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Development of pulse introduction membrane extraction for analysis of volatile organic compounds in individual aqueous samples, and for continuous on-line monitoring

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Abstract

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. Recently we have developed an alternative approach to membrane extraction referred to as pulse introduction membrane extraction (PIME). Here a pulse of sample is injected into the membrane, and steady state is not reached. This approach results in analytical system that has faster response and the capability to analyze individual samples. This concept can be used in conjunction with gas chromatography, mass spectrometry, as well as other analytical techniques. In this paper, the application of PIME for continuous monitoring of trace level organics in water is presented. The system demonstrated sub-ppb level detection limits, high precision and linear calibration curves. In this study, conditions for shorter analysis time and high sensitivity were studied. A comparison of PIME with steady state, continuous sample introduction is also presented. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Pulse introduction membrane extraction; Membrane extraction; Extraction methods; Purge-and-trap methods; Continuous monitoring; Volatile organic compounds; Benzenes; Toluene

1. Introduction

Conventional analytical techniques for measurement of volatile organic compounds (VOCs) in water are purge-and-trap, headspace analysis and solid-phase microextraction. These processes usually involve distinctive steps, such as, sampling at site, transportation, storage and sample preparation before gas chromatography (GC). 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 sample that can be analyzed. In these techniques each sample represents concentration of the sample at a given point in time

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or space and the information on temporal variations in a sample stream are not obtained. At present, there is a real need for instrumentation for continuous monitoring of trace level organic compounds in wastewater discharge and process streams. This is especially true as clean fresh water become scarce and water recycling becomes more prevalent. Continuous monitoring of high-purity water in semiconductor 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 has been used in a variety of applications such as gas separation, dehumidification, dialysis, osmosis and reverse osmosis [1]. Although industrial-scale membrane processes 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 for mass spectrometry (MIMS) [2–8], 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. MIMS has been used in continuous monitoring water and air stream [4–8]. Continuous in vivo mass spectrometric determination of select organics in blood with a membrane probe has also been reported [2]. 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 GC, 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) [9–12] for continuous monitoring of organics in water and air. In OLMEM–GC, water or air sample continuously flowed into membrane module and nitrogen flowed countercurrent at the permeate side to strip the permeated organic compounds into the 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 s pulse of electrical current. Running the water continuously though the membrane and periodically making microtrap injections performed continuous monitoring of water stream. 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. Similar membrane extraction techniques with GC interfaces have also been published by other investigators [13].

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.

Recently we have developed an alternative approach for continuous on-line membrane extraction referred to as pulse introduction membrane extraction (PIME) and it has also been referred to as membrane purge-and-trap [14]. Here a pulse of sample is injected into the membrane for extraction. This concept can be used in GC, mass spectrometry

(MS), as well as other analytical techniques. In this paper, a 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 defined, as the time required for all the analyte to permeate across the membrane. It is an important parameter since it determines the frequency at which the analysis can be carried out. It has been reported [15–19] that the mass transfer resistance in the stagnant aqueous boundary layer formed on the membrane surface due to poor mixing of water with the membrane is the major resistance to analyte permeation. In the PIME–GC system, a pulse of nitrogen is used before and after the sample injection to eliminate the boundary layer and to reduce the lag time. The nitrogen purge before the sample elution eliminates the existing boundary layer and increases permeation flux. Nitrogen purge after the sample has passed through eliminates the sample tailing (or carryover). This reduces lag time and eliminates the boundary layer that is formed as sample passes membrane module.

In this paper, 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.

2. Experimental

The PIME–GC system is shown in Fig. 1. The water sample was injected using an automatic six-port valve. The membrane module was made of 20 pieces of 10 cm×0.290 mm O.D.×0.240 mm I.D. composite silicone membrane. The membrane is comprised of 1 μm thick film of homogenous siloxane supported on microporous polypropylene

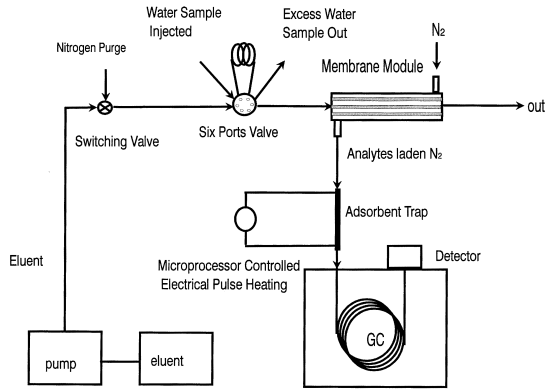

Fig. 1. Schematic diagram of the PIME–GC system.

fiber. The membrane module was constructed by inserting the hollow fiber membranes into a 1/8 in. O.D. stainless tubing (1 in.=2.54 cm). Details about the membrane module have been presented elsewhere [14].

