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Liquid-Phase Microextraction in a Single Drop of Organic Solvent by Using a Conventional Microsyringe

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Two modes of liquid-phase microextraction (LPME) were developed for capillary gas chromatography. Both methodologies, i.e., static LPME and dynamic LPME, involve the use of very small amounts of organic solvent (<2 μL) in a conventional microsyringe. The performance of the two techniques is demonstrated in the determination of two chlorobenzenes extracted into a single drop of toluene by the use of a 10-μL syringe. Static LPME provided some enrichment (∼12-fold), good reproducibility (9.7%), and simplicity but suffered relatively long extraction time (15 min). Dynamic LPME provided higher (∼27-fold) enrichment within much shorter extraction time (∼3 min), and relatively poorer precision (12.8%), primarily due to repeated manual manipulation. Both methods allow the direct transfer of extracted analytes into a gas chromatograph.

Liquid−liquid extraction (LLE) is among the oldest of the preconcentration and matrix isolation techniques in analytical chemistry. However, conventional liquid−liquid extraction uses large amounts of solvent, which are often hazardous, and is time consuming to perform. Techniques such as flow injection extraction (FIE),[1,2] solid-phase extraction,[3,4] and solid-phase microextraction[5−7] have been developed to overcome these disadvantages.

FIE was first described in 1978 by Karlberg and Thelander.[1] In conventional FIE procedures, an aqueous sample is injected into an aqueous carrier stream. Organic segments are then continuously inserted into this stream. After the segmented stream passes through a coil in which extraction occurs, the organic phase is separated from the aqueous phase and is led through a flow cell for measurement. As compared with traditional LLE, FIE offers the advantages of low consumption in reagent, sample, and organic solvent, high speed, and low cost. However, the consumption of organic solvent was still at the level of several hundred microliters per analysis.

In 1979, Murray[8] developed another kind of liquid microextraction system for gas chromatography (GC). The method involved the use of 200 μL of organic solvent as extractant. More recently, Cantwell and Jeannot[9] developed a liquid−liquid microextraction system by which solvent microextraction was achieved into a single drop (8 μL). However, one common disadvantage of both methods is that extraction and injection are performed separately in two different instruments. Solid-phase microextraction (SPME) developed by Pawliszyn et al.[5] is a solvent-free and environmentally sound extraction technique. An important feature of SPME is the integration of extraction and injection in the same fiber, which can be considered to function as both a SPME sorbent and a microsyringe.

In this article, we report on a concept to perform liquid−liquid microextraction and injection in one instrument, i.e., the commonly used microsyringe which functions as a microseparatory funnel for extraction as well as a microsyringe for injection into the gas chromatograph. The technique is termed liquid-phase microextraction (LPME). Two modes of LPME, static and dynamic, were investigated. It is believed that this technique, especially dynamic LPME (which can also be considered as micro-FIE in some sense), can provide an attractive alternative to conventional FIE and SPME for GC analysis.

EXPERIMENTAL SECTION

Apparatus. Experiments involving toluene as extraction solvent (Figures 1−6) were carried out on a Hewlett-Packard (Avondale, PA) Model 5890 gas chromatograph with an electron capture detector (ECD). Separation was performed on a 25 m × 0.32 mm i.d. fused-silica capillary column with 0.5-μm Ultra-2 coating (Hewlett-Packard). Nitrogen was used as carrier gas with flow rate of 1.2 mL/min. Experiments involving chloroform as extraction solvent (Figures 7 and 8) were carried out on a Shimadzu GC/MS Model QP5000 (Kyoto, Japan) under full-scan mode. Separation was performed on a 30 m × 0.32 mm i.d. fused-silica capillary column with 0.5-μm DB-5 coating (J&W Scientific, Folsom, CA). Helium was employed as carrier gas at 2 mL/min. Temperatures, detector, 250 °C; injector, 240 °C; column, 80−220 °C (programmed at 8 °C/min).

A microsyringe, with an angled-cut needle tip (Model 10R, glass barrel i.d., 0.60 mm; needle i.d., 0.11 mm), used for extraction and injection, was made by SGE Scientific (Sydney, Australia). The syringe plunger operated within the glass barrel, not in the needle.

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Reagents. 1,2,3-Trichlorobenzene and 1,2,3,4,5-pentachlorobenzene were bought from Aldrich (Milwaukee, WI). HPLC-grade toluene was bought from J. T. Baker (Phillipsburg, NJ). Deionized water was prepared on a water purification system supplied by a Milli-Q system (Millipore, Bedford, MA).

Extraction Process. Two modes of LPME were investigated and compared in our experiments.

