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Gas Injection Membrane Extraction for Fast On-Line Analysis Using GC Detection

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Membrane extraction has been interfaced with gas chromatography and mass spectroscopy for the analysis of volatile organics in water. The vacuum in a mass spectrometer provides fast mass transport. The time required to complete permeation in a GC interface can be fairly long, because the positive pressure of the carrier gas on the permeate side slows down the analyte permeation. The aqueous boundary layer formed on the membrane is considered to be the biggest contributor to the resistance to mass transfer. Another issue is the dispersion of analyte in the aqueous stream, which broadens the input pulse to the membrane. The overall effect of these two factors is to increase the analysis time. Gas injection of aqueous samples is presented in this paper to address these issues. Gas injection reduces the formation of boundary layer, and increases the overall diffusion coefficient seven times. Axial mixing of the sample with a gaseous eluent is minimal, and this eliminates the tailing in permeation profiles. The overall membrane extraction is found to be significantly faster when a gas is used to inject an aqueous sample. This method is also simpler in terms of instrumentation and operational procedures.

In the determination of volatile organic compounds in water, the first step is usually separation of analytes from the matrix. Conventional sample preparation techniques, such as purge-and-trap and headspace analysis, are mainly used for laboratory analysis of discrete samples. Membrane separation has emerged as a promising alternative.[1−24] It offers high selectivity and high enrichment factors and can be used for on-line, automated analysis. Membrane extraction has been used in conjunction with a mass spectrometer (MS)[2−12] or a gas chromatograph (GC).[13−23] The vacuum in an MS provides fast permeation through the membrane. The permeation is much slower in a GC or GC/MS interface, because a positive pressure is required for carrier gas flow. As instrumentation for faster GC becomes commonplace, there is a real need to develop faster membrane techniques that can speed up extraction.

Both hollow-fiber and flat membranes have been used in developing GC interfaces.[13−23] Generally, hollow fibers are preferable because they offer the advantage of larger surface area per unit volume and high packing density. A large number of parallel fibers can be packed into a small volume. All hollow-fiber modules share a common feature, that is, the sample contacts the membrane on the feed side while a stripping gas flows on the permeate side to transport analytes to GC. Contact between the sample and the membrane can be done in two ways. The membrane can be introduced into the sample (referred to as Membrane In Sample, or, MIS), or the sample can be introduced into the membrane (referred to as Sample In Membrane, or, SIM).

In the MIS configuration, the membrane is either directly submerged in the sample or in its headspace while the stripping gas flows inside the membrane.[23] At any point in time, only a small fraction of the sample directly contacts the membrane. The ratio of membrane surface area to sample volume is fairly low. The sample is usually stirred to enhance the analytes' diffusion through the aqueous phase. In the case of headspace extraction, analytes first vaporize and then permeate through the membrane. Diffusion in the gas phase and the gas-membrane interface is faster than in the aqueous phase and the liquid-membrane interface. However, slow mass transfer from the sample into headspace prolongs the overall process. It takes a rather long time to achieve high extraction efficiency. It was reported that quantitative extraction of a 2-mL sample required 100 min to complete.[23]

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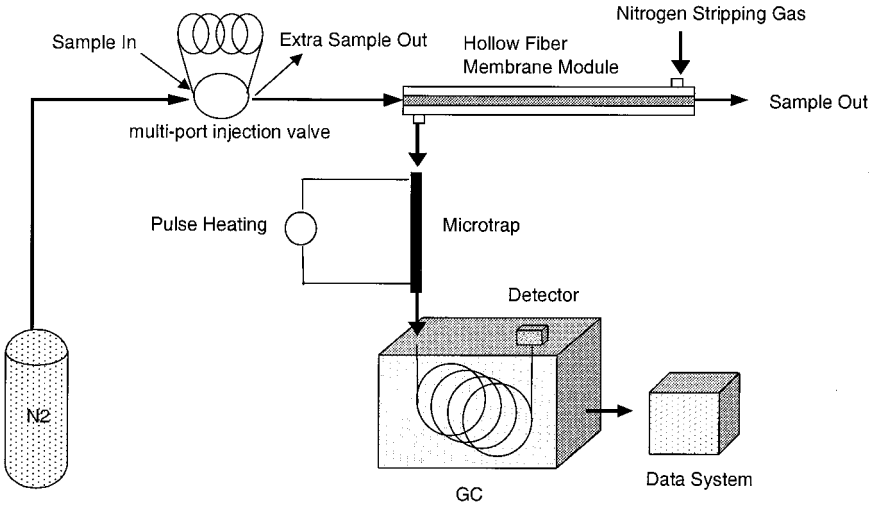