The microtrap was made from 15 cm×0.5 mm I.D. silcosteel tube (Restek) packed with Carbotrap C (Supelco, Supelco Park, PA, USA). The microtrap was heated with a 1.2-s pulse of 10 A current supplied by a Variac. The working principle of the microtrap and the operational details have been presented previously [10,20]. Milli-Q water was used as the eluent and was pumped through the system using an high-performance liquid chromatography (HPLC) pump. A HP 5890 series II GC system (Hewlett-Packard, Avondale, PA, USA) equipped with a flame ionization detector and a 30 m×0.53 mm O.D.×0.21 mm I.D. SE-54 column (Supelco) with 2.4-μm thick stationary phase were used for analysis. A HP Chemstation 3365 software package was used for data acquisition. Carrier gas flow-rate was around 5 ml/min. All standard solutions were made with high-purity reagents purchased from Aldrich, USA.

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 through configuration was used, i.e., water sample passed inside the membrane while nitrogen stream flowed countercurrent on the outside. 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, stripped by nitrogen gas and concentrated by the microtrap. After the permeation was complete, the microtrap was thermally desorbed to inject the sample into the GC system. For a large sample volume when lag time is long, 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 [10]. All transfer lines between the membrane module and the microtrap were heated to 70°C to prevent condensation of organics.

3. Results and discussion

Continuous, on-line monitoring involves making a series of injections. An important consideration in membrane extraction is the slow permeation of the analytes through the boundary layer and the membrane. For each sample injected, the permeation must be complete before the next injection can be made. To determine the time required for extraction, a sample was injected and the microtrap was pulsed every 30 s to monitor the permeate concentration. Permeation profiles as shown in Fig. 2 were obtained. The lag time, which is the duration of the permeation, profile increased with sample size, and can be reduced by nitrogen purge as mentioned before.

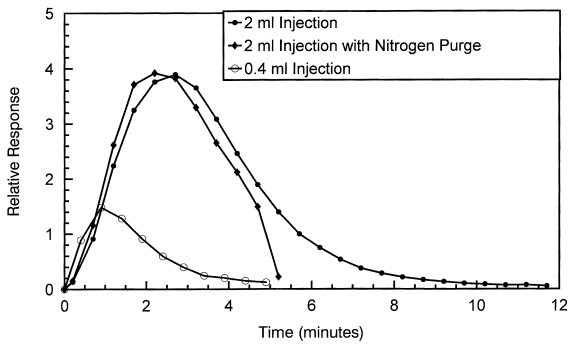

Fig. 2. Permeation profiles for 0.4, 2.0 ml injection, and for 2.0 ml injection with nitrogen purge.

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 lag time of 5 min. A small volume sample passes rapidly through the membrane resulting in a reduced lag 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 nitrogen purge to reduce the lag time. For the 2 ml sample, the lag time was 12.5 min. However, by initiating nitrogen purge 4 min after sample injection, the lag time decreased to 5 min. From the response profiles shown in Fig. 2 it can be seen that lag time was limited to 5 min 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. 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 the GC column rather than the lag time of membrane permeation. Each injection represented concentration of the sample stream at a point in time. Since any carryover from a previous injection would introduce error, it was important that the response in Fig. 2 came down to zero before the next injection was made.

Fig. 3 shows good reproducibility of retention time, peak shape as well as peak area, and demonstrated the applicability of PIME in continuous monitoring. Relative standard deviations (R.S.D.s) 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. This demonstrates high precision of the analytical system. Typical calibration curves for

