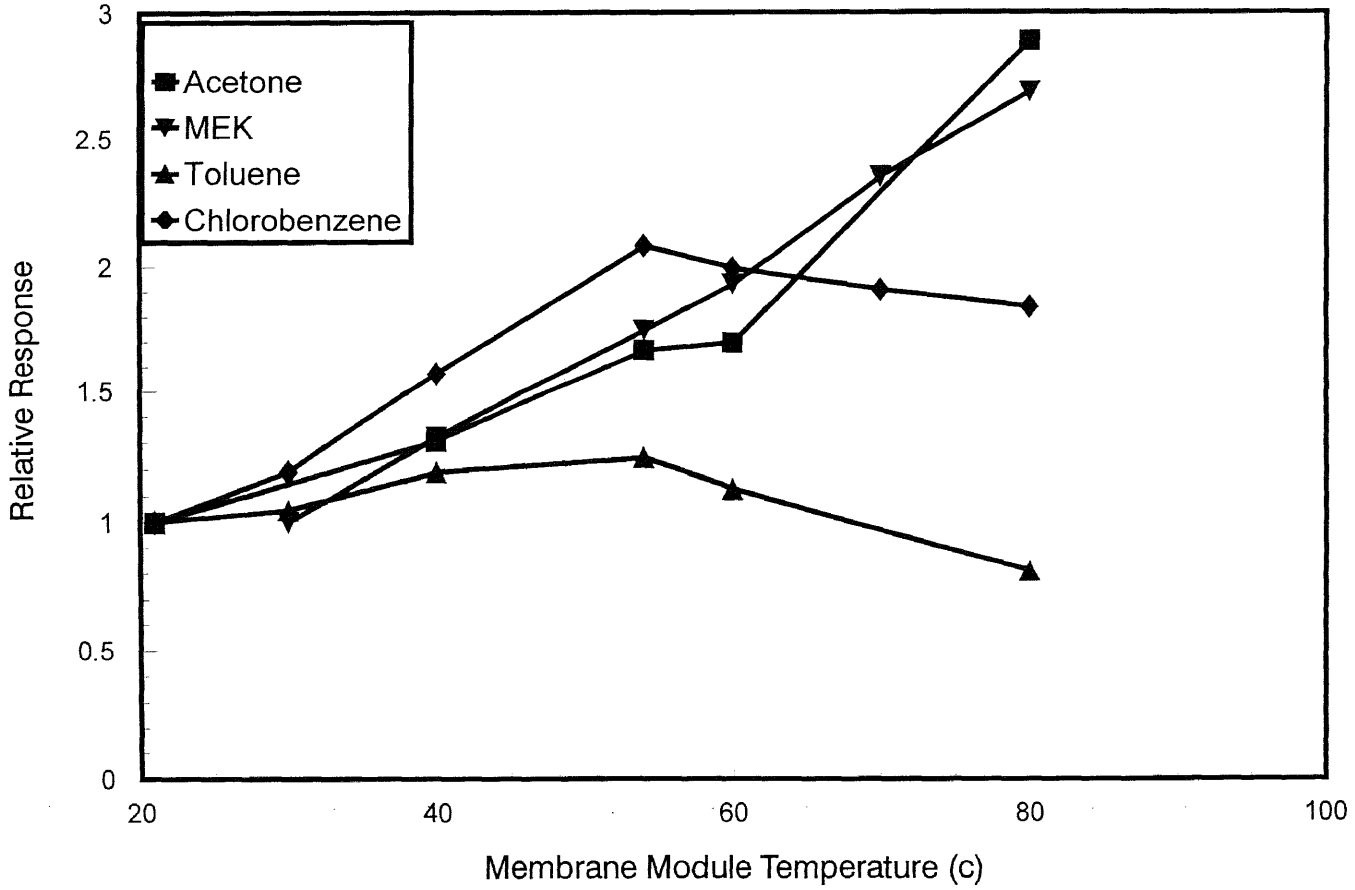


Fig. 6.3 System response as a function of membrane module temparature

responses of toluene and chlorobenzene over the temperature range studied here clearly illustrated the balance between these factors. At low temperature range, diffusivity increase results in higher permeation, and at higher temperature the drop in solubility reduces permeation. As a result, the optimum temperature for maximum permeation was between 50-60 ^{o}C as shown in Fig. 6.3. However, the response of ketones continued to increase at the temperatures studied here. The possible reason is that ketones have strong affinity for water. An increase in temperature increases the Henry's law constant k_D, and thus the partial pressure P_i according to:

$$\frac{d(\ln k_D)}{d(1/T)} = \Delta H / R \qquad (6\text{-}5)$$

$$P_i = k_D \times C_w \qquad (6\text{-}6)$$

where ΔH is heat of absorption which is negative and C_w is the concentration of analytes in water. The increased volatility of acetone and MEK in the aqueous phase along with increased diffusivity dominated the pervaparation rate at this temperature range. Therefore, an increasing response was seen.

6.3.3 Effect of Salinity

The real sample may contain salts, so it is necessary to study the salinity effect on PIME system response. The effects of salt concentration on system response was studied by adding NaCl into the sample. NaCl concentration range was from 0.2 to 3 M in the aqueous sample. The effects of salinity on the system response of 5 ml aqueous sample containing 50 ppb of benzene, 50 ppb toluene, 200 ppb acetone and MEK are shown on Fig. 6.4. At low ion concentration, the system response of these components were not