Static LPME consists of the following steps: (1) Withdraw 1 μL of toluene into a 10-μL microsyringe. (2) Pass the needle of the microsyringe through the sample vial (4 mL) septum, and immerse the tip of needle in the liquid sample. (3) Depress the plunger to expose a 1-μL drop of toluene to the sample. The analytes are then partitioned between the aqueous solution and the toluene for 15 min. (4) Retract the drop of toluene into the microsyringe and remove the latter from the sample vial. (5) Insert the needle into the GC injector port and inject.

Dynamic LPME consists of the following steps: (1) Withdraw 1 μL of toluene into a 10-μL microsyringe. (2) Pass the microsyringe needle through the sample vial (4 mL) septum and immerse the needle tip in the liquid sample. (3) Withdraw a 3-μL aqueous sample within ~2 s, wait for ~3 s, then push out 3 μL of sample within another 2 s, and wait for 3 s. The same process was repeated 20 times within ~3 min. Finally, the aqueous sample is pushed out with 1 μL of toluene left in the microsyringe. (4) Retract the needle from the sample vial. (5) Insert the needle into the GC injector port and inject.

RESULTS AND DISCUSSION

In this work, we investigated the two modes of LPME, i.e., static and dynamic LPME, outlined above. Both modes can be carried out in a conventional microsyringe but are different from each other in terms of plunger movement and the consequent performance.

Static LPME of Chlorobenzenes. In static LPME, the organic drop is exposed to the static aqueous sample solution. The analyte in the aqueous solution is transferred to the organic drop by diffusion. To characterize the performance of this method, several parameters were studied: organic drop volume, sampling time, reproducibility, linearity, and enrichment factor.

Organic Drop Volume. The experiment was first conducted to study the effect of organic drop volume on the analytical signal. The toluene drop was exposed to aqueous sample solution for 10 min prior to injection for GC analysis. Figure 1 shows that the analytical signal increases almost linearly with toluene drop volume in the range of 0.5−3 μL and then deviated from the straight line. When drop size exceeded 5 μL, the toluene drop became more buoyant, crept up along the outside of the needle, and could not be withdrawn back into the syringe.

Figure 2 shows the expanded view around the needle tip. It should be noted that the needle tip is an angled cut (to facilitate piercing of the septum in the GC injection port), not a flat cut. The toluene drop is impacted by three forces: upward floating force ($F_f = V_{tol}\gamma_{wat}$) ($\gamma$ = density), and downward gravity ($F_g = V_{tol}\gamma_{tol}$), and adhesion forces ($F_a$) resulted from surface tension (σ). Under experimental conditions, σ is constant.[10] When $F_f - F_g$ is bigger than F_a due to increased V_{tol} (since $\gamma_{wat} > \gamma_{tol}$), the toluene drop begins to move upward slowly away from the tip outlet.

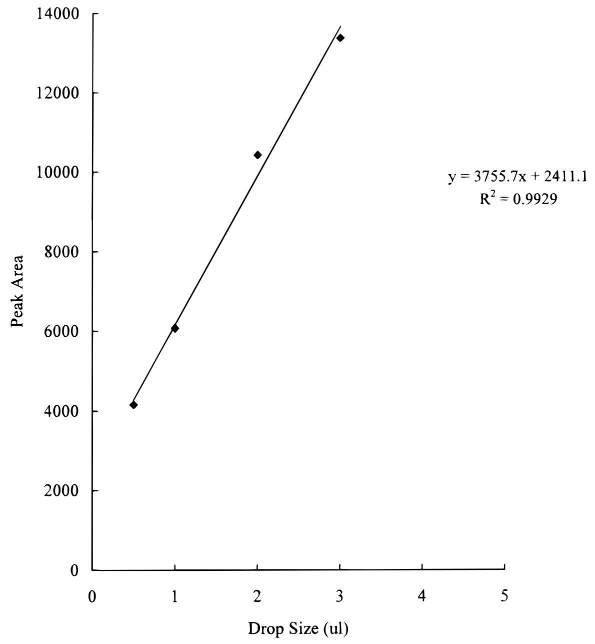

Figure 1. Effect of organic drop volume on the analytical signal.

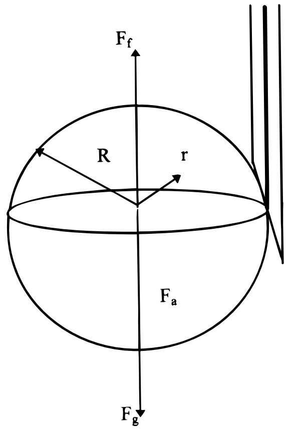

Figure 2. Enlarged view of organic drop attached to the needle tip.