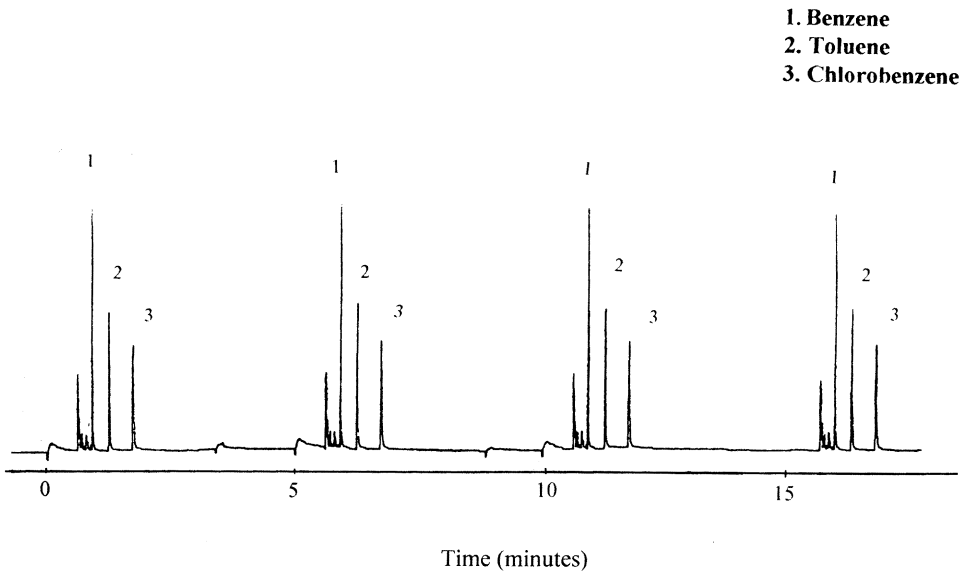

Fig. 3. Series of chromatogram obtained by consecutive injections of water sample containing 30 ppb benzene, 30 ppb toluene and 40 ppb chlorobenzene.

different organics are shown in Fig. 4. The data presented here is for a 1-ml sample injection followed by nitrogen purge of the membrane. The system demonstrated linear response in the low ppb levels studied here.

Short lag time could be obtained by both approaches mentioned above and both are suitable for continuous monitoring. The advantage of large sample with nitrogen purge is that a larger amount of sample is injected resulting in a larger detector response thus higher sensitivity. This can be seen in Fig. 2, where the maximum response for the 2 ml sample was significantly higher than the 0.4 ml injection. The advantage of using a small injection volume without nitrogen purge is that the instrumentation and the operation are simpler. The method detection limits (MDLs) for a 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 seven replicates and calculated according to the US Environmental Protection Agency (EPA) standard method [21]. Based on Fig. 2, lower detection limits are expected with a 2-ml sample (with nitrogen purge) since more sample is analyzed here.

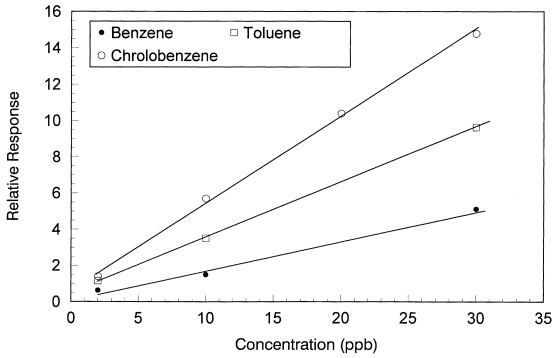

Fig. 4. Calibration curves for different VOCs in PIME.

3.1. 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 countercurrent gas stream continuously stripped the permeated organics. The organics were concentrated and injected by the microtrap at regular intervals into the GC system. Since the sample flows continuously, nitrogen purge

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:

$$J = -D(\partial C/\partial x) \quad (1)$$

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:

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

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 Eq. (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 Eq. (1) along the membrane thickness results in a steady state permeation flux J_{ss}:

$$J_{ss} = D(C/L) \quad (3)$$

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

C is the analyte concentration at membrane surface, C^* is the concentration in water and k is the distribution coefficient of the organic between water and membrane. The mathematical solution for Eqs. (1) and (2) for the PIME system is [22,23]

$$J_{ns} = J_{ss}\left(1 + 2\sum_{n=1}^{\infty}(-1)^n \exp\left\{-n^2(\pi)^2\left[D(t)/l^2\right]\right\}\right)$$
when $t < \Delta t$ (4)

$$J_{ns} = J_{ss}\left(2\sum_{n=1}^{\infty}(-1)^n \exp\left\{-n^2(\pi)^2\left[D(t)/l^2\right]\right\} - 2\sum_{n=1}^{\infty}(-1)^n \exp\left\{-n^2(\pi)^2\left[(D/l^2)(t-\Delta t)\right]\right\}\right)$$
when $t > \Delta t$ (5)

So, along with the sample concentration, the permeation flux is also a function of time in the PIME system. The permeation profile is as shown in Fig. 2 and is somewhat similar to a Gaussian distribution. The Δt value, which is determined by the sample size and flow-rate, is an important parameter for system response (i.e., sensitivity) as well as lag time. The analysis time is limited by the lag time for a complete permeation. According to Eq. (4), if 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 certain internal volume. Thus it takes certain amount of time for reaching steady state. In this study, the time required to reach steady state was experimentally determined. Fig. 5 shows the response of the analytical system to a step change in