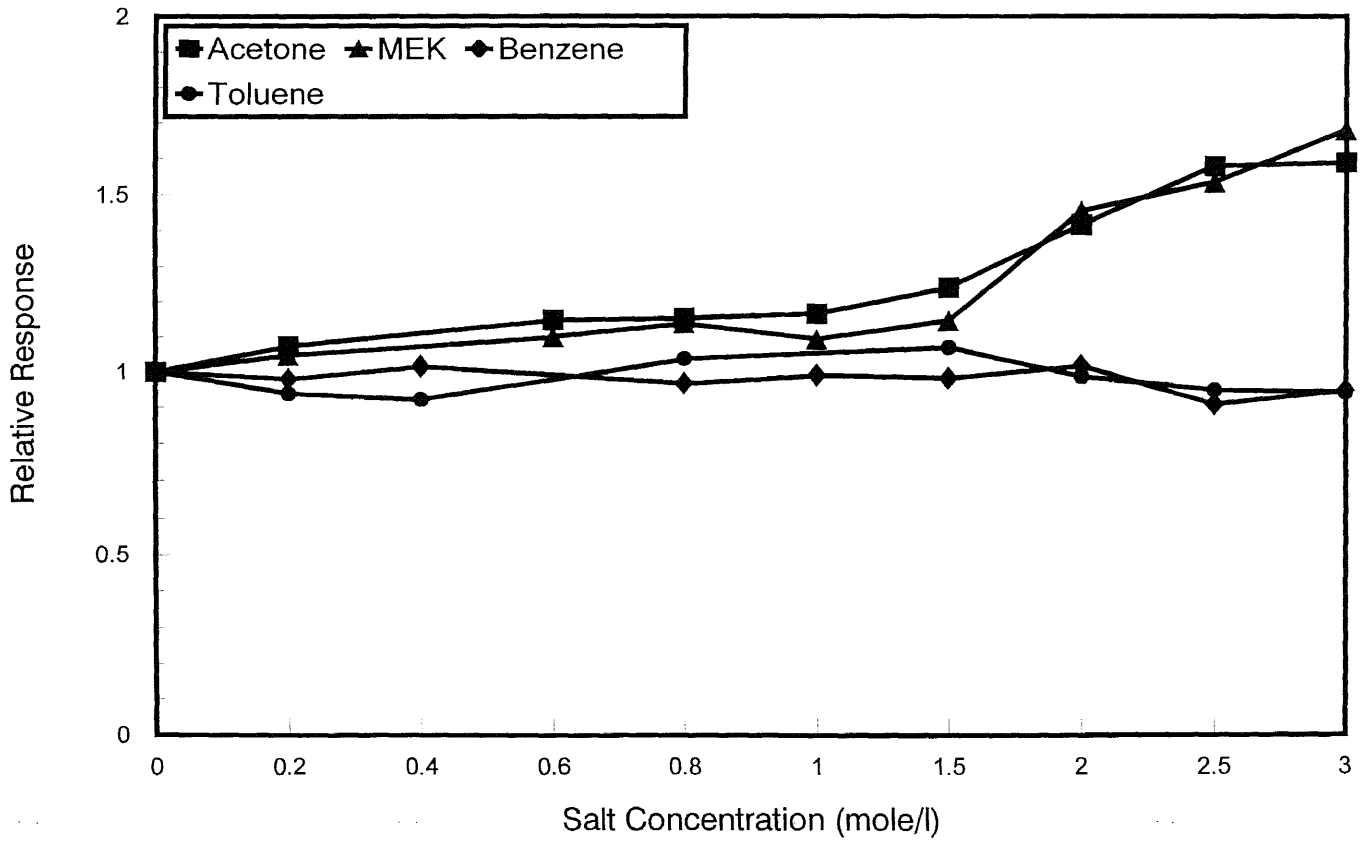


Fig. 6.4 Salinity effect on system response. Assume the response to be 1 when the salt concentration in the sample was zero.

significantly affected by the existence of ion. A typical real environmental sample's ion concentration is usually below 0.5 M, therefore the existence of ion has no effect on the system response. So, generally speaking, the analytical method is suitable for the analysis of environmental samples containing salts.

At high NaCl concentration (1.5 mole/L), the response of acetone and MEK increased as shown in Fig. 6.4. The possible reason could be that at high ion strength, the solubility of polar compounds in the solution may decrease. It also may weaken hydrogen bond between polar solutes and water, thus can facilitate the transfer from water to membrane. So a higher membrane permeation was observed for polar compounds. For nonpolar solutes, the major interaction between water and solutes is Van Der Waal force which are not effected by the existence of ion, thus their response were not effected. So a moderately high ion concentration in sample could be an approach to improve membrane extraction efficiency of polar compounds without interfering with the permeation of nonpolar compounds.

6.3.4 Multiple-bed Adsorbent Trap

In real world environmental samples, a large variety of VOCs with different molecular size, weight and volatility are encountered. It is important that the microtrap retain all the pollutants. At the same time, it should be possible to desorb them quantitatively. Common adsorbent of Carbotrap C is suitable for retaining compounds having 8 or more carbons. Small or light compounds have short breakthrough times in a Carbotrap C microtrap [70].

In order to increase the breakthrough time for small molecules on the microtrap, a multibed microtrap packed with 3 adsorbents with different absorbtion capacity was prepared. It was desorbed in a back-flush as shown in Fig. 6.1. The adsorbents in series were Carbotrap C, Carbotrap B and Carbosieve S-III. The sorption ability in terms of breakthrough volume increases, and the ease of desorption is decreased in this order. During trapping, the analytes first encounter Carbotrap C where heavy compounds were trapped. The smaller analytes breakthrough to Carbotrap B and Carbosieve S layers. During desorption, the flow direction was reversed, i.e. the flow is from Carbosieve to Carbotrap C. Consequently, the heavy compounds never come to contact with Carbosieve from which they are not desorbed easily. Details of the multibed microtrap and its breakthrough, and desorption characteristics have been studied in our research group [70].

A water sample containing molecules such as methanol and acetone which tend to breakthrough the Carbotrap C trap was analyzed by PIME with a multibed trap with back flush desorption. No breakthrough was observed. A typical chromatogram is shown in Fig. 6.5. Good separation and sharp peaks were observed which demonstrated the PIME system equipped with multibed trap can be used for analysis of a large variety of VOCs.

6.3.5 Comparison with Purge and Trap System

Purge and trap is the most common methods for VOCs analysis in water. The instrumentation of purge and trap is fairly complex and expensive. The analysis time is fairly long because purging, trapping, desorbtion, and cooling down of the heated trap take time. Compared to purge and trap, the instrumentation for PIME is much simpler