Although a bigger organic drop gives higher signal response, its manipulation is more elaborate and less reliable. Further, large injection volumes bring about bigger band broadening in capillary GC.[11] Taking these into consideration, we fixed drop size at 1 μL in the following investigations.

Sampling Time and Reproducibility. The extraction−time profile was investigated by monitoring the variation of analytical signal with exposure time. As the toluene drop is exposed to aqueous sample solution, more and more chlorobenzenes are transferred into the toluene drop from the aqueous sample solution. Figure 3 shows that the analytical signal increases quickly with sampling time in the range of 1−15 min, and after 15 min the rate of increase slows down. It can be seen, however, that equilibrium has not been reached even after 35 min. Since it is not considered practicable for exposure time to be excessively long to allow equilibrium to occur, it should be just long enough for the extraction rate to have slowed for improved precision.[6,9] On the basis of Figure 3, an exposure time of 15 min was selected for this application, and the reproducibility in peak area was

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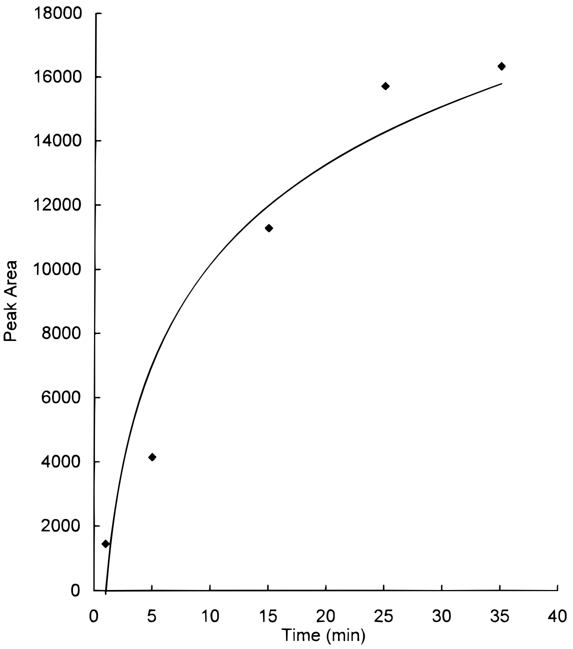

Figure 3. Extraction−time profile for 1,2,3-trichlorobenzene by static LPME in unstirred aqueous solution. Concentrations, 20 μg/L.

investigated on nine replicate experiments. The RSD, 9.7%, is not completely satisfactory but is comparable to that (~10%) in SPME.[6] There are three possible reasons for this. First, similar to that in SPME, the partition equilibrium was not reached in the experiments, so precise timing is essential for good precision. Second, unlike the solid fiber in SPME, the liquid organic drop (e.g., toluene) dissolved slightly with increasing exposure time. It was found that less than 0.1 μL of toluene was dissolved when sampling time was at 15 min. Third, the plunger was stopped on the basis of only visual inspection when the organic drop was withdrawn back into syringe after sampling was completed. This conceivably contributed to the error.

Linearity and Enrichment Factor. In an analysis, it is desired to evaluate the initial concentration of analytes in an aqueous sample solution based upon the measured value of the analyte concentration in the organic drop at sampling time. Similar to that in SPME,[6] an exhaustive extraction does not occur in LPME. Instead, the analyte is partitioned between the bulk aqueous solution and the small organic drop. Since the volume of aqueous solution is much bigger than that of the organic drop (4000 vs 1 μL), variation of analyte concentration during the extraction process is negligible. The five aqueous solutions containing different concentrations of chlorobenzenes were each subjected to extraction by 1 μL of toluene drops for 15 min, and the measured GC signals were plotted against initial aqueous concentration of chlorobenzenes. Two calibration curves were linear with correlation coefficients (R^2) of 0.994−0.996.

It should be noted that over 10-fold enrichment of chlorobenzenes from a water sample was achieved when the toluene drop was exposed to the aqueous solution for 15 min. Further increase in exposure time brought about only slight enhancement in the enrichment. Further, the dissolution of the toluene drop in aqueous solution became more serious with longer exposure time, with trade-off in the enhancement to some extent. In SPME, the extraction process can be accelerated by stirring or sonicating the aqueous solution. In the present case, however, stirring or sonication would break up the toluene drop. This is a limitation of the static LPME procedure. In order to address this problem, and accelerate the extraction process to obtain significantly higher enrichment within a reasonable time, dynamic LPME was developed and evaluated.