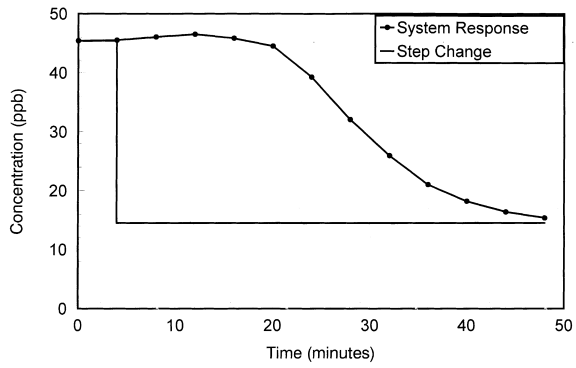

Fig. 5. Response to a step change in concentration during continuous sample introduction into a membrane.

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 min 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.

3.2. Advantage of "fresh membrane"

The theory of "sorption and diffusion" is widely used to describe permeation through nonporous membrane. The solute first partition on the 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:

$$C = kC^*$$

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. 2, where the sample was in contact with the membrane for only 0.5 min, but the lag time was 5 min 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:

$$\Delta M_f = V_m C - 0 = V_m kC^*$$

ΔM_f is the mass uptake for the front part of the pulse encountering "fresh membrane", 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:

$$\Delta M_l = V_m C - V_m C_0 = V_m(kC^* - C_0)$$

It is evident that the analytes uptake of the later part of the sample pulse is less than that of front part. Fig. 6 is plot of response per unit volume sample vs. 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 for the 5 ml sample was used to normalize the response of other injection volumes. As the sample volume increased, the response per unit volume decreased because relatively lesser amount of analyte encountered the "fresh membrane". The curve more of less flattened past 3 ml. 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 a sample continuously flowing into the membrane. A sensitivity comparison

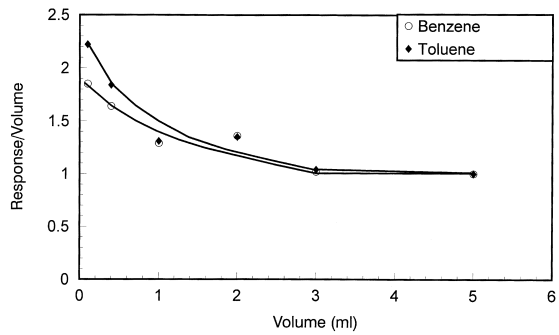

Fig. 6. Plot of response/sample volume vs. sample volume.

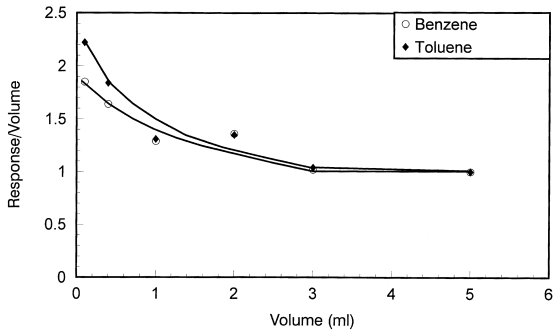

Fig. 7. Comparison of sensitivity between PIME and continuos sample introduction based on ''fresh membrane'' effect.

of the 0.4-ml sample introduced by PIME and OLMEM systems under similar operating conditions was carried out and the results are shown in Fig. 7. In PIME, the 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 equilibrium with diffusing analytes in the membrane thus reducing the driving force 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. MDLs for the 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.

3.3. 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 [15–19]. 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 the Reynolds number [24]:

$$\mathrm{Re} = (\nu d \rho)/\mu$$

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 [15–17] have shown that at these conditions, the boundary layer is well formed and results in a significant resistance to mass transfer.

In the PIME system, a nitrogen purge was used to break up the boundary layer and eliminate sample tailing to increase system response and reduce lag 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 a 1-ml sample in continuous introduction and PIME with nitrogen purge membrane was carried out. The result were similar to Fig. 7 and are not presented here for brevity. At the same concentration, the response was higher in PIME than in continuous introduction. The ratio of the slopes of the calibration curves for PIME to that of continuous introduction was 1.57 demonstrating higher sensitivity of PIME. This can be attributed to ''fresh membrane'' effect along with the reduction in boundary layer with nitrogen purge.

4. Conclusions

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

a faster response and a higher sensitivity than the sample continuous introduction system.

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