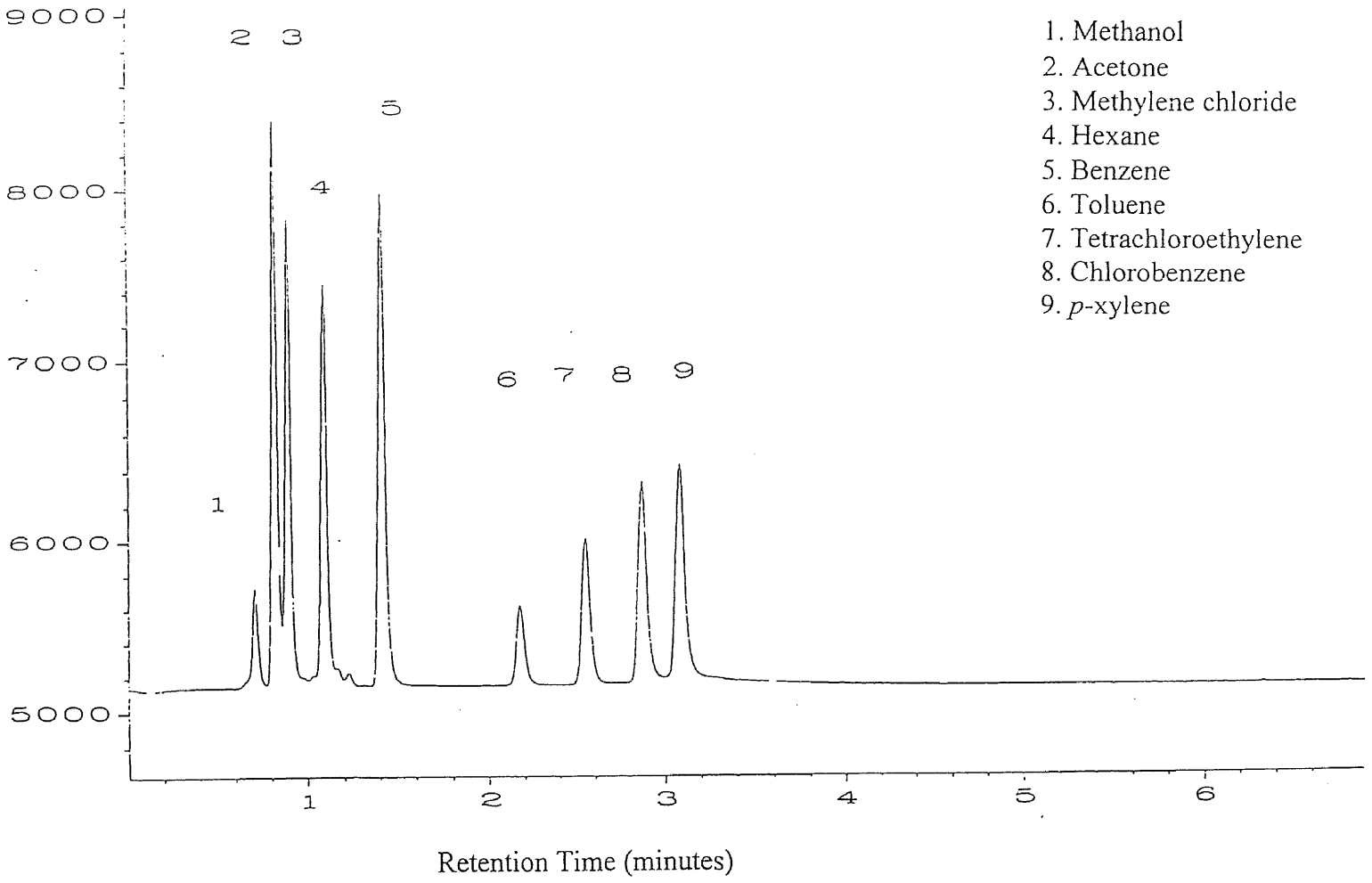


Fig. 6.5 Chromatogram of a multibed trap with back flush desorption

and more compact. It can be easily modified for on-line monitoring a process stream [39]. A PIME analysis can be complete in a few minutes depending on separation time of GC column, which is much shorter than about 30 minutes typically needed in purge and trap analysis. The high sensitivity of membrane extraction in the PIME system results in low detection limits. The method detection limits for PIME systems are presented in Table 6.2 and compared to that for purge and trap. It shows the method detection limits for PIME system are in part per trillion range and are lower than that of purge and trap.

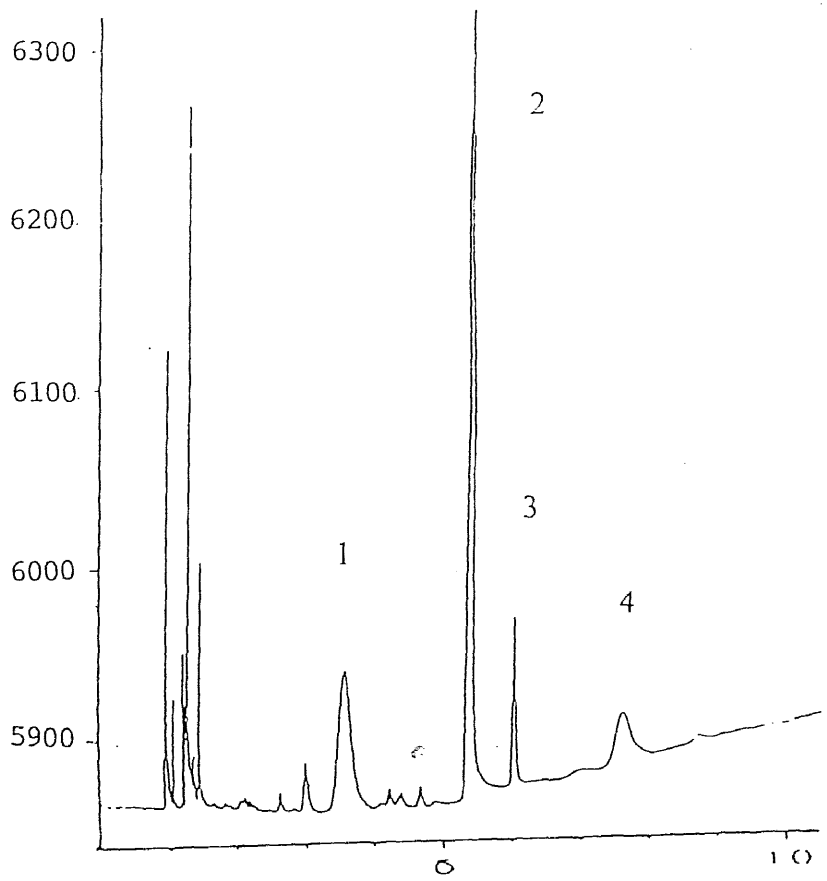
Table 6.2 Method detection limits for PIME system and compared to that for purge and trap system

Compounds	MDL of PIME (μg/L or ppb)	MDL in purge and trap (ppb)
Benzene	0.0012	0.04
Toluene	0.0063	0.11
Ethylbenzene	0.045	0.06
1,1,1-trichloroethane	0.010	0.08

A comparison of analysis of a typical water sample containing VOCs using PIME and purge and trap was carried out and the results are presented in the Table 6.3. As the table shows, good agreements for both method results were observed and the precision of PIME system was slightly higher.

Table 6.3 Comparison of PIME with purge and trap

Components		Pulse Introduction Membrane Extraction	Purge and Trap	Sample Value
Benzene	Concentration	70.3 ppb	72.5 ppb	69.0 ppb
	RSD	1.3 %	2.8 %	
Toluene	Concentration	71.3 ppb	80.1 ppb	74.2 ppb
	RSD	1.6 %	1.7 %	
1,1,1- Trichloroethane	Concentration	65.7 ppb	68.9 ppb	69.5 ppb
	RSD	1.6 %	6.6 %	



1. *cis*-1,2-Dichloroethene
2. 1,1,1- Trichloroethane
3. Trichloroethene
4. Tetrachloroethene

Fig. 6.6 Chromatogram of a ground water sample contaminated with chlorinated solvent from Naval Engineering Research Station at Toms River, NJ

Table 6.4 Analysis of ground water samples from contaminated sites from naval engineering research station at Toms River, NJ

Sample		*cis*-Dichloroethene	Trichloroethene	Tetrachloroethene
Well LF	Concentration	43.72 ppb	13.03 ppb	5.03 ppb
	RSD	3.8 %	5.3 %	12.2%
Well LI	Concentration	3.06 ppb	3.96 ppb	Not Detected
	RSD	3.3 %	11.9%	----
Well LK	Concentration	8.36 ppb	44.38 ppb	14.14 ppb
	RSD	13.8 %	4.6 %	11.9 %

6.3.6 Application

The PIME instrumentation was used for analysis of a variety of VOCs such as benzene, toluene, ethylbenzene and xylene (BTEX), oxygenated and chlorinated compounds. These are common water pollutants. The system was applied to analyze contaminated ground water from a Superfund site in NJ. A typical chromatogram for chlorinated compounds in a contaminated water is shown Fig. 6.6. The pollutants were identified as cis-1,2-dichloroethene, 1,1,1-trichloroethane, trichloroethene and tetrachloroethene. A syringe with a filter was used to eliminate soil and particles. A 5 ml sample was used for each analysis. Eluent flow rate was 0.6 ml/min. Membrane was heated to 43° C. The quantitative analytical results are presented in Table 6.4 which shows contamination of ground water wells at sub ppb levels.

6.4 Conclusion

A comparison of PIME and purge and trap showed good agreement. PIME appeared to have higher precision. This system was used for analysis of real ground water samples.

CHAPTER 7

ON-LINE MEMBRANE EXTRACTION FOR CONTINUOUS MONITORING OF SEMIVOLATILE ORGANIC COMPOUNDS IN WATER

7.1 Introduction

Contamination of ground water and surface water resources have posed a major threat to public health. From an analytical perspective, the organic pollutants in water can be classified to as volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs). US Environmental Protection Agent (USEPA) has listed numerous VOCs such as BTEX (benzene, toluene, ethylbenzene and xylene), and SVOCs, such as, pesticides of diuron, prometon, PAH, phenol as regulated compounds. Conventional analytical methods for VOCs include head space, purge and trap and solid phase microextraction. The purge and trap is the most common method where an inert gas purges the VOCs from water. The organics are purged out and focused on a sorbent trap and then is thermally desorbed for GC or GC/MS analysis. The conventional measurement methods for SVOCs include liquid-liquid extraction (e.g. EPA method 1625) solid-phase extraction and large volume injection. Of these solid phase extraction is evolving as the method of choice due to the lower solvent use, and shorter analysis time.