Dynamic LPME of Chlorobenzenes. Liquid−liquid extraction involves the distribution of a solute between two immiscible liquid phases. Most often, a solute is extracted from an aqueous solution into an immiscible organic solvent. The extraction speed is strongly affected by observed rate constant (s^{-1})[9,12,13] given by

$$k = A\beta_0\left(\frac{\kappa}{V_{\mathrm{aq}}} + \frac{1}{V_{\mathrm{o}}}\right) \tag{1}$$

where V_{o} and V_{aq} are the volumes of the organic and aqueous phases, respectively, A_i is the interfacial area, β_0 is the overall mass-transfer coefficient with respect to the organic phase, and κ is the distribution coefficient, defined by the ratio of analyte concentration in the organic phase ($C_{\mathrm{o,eq}}$) and the aqueous phase ($C_{\mathrm{aq,eq}}$) at equilibrium. It is obvious that fast extraction requires A_i to be maximized while V_{o} and V_{aq} be minimized. In their work on droplet extraction of gas samples, Liu and Dasgupta[14,15] also found that a spherical or ovoid shape was not preferred in terms of extraction speed because of the small surface/volume ratio. They utilized circular or U-shaped wire loops to form "filmlike" droplets for quick sampling. Similarly, we developed a method described as dynamic LPME, to permit the formation of a renewable microfilm within a microsyringe. Dynamic LPME features the repeated movement of the syringe plunger, as compared to static LPME. Figure 4 shows the expanded view of the extraction process in a microsyringe (chart not to scale). In order to simplify theoretical treatment, we assume that the internal diameter and material of the needle are the same as those of the glass barrel. Two features of the dynamic LPME should be explained.

First, a very thin organic film (OF) is left and formed on the inner surface of the microsyringe barrel and needle after the organic solvent is withdrawn,[16] followed by the aqueous sample solution. Similar to that in FIE, a bolus flow[2] (convection of liquid) was also formed in the opposite direction in the organic plug (OP) and aqueous sample plug (ASP) during the movement of the plunger. Therefore, the analyte is transferred fast from the ASP into the OF (Figure 4b). After a dwell time of several seconds to achieve equilibrium, the ASP is completely discharged. The analyte is then rapidly transferred from the OF into the OP (Figure 4c). The OF works as a transporter by which analyte is transferred from the ASP to the OP. In addition, a little percentage of analyte in the ASP is transferred directly to the OP across their boundaries. Direct transfer is probably negligible as compared with the indirect transfer by the OF, as $A_{\mathrm{asp-of}}$ (interfacial area between OF and ASP) is much bigger than $A_{\mathrm{asp-op}}$ (interfacial area between OF and ASP).

Second, the repeated aspiration of the ASP, following the first sampling cycle, ensures that both the OF and the ASP are periodically renewed, and thus the OF would be in contact with

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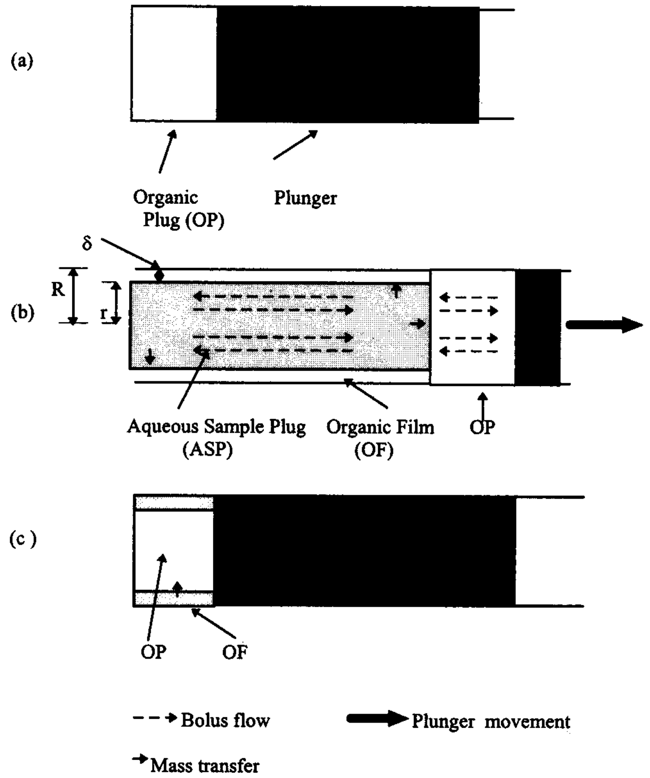

Figure 4. Expanded views of dynamic LPME within the microsyringe.

fresh aqueous sample having the initial analyte concentration in the sample vial.