Figure 1. Schematic diagram of gas injection membrane extraction.

In the SIM configuration, the membrane modules have the classical shell and tube design.[25] The sample is either made to "flow through" or "flow over" the membrane. In both cases, the sample contact is dynamic, and the extraction is over once the sample has passed through. This allows multiple samples to be analyzed in quick succession. In either case, the contact surface-to-volume ratio is much higher than in the MIS extraction, and quantitative extraction can be achieved faster. It was reported that it took 4 min to extract 90% of analytes from a 2-mL sample in the flow-through mode, although an additional 10 min was needed to complete permeation.[18] Between the flow-through and the flow-over mode, the former provides higher extraction efficiency, because the tube-side volume is smaller than the shell-side volume. Comparison studies show that under similar experimental conditions, flow-through extraction provides the highest sensitivity among all available SIM and MIS configurations.[23,26]

In the flow-through extraction, the sample can be introduced into the membrane continuously.[13−15] Permeation may take a relatively long time to reach steady state, and any measurement during the transitional period provides erroneous results. To avoid this problem, a non-steady-state membrane extraction method referred to as pulse introduction membrane extraction (PIME) was developed recently.[16−19] Deionized water (or an aqueous solution) has been used as the carrier stream to transport the sample to the membrane[17−19] in PIME. A static analyte-depleted boundary layer is formed between the membrane and the aqueous phase.[27−30] The overall mass transfer resistance is the sum of the mass transfer coefficients of the aqueous boundary layer on the feed side, the membrane, and the gaseous boundary layer on the permeate side. In analytical applications where thin membranes, and relatively low sample flow rates are used, mass transfer through the aqueous boundary layer is the rate-limiting step.[23] The concentration gradient is the driving force for the analyte permeation across the membrane. The analyte-depleted boundary layer reduces the effective concentration gradient for mass transfer.[16] In PIME, gas purging at a predetermined delay following the sample injection was used to break up the boundary layer. It improved extraction efficiency and shortened response time to a limited degree.[17−19]

Sample dispersion is another cause of slow permeation in PIME[18,19] and other flow injection-type techniques in which an aqueous carrier stream is used.[6] The aqueous sample is diluted by axial mixing with the carrier stream. Dilution reduces the effective concentration on the feed side of the membrane, which is the driving force for diffusion. Moreover, dispersion increases sample volume and sample residence time in the membrane. The overall effects are slower extraction and lower sensitivity.

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

EXPERIMENTAL SECTION

Figure 1 shows the schematic diagram of the GIME system. An aqueous sample is introduced into a N_2 stream by a pneumatically controlled 10-port valve (Valco Instruments Co. Inc., Houston, TX). The N_2 stream injects the sample into the membrane. The membrane serves as a selective barrier through which organic analytes permeate. On the permeate side, a counter-current gas stream strips the organics and transports them to a microsorbent trap (referred to as the microtrap). The microtrap concentrates and then desorbs the analytes into the GC. After the GC run, a chromatogram is obtained. The system can be used for the analysis of individual samples by discrete injections or for continuous on-line monitoring by sequentially injecting a series of samples. A chromatogram is obtained corresponding to each injection.

The membrane module was constructed using three 50-cm-long membranes in a 0.318-cm o.d. spiraled, stainless steel tube.