All the above measurement process involve sampling at site, sample transportation, storage, sample preparation and analysis. These independent steps increase the probability of analytical errors due to contamination, sample loss etc. In addition, these techniques are not designed for automated on-line analysis. Although batch processes, by nature, attempts have been made to develop automated SPE and purge and trap for on-line analysis. The resulting instrumentation is complex, expensive and has relatively long

analysis. The resulting instrumentation is complex, expensive and has relatively long cycle times. At present these have found limited applications in process or environmental monitoring. There is a need for the development of instrumentation for on-line water monitoring which incorporates simple, rugged design while providing low detection limits for trace analysis. As the USEPA stated in its water quality guidance for the Great Lakes system [3], for some highly volatile, hydrolyzable, or degradable compounds, EPA strongly recommends to use only results of flow-through tests in which the concentrations of test compounds in test solutions were measured using acceptable analytical methods. A flow-through test is a test in which test solutions flow into constant-volume test chambers either intermittently (e.g. every few minutes) or continuously, with the excess flowing out.

Semipermeable membranes have been used for extracting and analyzing volatile organic compounds in water and air [14-19]. Membrane extraction is attractive because analytes can be isolated on-line from the air/water matrix in a continuous fashion and the whole process can be automated. In these applications, the membrane serves as an interface between water and an inert gas for GC column, or a vacuum for mass spectrometer. The organics migrate from the aqueous phase across the membrane to the permeate side of gas (or vacuum) under concentration gradient. The analytes are then introduced into a GC or a MS for analysis. The membrane interface with GC or GC/MS for continuous monitoring water and air have been reported [15-19, 23, 39].

The SVOCs offer additional challenges to on-line membrane extraction because these compounds are not easy to volatilize and can not be introduced easily into an

analytical instrument. Limited studies have been reported for analytical membrane extraction of SVOCs. Recently laser desorption of SVOCs from the membrane interface in membrane introduction mass spectrometry has been reported [40]. Application of dialysis with semipermeable membrane as an efficient method for lipid removal in the analysis of bioaccumulative chemicals has been published [41]. A membrane concentrator for SVOCs in water was designed by H. Nomura, J. Ahn, et al. [42] where water stream continuously flowed through a membrane module and a certain amount of organic solvent continuously circulated on the permeate side. After about 110 minutes of equilibrium, an eighty fold enrichment was obtained.

The objective of this study was to develop instrumentation for continuous, on-line monitoring of SVOCs in water stream using membrane extraction. The membrane serves as an interface across which liquid-liquid extraction takes place as shown in Fig. 7.1. The SVOCs transfer from aqueous phase and are concentrated in the organic phase. The enriched solvent continuously flows into a six port valve that intermittently injects sample into a HPLC for analysis. In this paper, continuous on-line monitoring of a simulated aqueous stream is demonstrated. The enrichment into the organic phase under different operating conditions, and the performance characteristics of the instrumentation are presented.

7.2 Experimental Section

The instrumentation includes hollow fiber extraction module, six port injection valve, HPLC with UV detector, extraction solvent and water delivery pumps. The schematic

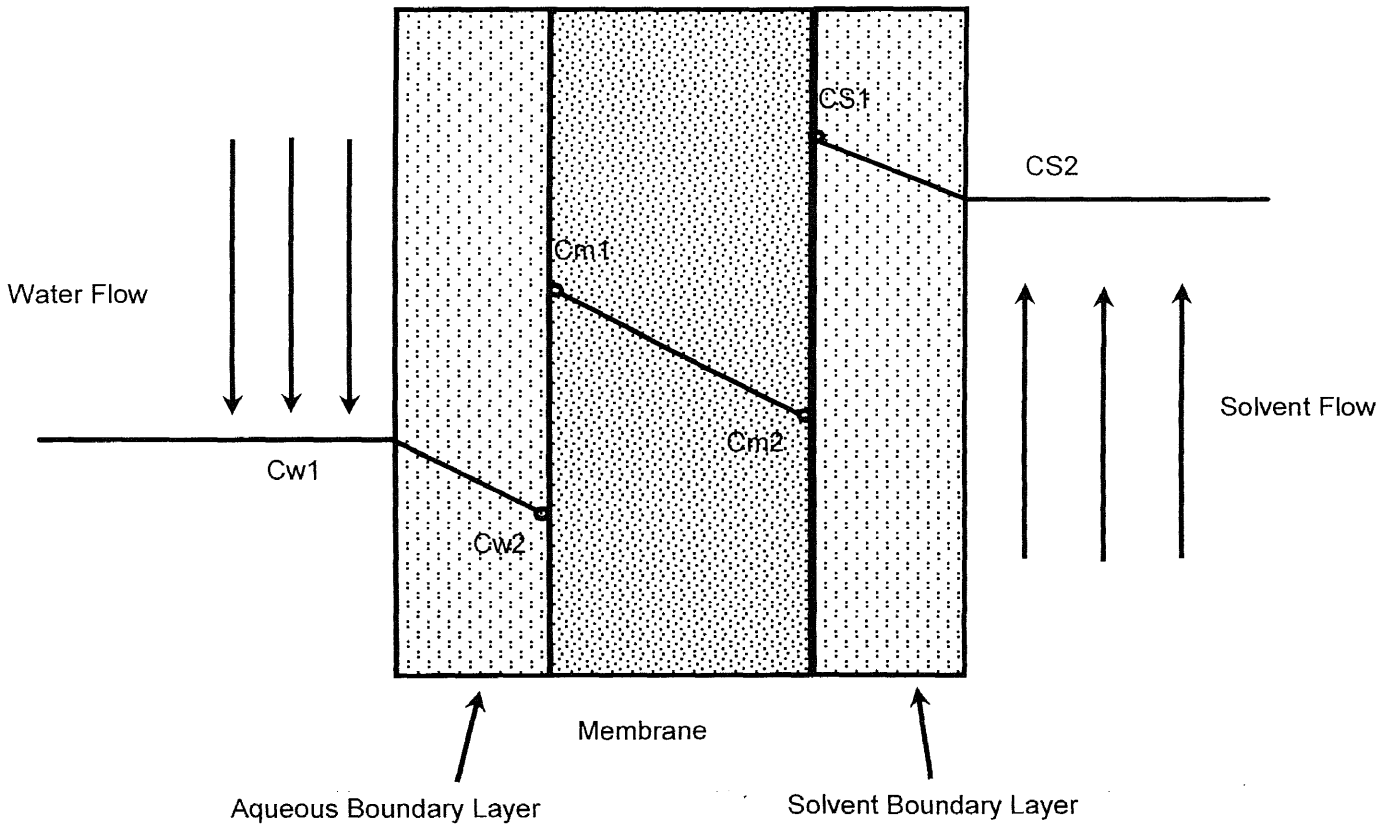


Fig. 7.1 Concentration profile in membrane extraction process. Cw, Cm, Cs are analyte concentration in water, membrane and solvent phase respectively. The subscript 1 and 2 stand for incoming and outgoing concentration in that phase.

diagram of the instrumentation is shown in Fig. 7.2. The water sample and extraction solvent flow on either side of the hollow fiber. Two flow modes were used for hollow fiber extraction. In "flow over" mode, water flowed outside and the solvent inside the membrane fiber. In "flow through" mode, water flowed inside and the solvent outside the membrane fiber. Here the flow over configuration is shown. Water flow rates were faster at 2-5 ml/min, while the extraction solvent flowed at rate of 0.03-0.24 ml/min. This provided an enrichment of the organics into the solvent phase. A Waters HPLC syringe pump was used for water sample delivery, and a reciprocating pump of model QG 150 (Fluid Metering, Inc., Orchard Oyster Bay, NY) was used for solvent delivery. In practice, the membrane module was spiraled to reduce the boundary layer effects [10] , and to shorten the physical module length. The enriched solvent phase flowed through the sample loop of the six port valve (Valco Instruments Co. Inc., Houston, TX). Injections were made at regular intervals onto the HPLC column for separation. Corresponding to each injection a chromatogram was obtained.