To characterize the performance of dynamic LPME, the following factors were studied: sampling volume, number of sampling, reproducibility, linearity, and enrichment factor.

Sampling Volume. The sampling volume is referred to the volume of aqueous sample plug (V_{asp}) that is withdrawn into the microsyringe each time. Dwelling time is the total time that the ASP remains within the microsyringe in one sampling cycle. One sampling cycle consists of four steps, withdrawal and discharge of the ASP, and two pauses in-between. In this experiment, sampling was performed one time, with the dwelling time of ~9 s, almost evenly allocated to the four steps as above. The influence of V_{asp} on extraction was studied by monitoring the variation of the GC signal with sampling volume (Figure 5). As can be seen, the GC signal increases linearly with V_{asp}. This result can be explained as follows.

In liquid–liquid extraction, the equilibrium concentration of analyte in the organic phase is given by[9–11]

$$C_{o,eq} = \kappa C_{aq,eq} = \frac{\kappa C_{aq,ini}}{1+\kappa V_o/V_{aq}} \qquad (2)$$

where $C_{o,eq}$ and $C_{aq,eq}$ are the equilibrium concentrations of analyte in the organic and aqueous phase. $C_{aq,ini}$ is the initial concentration of analyte in the aqueous phase. The amount of analyte transported from the ASP to the OP after the first sampling (m_1) is given by

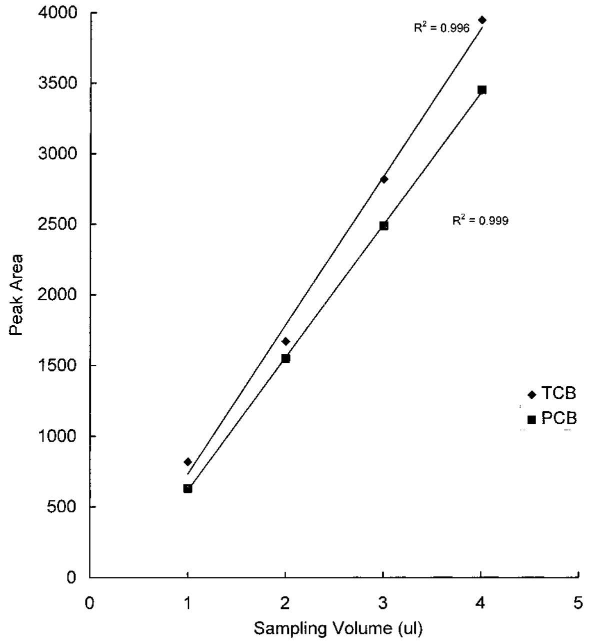

Figure 5. Effect of sampling volume on analytical signal. Concentrations, 1,2,3-trichlorobenzene (TCB), 20 μg/L; pentachlorobenzene (PCB), 10 μg/L.

$$m_1 = C_{of,1}V_{of} = C_{of,eq}V_{of} = \kappa C_{asp,eq}V_{of} = \frac{\kappa C_{asp,ini}}{1+(\kappa V_{of}/V_{asp})}V_{of} = \frac{\kappa C_{aq,ini}}{1+(\kappa V_{of}/V_{asp})}V_{of} \qquad (3)$$

where V_{of} and V_{asp} are the volumes of the OF and the ASP, $C_{of,1}$ and $C_{of,eq}$ are the analyte concentrations in the OF after the first sampling and at equilibrium, and $C_{asp,ini}$ and $C_{aq,ini}$ are the initial concentrations of the analyte in the ASP and the bulk aqueous solution in sample vial. As the mass transfer between thin OF and narrow ASP is very fast due to bolus flow,[2] the equilibrium between the ASP and the OF is instantly established. Hence, $C_{of,1}$ can be reasonably assumed to be equal to $C_{of,eq}$. In addition, $C_{asp,ini}$ is the same as $C_{aq,ini}$. The analyte concentration in the OP after first sampling is given by

$$C_{op,1} = \frac{m_1}{V_{op}} = \frac{\dfrac{\kappa C_{aq,ini}}{1+\kappa(V_{of}/V_{asp})}V_{of}}{V_{op}} = \frac{\kappa C_{asp,ini}V_{of}V_{asp}}{(V_{asp}+\kappa V_{of})V_{op}} \qquad (4)$$

where V_{op} is the volume of the OP. The volumes of the OF and the ASP are given by

$$V_{of} = \pi R^2 L - \pi r^2 L = \pi L(R-r)(R+r) \approx 2\pi R\delta L \qquad (5)$$

$$V_{asp} = \pi r^2 L \approx \pi R^2 L \qquad (6)$$

where L is the length of the ASP, r is its diameter, R is the inner diameter of the glass barrel of the microsyringe, and δ is the thickness of the OF. Since the OF is very thin, R can be considered as the same as r. Combining eqs 4–6 gives

$$C_{op,1} = \frac{\kappa C_{asp}(2\delta/R)V_{asp}V_{asp}}{\{V_{asp}+\kappa(2\delta/R)V_{asp}\}V_{op}} = \frac{2\delta\kappa C_{aq,ini}}{(R+2\delta)V_{op}}V_{asp} \qquad (7)$$