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The membrane was a 0.260 mm o.d. and 0.206 mm i.d. composite hollow fiber (Applied Membrane Technology, Minnetonka, MN). It had 1-μm-thick homogeneous siloxane as the active layer deposited on a film of microporous polypropylene as the support. A "T" unit (Components & Controls Inc., Carlstadt, NJ) was connected to each end of the tube, serving as the inlet and the outlet for the elution gas and the stripping gas. The space between the membrane and the "T" units was sealed with epoxy to prevent mixing of the two countercurrent nitrogen streams.

The microtrap was a small diameter silica-lined metal tube packed with a small amount of adsorbent. It had low thermal mass and could be heated and cooled rapidly. As the permeate stream flowed through the microtrap, the organics were trapped and concentrated. The microtrap was then resistively heated to desorb the analytes into the GC column as a sharp injection. Thus, the microtrap served as a concentration cum injection device for GC. The details of the microtrap and its working principles have been presented in previous publications.[31−33] In this study, a 15-cm-long, 0.53-mm-o.d. silica-lined tube (Restek Corp., Bellefonte, PA) packed with 0.02 g of Carbotrap C (Supelco, Supelco Park, PA) served as the microtrap. A 7−10 A current was supplied from a 30 V AC power source to heat the microtrap. The duration and frequency of the heating were controlled by a microprocessor-controlled device fabricated in-house.

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

RESULTS AND DISCUSSION

A major issue with membrane extraction has been the speed of analysis. Diffusion through the membrane and the boundary layer on its surface is a slow process.[13−19] To prevent carryover, a sample cannot be analyzed until permeation from the previous injection is completed. The time required to complete permeation is referred to as lag time, which is defined as the time interval between the points corresponding to 10% of maximum response in the ascending and descending parts of the permeation profile.[18]

Typical profiles of permeate flux through the membrane using aqueous elution, aqueous elution followed by gas purging, and GIME are shown in Figure 2. The permeation profiles were obtained by injecting a 1-mL sample into the membrane and then monitoring the output every 10 s. When compared to aqueous elution, the lag time in membrane extraction reduced by 75%, from 8 to 2 min with gas injection. In the case of aqueous elution with gas purging at the 4th minute, the lag time was 5 min, and the reduction in lag time by gas injection was 60%.

The system response with GIME was 97% of that with aqueous elution; that is, sensitivity remained the same. The profile during aqueous elution exhibits a long drawn-out tailing, which increases

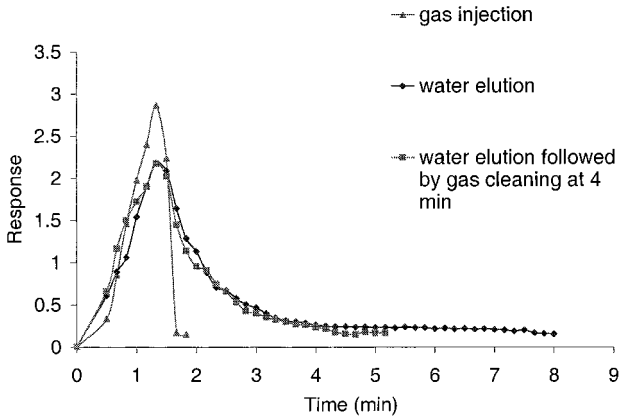

Figure 2. Permeation profiles for a 1-mL 500 ppb benzene sample at an eluent (gas or liquid) flow rate of 1 mL/min.

the lag time but makes little contribution to sensitivity. The permeation profile during GIME generated a symmetric, Gaussian profile with no tailing. Therefore, gas injection offers the advantage of shorter lag time with practically no loss in sensitivity.