The membrane module is made using 7 pieces, 121 cm long composite membrane 0.290 mm OD×0.240 mm ID (Applied membrane Technology, Minnetonka, MN). The membrane pieces were inserted into a 1/8'' ID Teflon tubing. A "T" unit (Components & Controls Inc., Carlstadt, NJ) was used at each end of the tubing to connect the solvent and the water line. Epoxy was used to seal the ends so that the water and solvent did not come in contact with one another.

A Waters HPLC system comprised of model 600E pump and model 484 tunable UV detector were used in this study. A 150 ×3.2 mm HPLC column with 5 μm Pinnacle

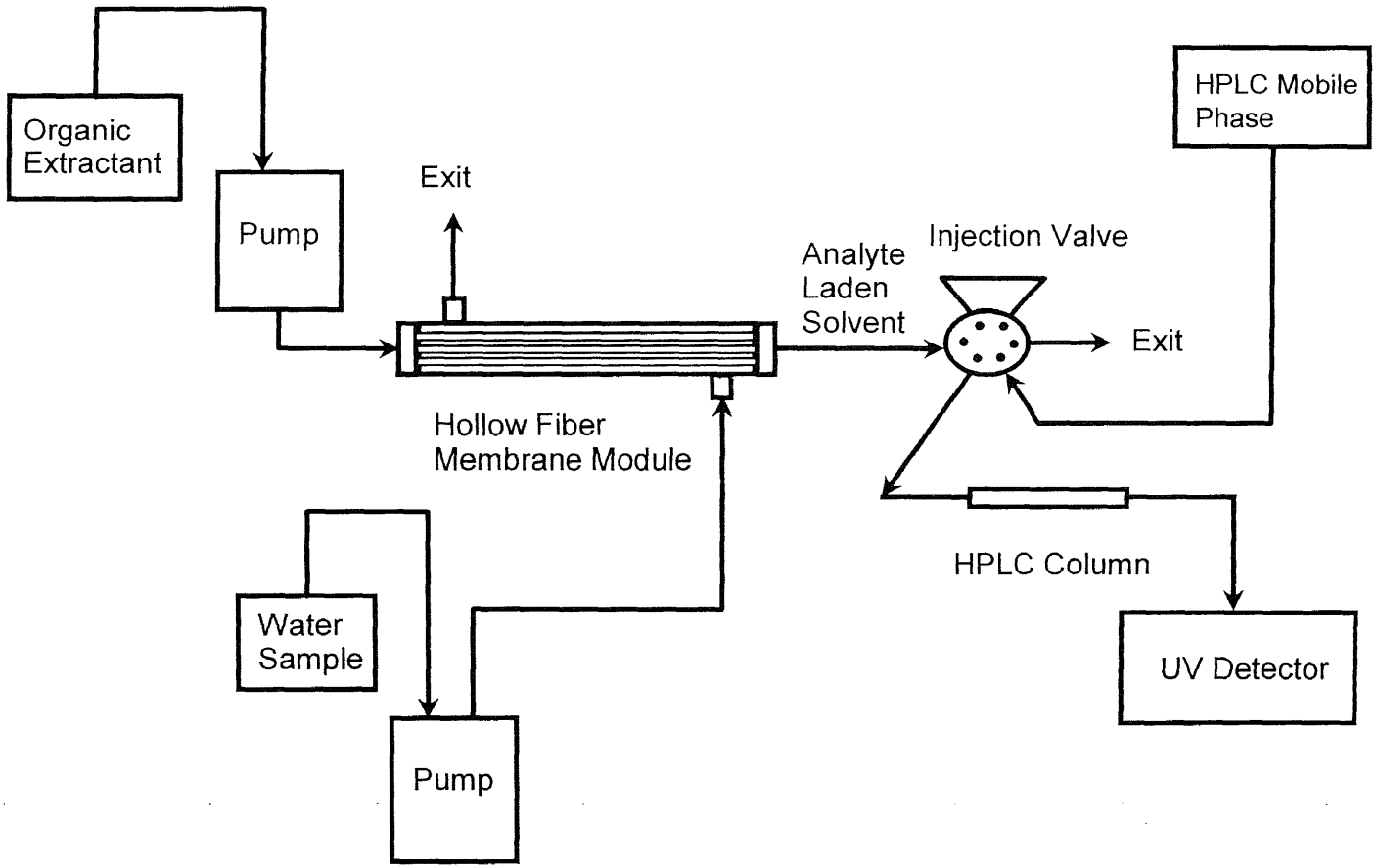


Fig. 7.2 Schematic diagram of continuous membrane extraction system for SVOCs from water. Flow over mode is shown here.

Cyano stationary phase of (Restek Corp. Bellefonte, PA) was used for separation. A Minichrom data system is used to acquire and analyze the data.

7.3 Results and Discussion

The mechanism of liquid-liquid extraction across the membrane is shown in Fig. 7.1. The extraction process consists of 5 distinct steps: 1. analytes diffuse from water and through the boundary layer; 2. dissolve in membrane; 3. migrate through membrane; 4. desorb from membrane and dissolve in solvent; 5. migrate through solvent boundary layer into the flowing solvent. In steps 1, 3, and 5 where the analytes are in homogeneous phase, migration is governed by concentration gradients. The thickness of boundary layer is determined by the degree of mixing of the fluid with the membrane surface. The thicker the boundary layer, the larger the mass transfer resistance. In steps 2 and 4, the transfer of analytes from one phase to another is driven by the partitioning from water to membrane, and from the membrane to organic solvent respectively.

7.3.1 Performance of the Instrumentation

The continuous monitoring of semivolatile organic compounds in water involves making analysis at a relatively high frequency. The analytes were continuously extracted through the membrane. The enriched solvent was injected into HPLC column every few minutes and the operation is demonstrated here by continuously monitoring a water stream containing spiked SVOCs. A series of chromatograms were obtained as shown in Fig. 7.3 corresponding to a series of equal interval injections. The concentration were 2.58, 0.818