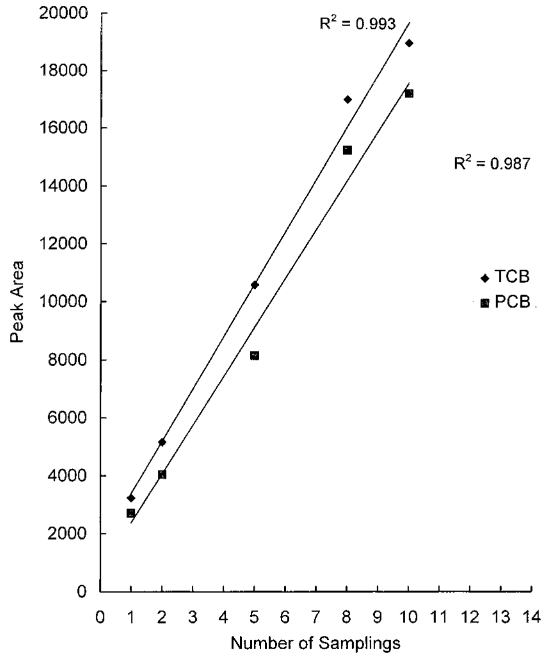

Figure 6. Extraction−number of samplings profile for TCB and PCB by dynamic LPME in unstirred aqueous solution. Dwelling time, ~10 s.

Equation 7 reveals that $C_{op,1}$ is proportional to sampling volume (V_{asp}), since δ, k, R, $C_{aq,ini}$ and V_{op} are constant under experimental conditions. Although $C_{op,1}$ increases linearly with sampling volume (V_{asp}) in the range of 1−4 μL, nonzero intercepts were attained for both TCB and PCB. One reason for this phenomenon may be that the film thickness formed in the needle is different from that in the glass barrel. When the sampling volume is smaller than 1 μL (capacity of needle is ~0.7 μL), almost all of the water sample is present in the needle rather than in the glass barrel.

In practice, V_{asp} cannot increase indefinitely. First, V_{asp} is limited by the volume of the microsyringe (e.g., 10 μL). Second, V_{asp} is limited by the increased difficulty of manually manipulating the plunger repeatedly. In this work, a V_{asp} of ~4 μL (~0.8 μL in needle is included) is the maximum volume that can be conveniently manipulated manually.

Number of Samplings. The key operation in dynamic LPME is the repeated up and down movement of the plunger. As the ASP is repeatedly withdrawn into the microsyringe and discharged, the ASP and the OF are periodically renewed, and more and more analyte is periodically transported from the bulk aqueous solution in the sample vial to the OP in the microsyringe. This is evidenced by the continuously increasing signal with the number of samplings (Figure 6). It should be noted that the GC signal increased linearly with the number of samplings in the range of 1−10 under investigation. This phenomenon may be explained as follows:

m_1, m_2, m_3, ..., m_n is the transported amount of analyte in the first, second, third, ..., and nth cycle of sampling. m_1 is already given by eq 4. After the first sampling, the ASP is periodically renewed completely, and $C_{asp,ini}$ is always the same as $C_{aq,ini}$. The OF is also periodically renewed. Unlike the complete renewal of the ASP, the OF is partially renewed, since a trace amount of the analyte ($V_{of}C_{of,eq}/V_{op}$) from the first sampling is left in the renewed OF. As V_{of} is much smaller than V_{op}, the trace amount of analyte left in the renewed OF is negligible; i.e., the OF can be assumed to be completely renewed. With the assumptions above, we can deduce that $C_{of,2}$ is the same as $C_{of,1}$, and $C_{of,eq}$. The transported amount of analyte in the second sampling is thus given by

$$m_2 = \left(C_{of,eq} - \frac{m_1}{V_{op}}\right)V_{of} = \left(C_{of,eq} - \frac{C_{of,eq}V_{of}}{V_{op}}\right)V_{of} \approx C_{of,eq}V_{of} \tag{8}$$