The advantage of GIME over aqueous elution can be realized from a theoretical standpoint as well. A mathematic model was previously reported for describing the permeation profile in non-steady-state membrane extraction [27,34] using an aqueous eluent. The model is applicable to GIME because the only thing that changes by going from a liquid to a gas is the transport properties of the eluent.[35] This change is reflected as the change in the overall diffusion coefficient. The permeation rate at time t, is given as $J(t)$

$$J(t) = J_{ss}\,[f(Dt/L^2) - \gamma f(D(t - \Delta t)/L^2)] \qquad (1)$$

where Δt is the duration of the sample pulse, D is diffusion coefficient, L is membrane thickness, and $f(Dt/L^2) = 1 + 2\sum_{n=1}^{\infty}(-1)^n \exp[-Dt(n\pi/L)^2]$

at $t < \Delta t$ and $\gamma = 0$,

$$J(t) = J_{ss}\{1 + 2\sum_{n=1}^{\infty}(-1)^n \exp[-Dt(n\pi/L)^2]\} \qquad (2)$$

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

$$J(t) = J_{ss}\{2\sum_{n=1}^{\infty}(-1)^n \exp[-Dt(n\pi/L)^2] - 2\sum_{n=1}^{\infty}(-1)^n \exp[-D(t - \Delta t)(n\pi/L)^2]\} \qquad (3)$$

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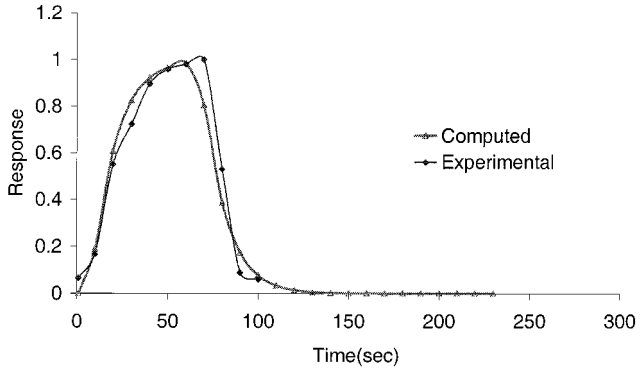

Figure 3. Experimental and computed permeation profiles for a 1-mL, 500 ppb benzene sample at a nitrogen flow rate of 1 mL/min.

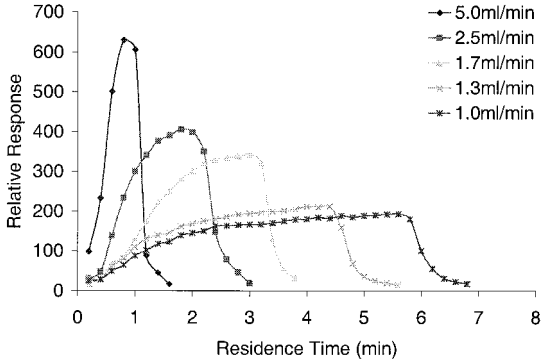

Figure 4. System response as a function of residence time for a 5-mL, 100 ppb toluene sample at different nitrogen flow rates.

The overall diffusion coefficient, D, can be calculated from eqs 2 and 3 as follows.[18] At the maximum point in the permeation profile,

$$J_{\max} = J_{ss}\{2\sum_{n=1}^{\infty}(-1)^n \exp[-Dt_{\max}(n\pi/L)^2] - 2\sum_{n=1}^{\infty}(-1)^n \exp[-D(t_{\max} - \Delta t)(n\pi/L)^2]\} \quad (4)$$

where $t_{\max}$ is the time corresponding to $J_{\max,}$ the maximum permeation flux. By injecting two different volume samples at the same N_2 flow rate, two different $t_{\max}$'s and $J_{\max}$'s were obtained, and eq 4 was solved numerically. The overall diffusion coefficient D for benzene (using a 500 ppb sample) was found to be 6.3×10^{-8} cm^2/s. This was seven times higher than that reported for benzene during aqueous elution.[18] Because the same membrane was used in both cases, the higher diffusion coefficient is attributed to the reduction of boundary layer effects in GIME. A permeation profile was computed using this value of D and is plotted in Figure 3. Good agreement between experimental and computed results is seen.