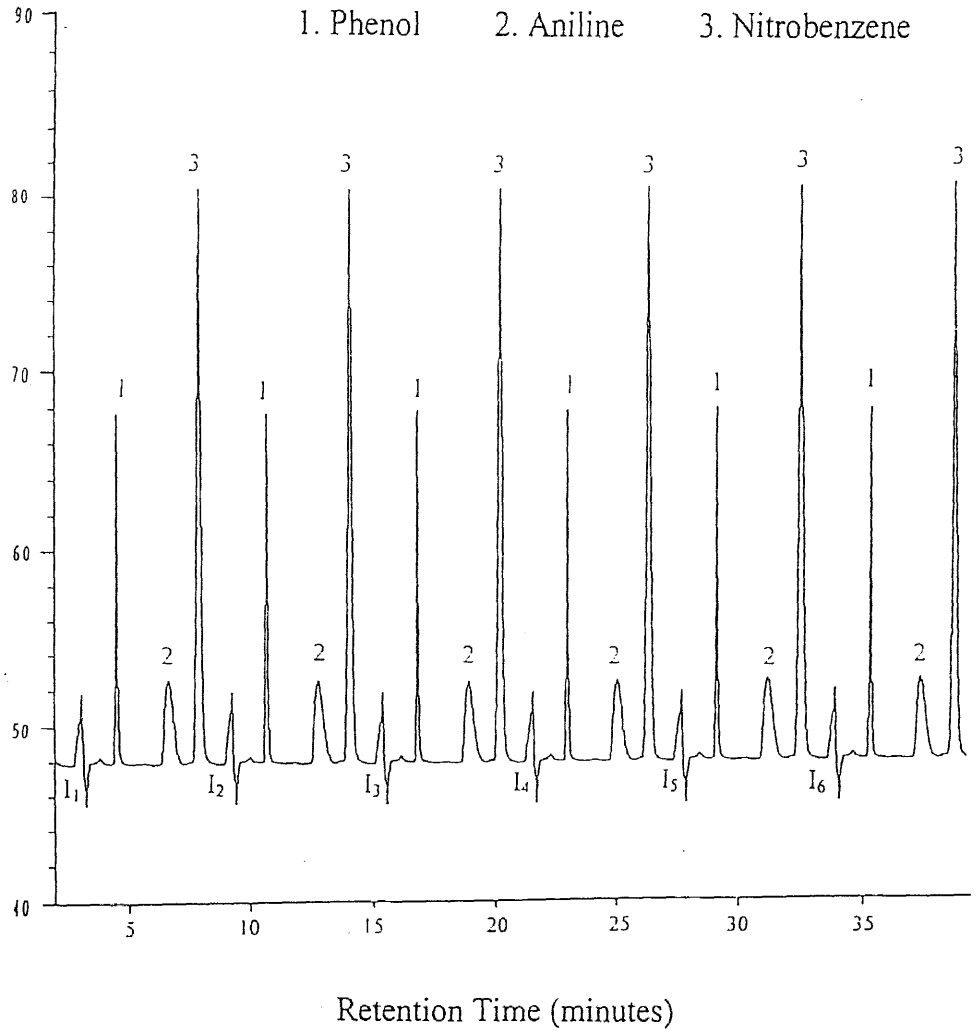


Fig. 7.3 Series of chromatograms of continuous monitoring a water stream

and 0.957 ppm for phenol, aniline and nitrobenzene respectively. Good reproducity in peak shape, peak height and retention time were observed. Here, the analysis frequency was limited by the HPLC column separation time rather then the system's extraction process.

Calibration curves for phenol, aniline and nitrobenzene are shown in Fig. 7.4. The linear curves demonstrate the linearity of the extraction process. The precision and method detection limits are presented in Table 7.1 which shows excellent reproducibility and high sensitivity of the instrumentation. The RSDs were based on 6 repeat injections. The MDLs were evaluated according to standard EPA method [67]. The MDLs were obtained in the "flow through" mode, at a water flow rate of 2.5 ml/min, and methanol as the extraction solvent at a flow rate of 0.04 ml/min. It should be noticed that the system response and consequently the MDLs are a function of extraction solvent, and operating parameters such as water flow rate, solvent flow rate and membrane module design.

Table 7.1 Method detection limits and precision of several semivolatile organic compounds

Compounds	MDLs[a] (μg/L or ppb)	RSD[b] (%)
Phenol	15.2	0.32
Aniline	8.2	0.78
Nitrobenzene	1.98	0.14

a. Method detection limits based on standard EPA method.
b. Relative standard deviation based on 6 replicates.

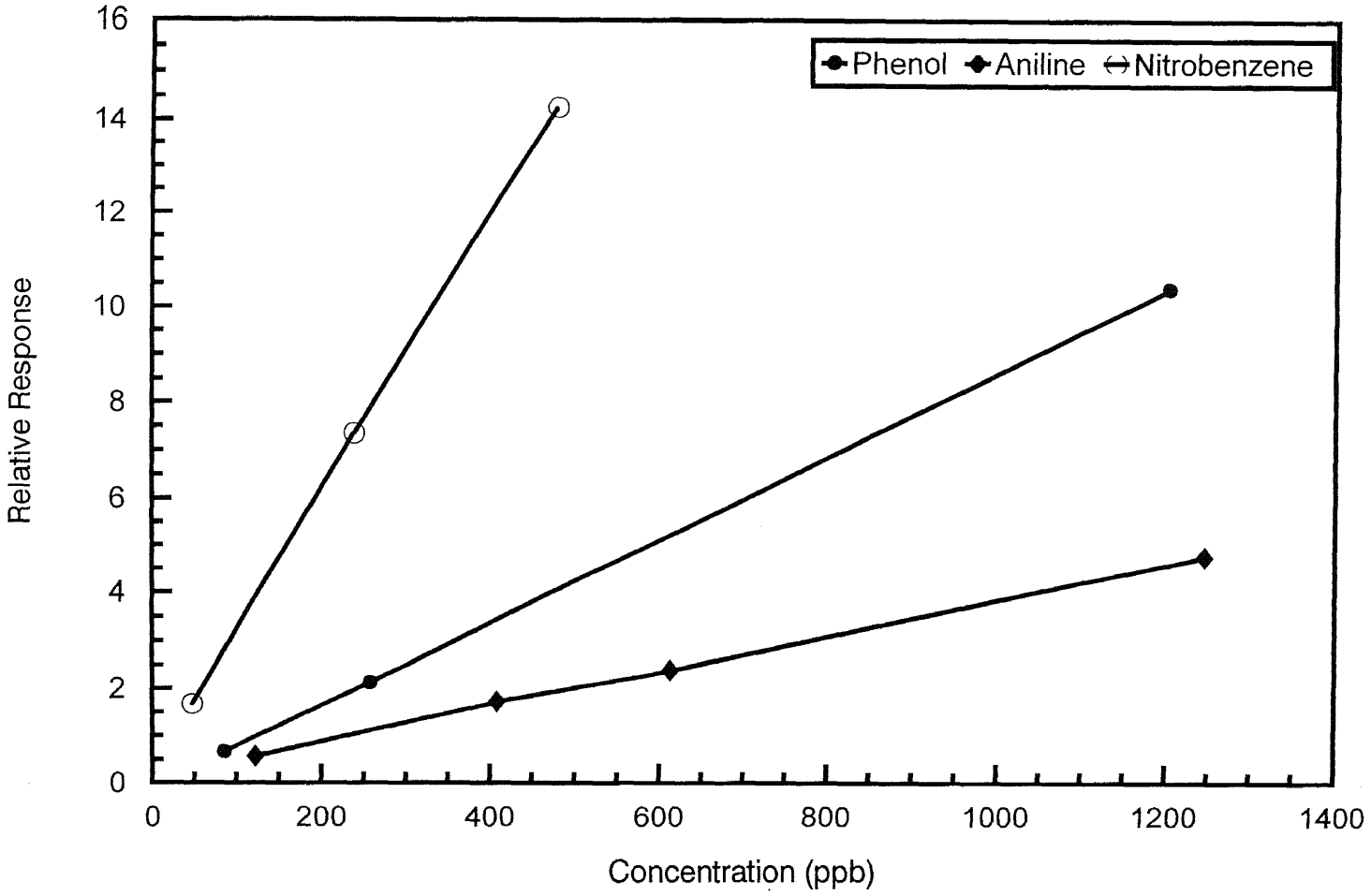


Fig. 7.4 Calibration curves of several organic compounds. Acetonitrile was used as the extractant at flow rate of 0.04 ml/min. Water flow rate was 2.5 ml/min in a flow through mode.