When n is relatively small, $(n - 1)V_{of}$ is much smaller than V_{op} and m_n is given by

$$m_n = \left(C_{of,eq} - \frac{m_1 + m_2 + m_3 + ..., m_{(n-1)}}{V_{op}}\right)V_{of} \approx \left(C_{of,eq} - \frac{(n-1)C_{of}V_{of}}{V_{op}}\right)V_{of} \approx C_{of,eq}V_{of} \tag{9}$$

Then, the analyte concentration in OP after n sampling ($C_{op,n}$) cycles is

$$C_{op,n} = \frac{m_1 + m_2 + ..., + m_n}{V_{op}} = \frac{C_{op,eq}V_{of}}{V_{op}}n \tag{10}$$

$$C_{op,n} = \frac{nV_{of}}{V_{op}}C_{op,eq} = \frac{nV_{of}}{V_{op}}\frac{\kappa C_{aq,ini}}{1+(2\kappa\delta/R)} = \frac{n\kappa RV_{of}}{V_{op}(R + 2\kappa\delta)}C_{aq,ini} \tag{11}$$

Equation 10 shows that there is a linear relationship between the analyte concentration in the OP ($C_{op,n}$) and number of samplings (n) when n is relatively small. In other words, the transported amount of analyte during each sampling cycle is approximately the same when n is relatively small. Accurately speaking, however, m_n is decreased very slowly even when n is small because OF is not completely renewed each time. This may be one of the reasons why nonzero intercepts were present in Figure 6.

Linearity, Reproducibility, and Enrichment Factor. Equation 11 shows that $C_{aq,ini}$ for an aqueous sample solution can be evaluated on the basis of the measured value of $C_{op,n}$ for the organic plug. It may be inferred that, when n is fixed, a calibration plot of GC signal vs $C_{aq,ini}$ for a series of standard concentrations should be linear. This is supported by the two calibration curves of GC signal vs initial aqueous concentration of chlorobenzenes, with correlation coefficient (R^2) of 0.989−0.990.

As with static LPME, it is not practical to sample repeatedly until equilibrium is achieved. It is obvious that, with a greater number of samplings, the enrichment factor is higher, the system more closely approaches equilibrium, and the number of samplings and other operational conditions are less critical. Since the ASP is periodically renewed, the OF would periodically be in contact with fresh aqueous sample solution having the initial analyte concentration, and as a consequence, the analyte concentration in the OF would be approaching a equilibrium value of $\kappa C_{aq,ini}$, when no more analyte can be transported by the OF. Hence, n should be as large as possible for improved enrichment and precision. On the other hand, manual manipulation of the syringe plunger becomes more difficult and less reproducible when n is increased. In our experiments, n is fixed at 10, and

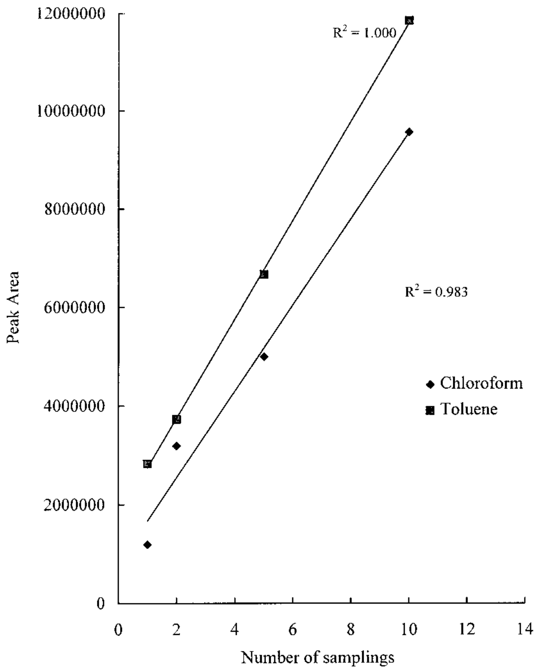

Figure 7. Extraction−number of samplings profile for PCB (1.0 μg/mL) by dynamic LPME using toluene and chloroform as extracting solvents, respectively. Dwelling time, ~10 s.

the reproducibility of GC signals (peak area) on eight replicate experiments was tested. The percent RSD is 12.8%, slightly worse than that of static LPME (9.7%), and of conventional SPME (10%).[6] When the number of samplings was increased to 20, an enrichment factor of ~27 was attained within ~3 min of sampling, which is much shorter than that in static LPME (15 min). The limit of detection was estimated to be 0.05 (pentachlorobenzene)−0.1 (1,2,3-trichlorobenzene) μg/L, 2 times lower than that of static LPME (0.1−0.3 μg/L) and comparable to that of SPME.[6] The precision and enrichment should be improved by automating the movement of the plunger.