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

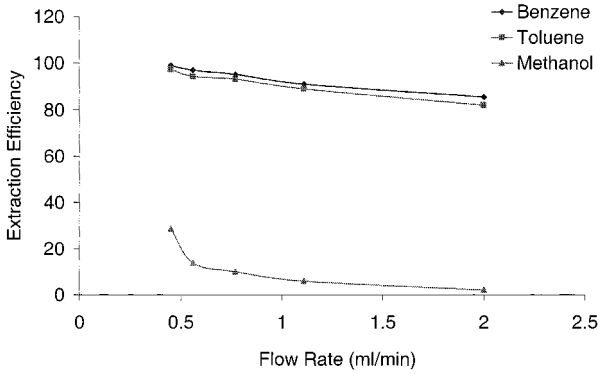

Figure 5. Extraction efficiency as a function of sample flow rate. A 5-mL of 50 ppm sample was used in each case.

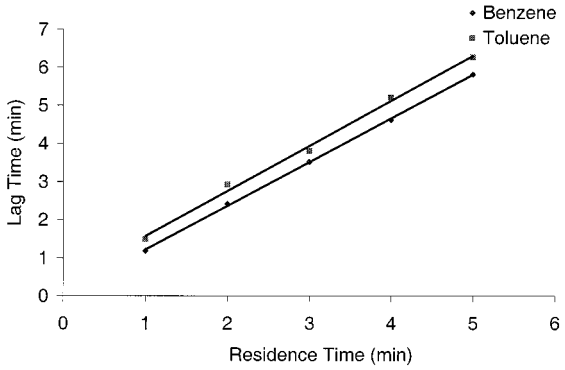

Figure 6. Lag time as a function of sample residence time. A 2-mL sample at a concentration of 50 ppm was used here.

Another issue with aqueous elution has been sample dispersion. It was reported that during aqueous elution in PIME, a 2-mL sample was dispersed into a 9 mL volume at a flow rate of 1 mL/min.[19] Similarly, a simulation of a membrane-introduction mass spectrometry (MIMS) showed that a 15-s block input produced a 60-s dispersed profile.[6] Dispersion increases with the increase in the aqueous eluent flow rate. As mentioned before, dispersion results in the increase in lag time and the decrease in analyte flux rate.[6,19] The phenomena of dispersion in flow injection analysis (FIA) have been studied.[36,37] The flow profiles here are similar to FIA, and the dispersion profiles are similar. The major causes of dispersion are convective and diffusive mixing of the sample with the carrier stream. Convection has been found to be the cause of tailing in the concentration profile. Diffusion is known to make minor contributions to the broadening of the sample pulse and does not change its symmetric shape.

The long tailing in the permeation profile during aqueous elution shows strong convective mixing between the eluent and the sample. On the other hand, the symmetric shape of the permeation profile during GIME indicates that there was no convective mixing with the N_2. The permeation profiles as a function of gas flow rate are shown in Figure 4. Higher N_2 flow rates generated higher flux rates. The opposite was observed during aqueous elution in PIME and MIMS, in which the analyte flux rate decreased with an increase of eluent flow rate.[6,19] The drop of flux rate was due to increased convective dispersion at the higher flow rate. This difference further demonstrates the elimination of dispersion by gas injection of aqueous samples.

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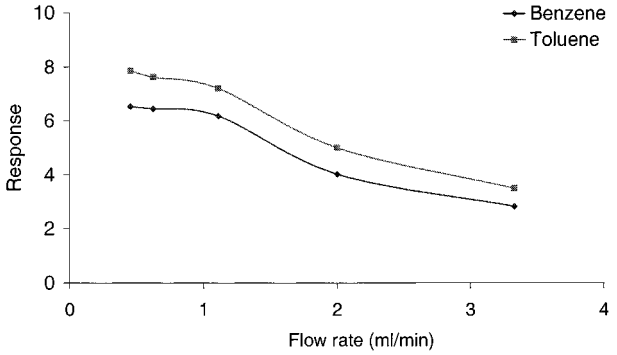

Figure 7. System response as a function of sample flow rate. Sample volume was 5 mL, and concentration was 50 ppb.