7.3.2 Enrichment Factor

The objective of the membrane extraction was to concentrate the organics from the aqueous phase into the solvent phase. The enrichment factor was defined as

$$F = \frac{Concentration\,in\,solvent}{Concentration\,in\,feed\,water}$$

The enrichment factor was evaluated for different flow conditions as well as for different extraction solvents. The results are presented at Table 7.2, 7.3 and Fig. 7.5 and 6. The enrichment factors were found to vary between 1 to 62 depending upon the analyte and the extraction conditions. From Table 7.2, it can be seen that the polar compounds such as phenol had low enrichment factors due to their strong affinity for water, and relatively low partition coefficients in the hydrophobic membrane used here. These results are consistent with other studies [23, 53]. Nonpolar compounds such as phenyl ether showed much higher enrichment factors. Comparison of Table 7.1 and 7.2 demonstrates that analytes with low enrichment factor had high detection limits, and vice versa.

The extraction solvent played an important role in determining the enrichment factor. Four solvents, methanol, acetonitrile, octanol and hexane were evaluated here. These represented a wide range of polarity. The enrichment factor was relatively lower in the polar solvents methanol and acetonitrile, and higher in nonpolar solvents. Even a polar analyte such as phenol had the highest enrichment factor in hexane, the most nonpolar of the solvents used here. Octanol-water and hexane-water partition coefficients from the literature [71] are also presented here. Although the partition coefficient of the analytes

Table 7.2 Enrichment Factor for Different Compounds Using Different Solvents

Solvents * \ Compounds	Benzyl alcohol	Phenol	Nitrobenzene	Phenyl Ether
Octanol at 0.07 ml/min	27.6	2.96	8.82	37.9
Hexane at 0.09 ml/min	35.1	4.84	11.3	62.7
Acetonitrile at 0.027 ml/min	2.02	2.78	2.12	2.58
Methanol at 0.05 ml/min	1.24	2.17	9.57	25.72
log P(hexane)***	-0.76	-0.96	NA**	NA**
log P(octanol) ***	1.1	1.46	1.88	4.4

*. Water flow rate was 1 ml/min for methanol extraction and 5 ml/min for the other solvents.
**. Not available
***. Partition coefficients in octanol-water or hexane-water system

are higher in the octanol-water system than in the hexane-water system, the enrichment factors in hexane were found to be higher than that with octanol. The presence of the membrane is the obvious cause of the anomalous behavior. One possibility is that when the solvent came in contact with the membrane, the polymeric material swells. These results in a more open structure that allows rapid diffusion of analytes through the membrane. It is possible that swelling in presence of hexane is more than that in presence of octanol. Consequently, the permeability of the membrane was higher when hexane was used. Another possible explanation is as follows. Octanol can more easily extract these compounds directly from water than hexane. However, octanol is more polar thus does not easily extract organics from polysiloxane membrane. Therefore hexane as a nonpolar solvent would have stronger extraction ability for organics from membrane (in the step 4 of the extraction process) than octanol.

Another variable in the extraction process is the flow mode. Flow over (water outside the fiber) and flow through (water inside the fiber) modes can be used for hollow fiber extraction. The enrichment factors were found to be consistently higher in the flow-over mode as shown in Table 7.3. The internal volume of the membrane was small as the fiber ID was only 0.240 mm. The volume outside of the membrane was much larger because the ID of the module was 3 mm. Thus in flow-over mode, a small volume of organic solvent was involved in the extraction so that the analytes could be concentrated into a smaller volume.

In flow-through mode where the water flows inside of the membrane, smaller fiber diameter leads to a lower Reynolds number which determines the degree of mixing:

$$Re = (\rho v d/\mu)$$

where Re is Reynolds number, ρ is the fluid density, v is the fluid velocity, d is tube diameter and μ is the fluid viscosity. The higher the Re, the better the mixing. Less mixing at the surface of the membrane results in a thicker boundary layer. Since the organics have higher solubility in the membrane than in water, a concentration depletion zone is formed. This increases the mass transfer resistance in step 1, and results in a lower enrichment factor. The boundary layer is not as critical for the organic solvent in which the analytes have very high solubility. In flow-over mode, the ID of membrane module is much larger than hollow fiber ID thus a higher Re was obtained. Also the presence of membrane fiber in the module shell acted as barriers to the flow path that introduced more turbulence and better mixing of the aqueous phase with the membrane.

Table 7.3 Effect of flow mode on enrichment factor

Flow Mode	Benzyl alcohol	Phenol	Nitrobenzene
Flow though[a]	1.12	1	1.01
Flow over[b]	12.8	6.56	6.33

a. Methanol flow rate was 0.023 ml/min and the water flow rate was 2.9 ml/min.
b. Methanol flow rate was 0.035 ml/min and the water flow rate was 2.9 ml/min.

The enrichment factor was also a function of water and solvent flow rates. Faster water flow leads to a higher Re number forming a thinner boundary layer and faster mass transfer in step 1. Higher flow rate also brought more sample, consequently a larger amount of analyte, into the module. Enrichment factor as a function of water flow rate (in the flow-over mode) using acetonitrile as the extractant is shown in Fig. 7.5. It can be clearly seen that as water flow rate increased, the enrichment factor increased. The effect