In addition to toluene ($\gamma = 0.867$ g/mL), we also investigated a heavier than water solvent, chloroform ($\gamma = 1.483$ g/mL), in dynamic LPME. Like toluene, chloroform remained as the upper layer in the syringe barrel above the aqueous layer, in contrast to what happens in a conventional separatory funnel. This phenomenon may be due to the fact that the surface tension of liquid (chloroform and water) within the narrow glass barrel is large enough to counter gravity.

Figure 7 compares the effect of number of samplings on the analytical signal when chloroform and toluene are used as extracting solvent. It is indicated that the GC signal is linearly related to the number of samplings in the range of 1−10 when either chloroform or toluene is used. However, the slope of curve 1 is higher than that of curve 2, which is primarily due to that distribution coefficient of pentachlorobenzene in toluene being higher than that in chloroform (eq 11).

When SPME is used to extract volatile or semivolatile organic chemicals in water, peak tailings is sometimes observed, caused by slower desorption from within the bulk of the film than the initial desorption of layers on the surface of the film.[6] By using dynamic LPME, peak tailing can be minimized, which is evidenced by the symmetric peaks in the chromatogram (Figure 8).

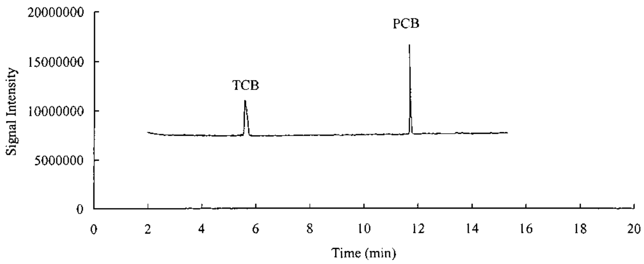

Figure 8. Separation of TCB and PCB at 1.0 μg/mL in water sample, extracted by dynamic LPME using chloroform as extracting solvent. Dwelling time, ~10 s; number of samplings, 10.

CONCLUSION AND FUTURE RESEARCH

A comparison of static LPME with dynamic LPME shows that the two methods are comparable in terms of organic solvent consumption (<2 μL). Static LPME provides better reproducibility but suffers limited enrichment and longer extraction time. Dynamic LPME provides higher enrichment within a much shorter time, but has lower reproducibility, which can conceivably be improved by automation. A conventional autosampler can probably be adapted to perform dynamic LPME.

Dynamic LPME shares the advantage with FIE in terms of high extraction speed and low operation cost. However, in FIE, the phase ratio,[2,15] which governs the ultimately enrichment factor, can only be adjusted over a limited range and not as conveniently as in our present system. The enrichment using dynamic LPME can be easily adjusted over a wide range by selecting the sampling volume and number of samplings. In regard to solvent consumption, the smallest scale FIE systems introduced to date utilize organic segments that are ~1 μL in volume.[17,18] One sample is extracted into many organic segments, typically consuming 150 μL of organic solvent per analysis, ~2 orders of magnitude higher than that in dynamic LPME.

The results also show that dynamic LPME may provide an attractive alternative approach to SPME for microscale preconcentration and matrix isolation. The two techniques are comparable in terms of precision, sensitivity, analysis time, and facility of automation.[6] SPME has the advantage that it can be easily used for head-space analysis. However, SPME requires more dedicated and expensive apparatus than is employed in LPME and suffers from the problem of peak tailing due to slow desorption of analyte from the solid-phase film.[6] Recently, SPME has also been applied to HPLC, which, however, involves the use of a sophisticated setup.[19] Dynamic LPME has the advantage that it can be easily performed in a microsyringe without any modification; also, the sensitivity can be quickly adjusted over a wide range by varying the number of samplings and the sampling volume. Further, the problem of peak tailing often encountered in SPME can be reduced or eliminated. The disadvantage of dynamic LPME is that manual operation is more elaborate and, because of this, gives rise to less reproducible results than SPME. Hence,it is desirable to develop an automated dynamic LPME method based on a conventional autosampler. In addition, as with SPME whereby several solid-phase coatings are available, a wide variety

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of organic solvents can be used in LPME for different target compounds. Preliminary studies have shown that even organic solvents heavier than water (e.g., chloroform) can be used in dynamic and probably static LPME. For enhanced selectivity in real sample analysis, the syringe can be rinsed in the usual way after extraction.

Finally, dynamic LPME can be extended beyond GC applications. It is more convenient than SPME for micro-HPLC and capillary HPLC analyses. These possibilities will be investigated in the future.

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