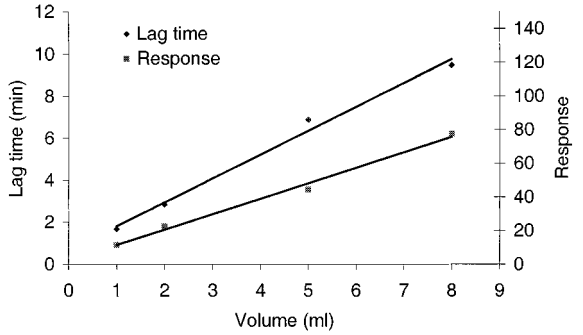

Figure 8. System response and lag time as a function of sample volume. Benzene samples used were 500 ppb at a nitrogen flow rate of 1 mL/min.

In addition, GIME did not need a pump for eluent delivery. It also eliminated the need for postinjection gas cleaning that had been used in PIME to break up the aqueous boundary layer. Therefore, gas injection resulted in simpler instrumentation and operational procedures.

Effects of Process Parameters. Figure 5 shows that extraction efficiency increased with an increase in sample residence time in the membrane. For a given sample volume, sample residence time decreased as the N_2 flow rate increased. In other words, the lower the sample flow rate, the higher was the extraction efficiency. Extraction efficiency is also a function of the membrane–water partition coefficient of the analytes. According to Figure 5, hydrophobic compounds such as benzene and toluene had much higher extraction efficiency than the polar, water-soluble methanol. Nonpolar organics in general have a higher partition coefficient in the hydrophobic membrane used here.

Sample flow rate also affects lag time and analytical sensitivity. Figure 6 shows that higher flow rates resulted in shorter residence time in the membrane, which in turn reduced lag time. Figure 4 shows the permeation profiles for 5-mL, 500 ppb toluene samples at different N_2 flow rates. When the flow rate decreased, lower amounts of analytes were brought into the membrane per unit time, resulting in a lower permeate flux rate. Figure 7 is a plot of instrument response as a function of flow rate. Despite lower permeate flux rate, the response increased with the decrease in flow rate. This was because lower flow rates resulted in longer residence times and higher extraction efficiencies. The system response was proportional to the cumulative flux. The response leveled off below the flow rate of 1 mL/min, because the extraction was nearly exhaustive.

Sample volume is another important variable that affects lag time and sensitivity. With all other parameters remaining constant,