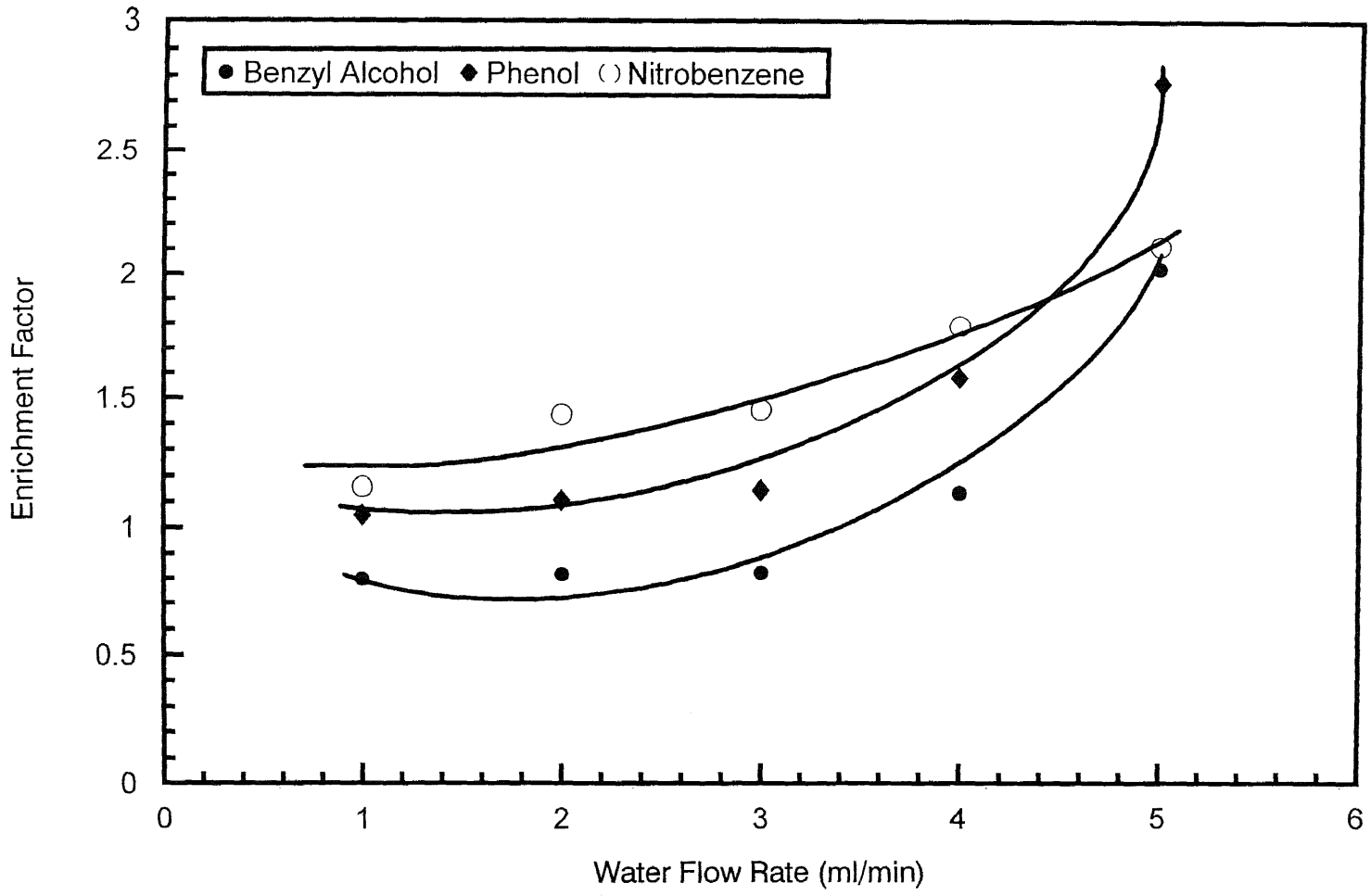


Fig. 7.5 Enrichment factor as a function of water flow rate. Acetonitrile was used as the extractant at flow rate of 0.027 ml/min. Flow over mode was used.

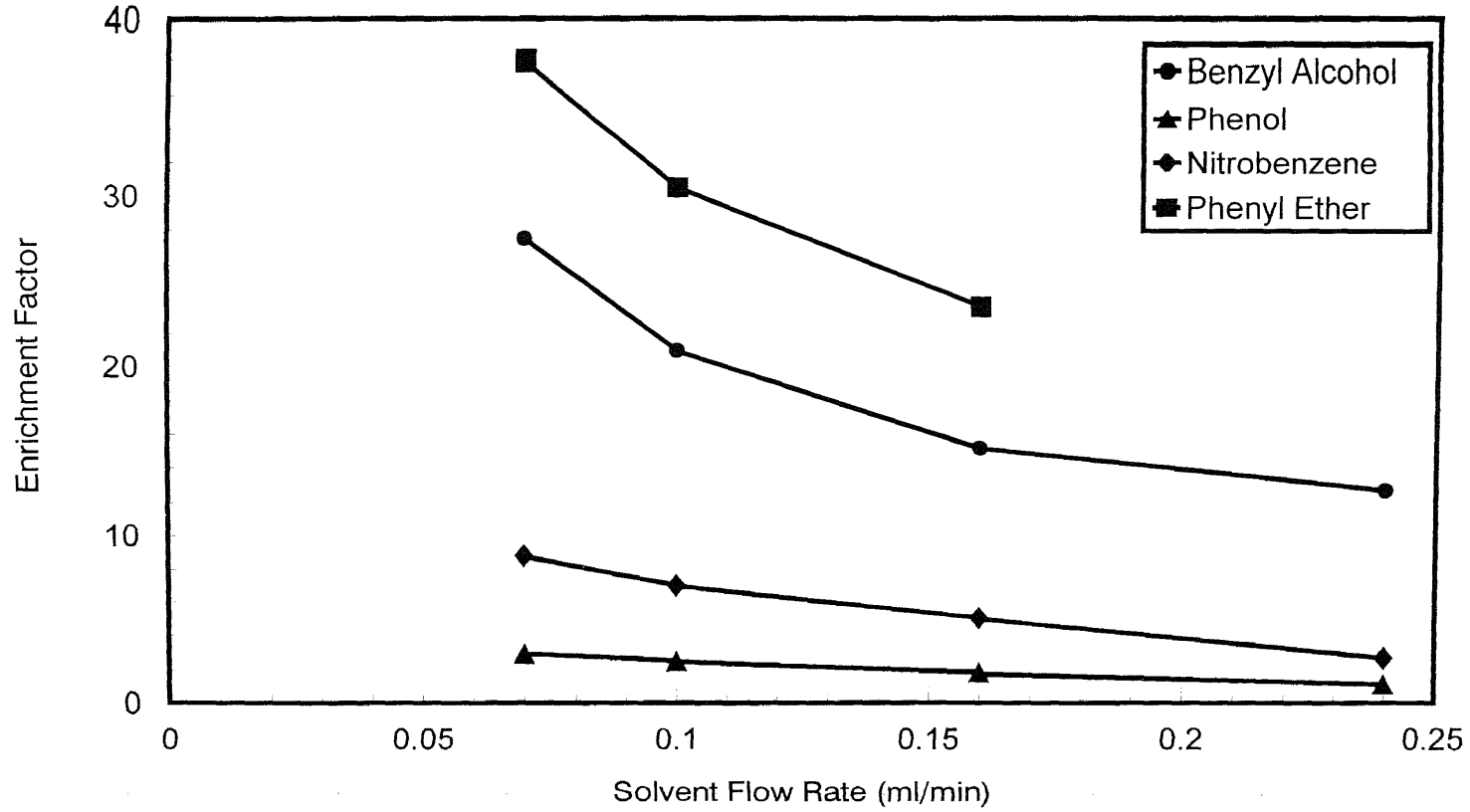


Fig. 7.6 Enrichment factor as a function of extractant flow rate. Octanol was used as the extractant. Water flow rate was 5 ml/min in a flow over mode.

of extractant solvent flow rate at a constant water flow rate is shown in Fig. 7.6. The lower the flow rate, the less solvent was involved in the extraction process. Thus a higher enrichment factor was achieved. On the whole, higher water and lower extraction solvent flow rates are favorable for high enrichment factor.

7.4 Conclusion

On-line membrane extraction using an organic solvent was an effective method for developing instrumentation for continuous monitoring of semivolatile organics in water. The instrumentation demonstrated low detection limits, linear calibration curve, and excellent precision. The enrichment factor in the membrane extraction varied from anywhere between 1- 62. It was a function of the analytes molecule, extraction solvent as well as flow conditions. The flow over mode was found to provide higher enrichment than the flow though mode.

CHAPTER 8

SUMMARY

Pulse Introduction Membrane Extraction-Gas Chromatography (PIME-GC) was developed for measuring trace level volatile organic compounds (VOCs) in water. This technique was based on non-steady state membrane permeation. A mathematical model developed here successfully described the system. The aqueous boundary layer provides the major mass transfer resistance for PIME. Reduction of the boundary layer using a gas purge of the membrane, and use of a spiral membrane module configuration resulted in significant improvements in system performance. The length of the membrane module had a major impact on extraction efficiency, and sensitivity increased with module length. The study showed that the sample duration on membrane module, flow rate, sample size, and temperature all affect the system response and lag time.

The system demonstrated good analytical performance in terms of linearity, detection limits, extraction efficiency, and precision. This instrumentation was compared to the system based on steady state membrane permeation. The nitrogen purge membrane was employed in PIME-GC to clean the membrane and reduce boundary layer effects. One major advantage of the PIME is that it could be used for continuous monitoring as well as for measuring discrete, individual samples. The comparison of the PIME with purge and trap system showed good agreement for both methods. The application of PIME to ground water analysis demonstrated the capability for real water measurement.

An exploratory continuous monitoring system for SVOCs in water using membrane extraction coupled with on-line HPLC analysis was also investigated. This technique

exploited the higher partition coefficient of organic compounds in the membrane and in an organic solvent to selectively extract the organics from water. Sixty fold enrichment in the organic phase was possible using this technique. This system showed good analytical performance in terms of low detection limits, high sensitivity and precision.

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