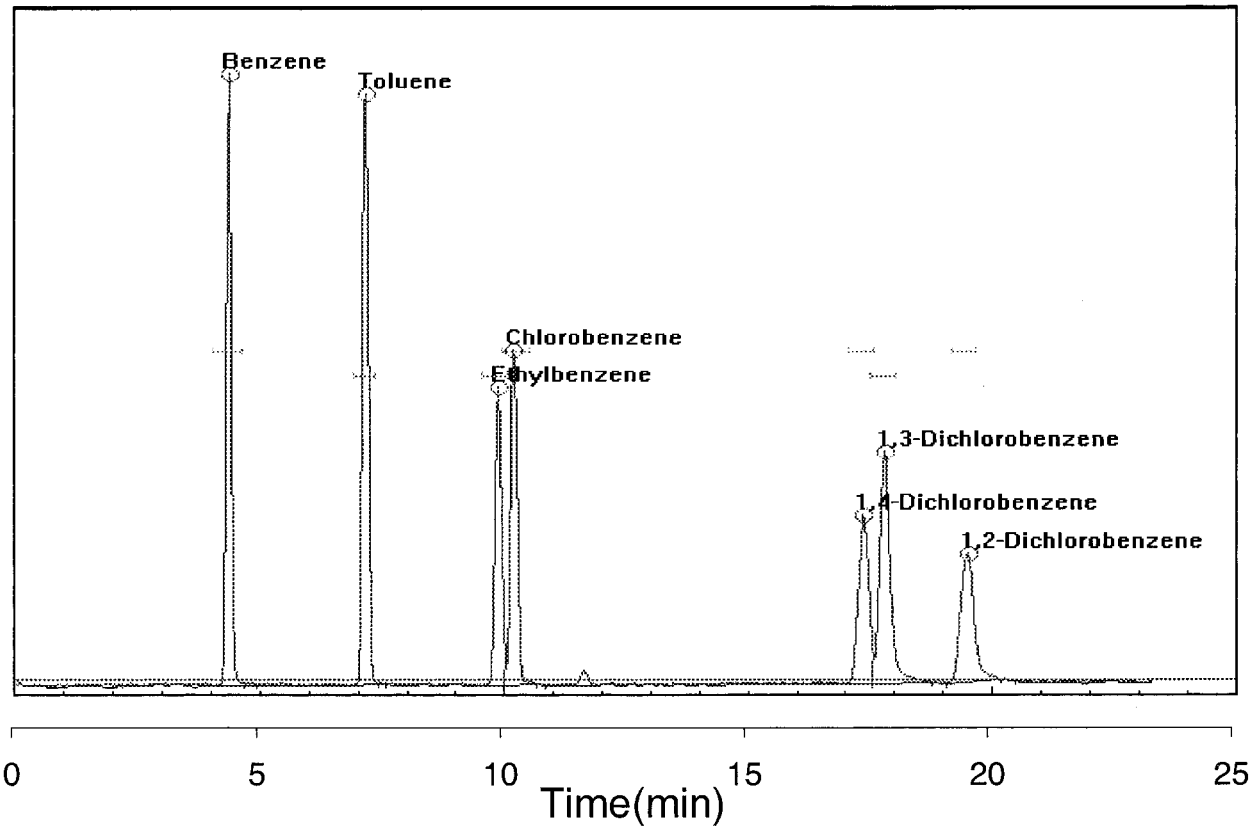

Figure 9. Chromatogram of an aqueous sample containing parts-per-billion level purgable aromatics as listed in USEPA Standard Method 602 by GIME.

the sensitivity was proportional to the sample volume, because a larger sample containing more analytes generated a higher detector response. On the other hand, a larger volume resulted in a longer lag time. The system response and lag time as a function of sample volume are shown in Figure 8. Both increased linearly with sample volume.

In summary, there was a compromise between the lag time and the sensitivity in GIME. Nevertheless, using the same sample volume and flow rate, gas injection was much faster than aqueous elution. This could significantly increase sample throughput if fast GC was coupled with GIME. If the analysis frequency in continuous monitoring were to be the same for aqueous elution and gas injection, a larger sample volume and a lower flow rate could be used in GIME to increase sensitivity.

Analytical Performance. In GIME, individual samples can be analyzed by discrete injections, and continuous monitoring can be carried out by sequential injections. Figure 9 shows a chromatogram of the seven aromatic compounds listed in EPA Standard Method 602 by GIME. The Method Detection Limits (MDLs) for benzene, toluene, and ethylbenzene were 0.1, 0.1, and 0.9 ppb, respectively, using 2-mL samples at a N_2 flow rate of 1 mL/min. The MDLs were calculated using a standard EPA method.[38] The experiments were performed using a portable GC fitted with a PID. This instrument was not so sensitive as the laboratory instruments. The direct comparison presented earlier indicated that the sensitivity by gas injection was comparable to that by water elution. On the basis of prior experiences,[17,18] it is estimated that significantly lower detection limits could be achieved using a regular benchtop GC/FID. In aqueous elution, the maximum volume that can be injected is limited by lag time.[18,19] Because permeation is much faster with gas injection, it is conceivable that the detection limits could be lowered by increasing injection volume. It should also be noted that MDLs depend on parameters such as membrane length, number of fibers, and the N_2 flow rate.[18,19]

The relative standard deviations (RSDs) obtained by seven replicate analyses of a 1-mL, 10 ppb sample were 1.7, 2.3, and 2.8% for benzene, toluene, and ethylbenzene, respectively. The calibration curves in the 1−1000 ppb concentration range were linear, and regression coefficients for benzene and toluene were 0.995 and 0.999.

(38) Code Fed. Register. 1994, Part 136, Appendix B.

CONCLUSION

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

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