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Liquid-Phase Microextraction Combined with Hollow Fiber as a Sample Preparation Technique Prior to Gas Chromatography/Mass Spectrometry

Limian Zhao and Hian Kee Lee*

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Republic of Singapore 117543

Two modes of liquid-phase microextraction (LPME) combined with hollow fiber (HF) were developed for gas chromatography/mass spectrometry (GC/MS). Both methodologies, that is, static LPME with HF and dynamic LPME with HF, involved the use of a small volume of organic solvent impregnated in the hollow fiber, which was held by the needle of a conventional GC syringe. In static LPME/HF, the hollow fiber impregnated with solvent was immersed in the aqueous sample, and the extraction processed under stirring; in dynamic LPME/HF, the solvent was repeatedly withdrawn into and discharged from the hollow fiber by a syringe pump. This is believed to be the first reported instance of a semiautomated liquid microextraction procedure. The performance of the two techniques was demonstrated in the analysis of two PAH compounds in an aqueous sample. Static LPME/HF provided ∼35-fold enrichment in 10 min and good reproducibility (∼4%). Dynamic LPME/HF could provide higher enrichment (∼75-fold) in 10 min and even better reproducibility (∼3%). Both methods allow the direct transfer of extracted analytes to a GC/MS system for analysis.

Liquid−liquid extraction (LLE) is the classical technique for sample preconcentration and isolation in analytical chemistry. However, it is time-consuming, generally labor-intensive, and requires use of large amounts of expensive high-purity organic solvents, which are often hazardous. Techniques such as flow injection extraction (FIE),[1,2] solid-phase extraction (SPE)[3,4] and solid-phase microextraction (SPME)[5−7] have been developed to overcome some of these disadvantages.

Miniaturization has become an important trend in the development of sample preparation techniques. SPME is a very well established microscale sample pretreatment technique. It has been developed swiftly in terms of its theory, technology, and applications, illustrated by numerous published papers in the past decade. However, there are still some limitations in SPME, such as the quality of the fibers depending on commercial and noncommercial sources, sample carry-over, and fiber damage during the agitation, as well as the effect of added salt, although these problems can be circumvented by the use of headspace SPME or an appropriate isotopically labeled internal standard. However, not all analytes can be extracted by headspace SPME, and it is rather expensive and difficult to find suitable isotopically labeled standards.

In 1979, Murray[8] developed a type of liquid microextraction technique for gas chromatography, in which 200 μL of organic solvent was used as the extractant. More recently, a novel technique termed solvent microextraction (SME) or liquid-phase microextraction (LPME)[9−14] has been developed. This relatively new technique is performed by suspending a microliter drop of organic solvent on the tip of either a Teflon rod or the needle tip of a microsyringe immersed in the stirred aqueous solution. The analytes partition between the bulk aqueous phase and the organic solvent microdrop. The applications of SME or LPME in environmental analysis and drug analysis have been described in several papers.[15−19] Compared to LLE and SPE, LPME gives a comparable and satisfactory sensitivity and much better enrichment of analytes. In addition, the consumption of solvent is significantly reduced by up to several hundred or several thousand times, and the method is extremely affordable, simple to operate, and fast.

Some practical considerations, however, limit the applications of LPME. The major problem of LPME is that the microdrop suspended on the needle of microsyringe is easily dislodged by the stirred aqueous sample. Although the selection of a syringe with a beveled needle tip,[11] suitable solvent,[17] and a very small volume of solvent (∼1 μL) can obviate this difficulty, they cannot solve this problem completely, thus limiting the development and

* Corresponding author. Fax: (65)-6779-1691. E-mail: chmleehk@nus.edu.sg.

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application of LPME. Furthermore, drop-based LPME works best with clean matrixes, because particles or bubbles in the sample affect the extraction by making the drop unstable, and (for particles) are potentially detrimental to the analytical instrument. Although LPME has been applied to soil matrixes, the exposure time and stirring speed are limited by the drop stability, thus compromising extraction performance (since in general, higher stirring speeds and longer extraction time would enhance the extraction yield[18]). There is certainly room to improve on the microdrop stability.

Petersen-Bjergaard and Rasmussen introduced the use of a hollow fiber in a three-phase (liquid−liquid−liquid) microextraction procedure .[20−23] In this method, the analytes were extracted from aqueous samples through a thin phase of 1-octanol inside the pores of a polypropylene hollow fiber and,finally, into a 25-μL acceptor solution inside the hollow fiber itself. Following this LLLME, the acceptor solution was analyzed by capillary electrophoresis (CE) or high performance liquid chromatography (HPLC). They also applied this technique to gas chromatography (GC), in which a hollow fiber impregnated with 25 μL of solvent was used to extract analytes from aqueous samples.[23] The results suggested that using a hollow fiber to protect the extraction solvent might be an effective method to solve the aforementioned problems.

Previous work on dynamic LPME[11,12] was based on manual manipulation of the syringe plunger, a tedious operation. At the same time, the repeatability of the procedure (RSD 12.8%)[11] was relatively high as a result of difficulty in ensuring good reproducibility of the to-and-fro movements of the plunger. Hence, it is desirable to develop an automated dynamic LPME to overcome these problems.

In this article, we report on a concept of LPME combined with a hollow fiber (LPME-HF). A hollow fiber unit serves as the "holder" and "protector" of 2−3 μL of organic solvent and simultaneously, owing to its porous property, increases the interfacial area between solvent and aqueous sample, thus increasing the extraction efficiency. Two modes of LPME/HF, static and dynamic, were preliminarily investigated in the analysis of PAH. For the first time, the latter mode was conducted in a semi-automated fashion with a programmable syringe pump. Both extraction modes provided good extraction efficiency in only 10 min, and furthermore, reproducibility was improved significantly as compared to that of LPME conducted without the use of the hollow fiber.

EXPERIMENTAL SECTION

Reagents and Apparatus. Fluoranthene and pyrene were bought from Supelco (Bellefonte, PA). 1-Octanol was from Merck (Darmstadt, Germany). Ultrapure water was provided by a Milli-Q water purification system (Millipore, Bedford, MA).

The Q3/2 Accurel polypropylene hollow fiber was bought from Membrana GmbH (Wuppertal, Germany). The inner diameter of the hollow fiber was 600 μm, the thickness of the wall was 200 μm, and the pore size was 0.64 μm.

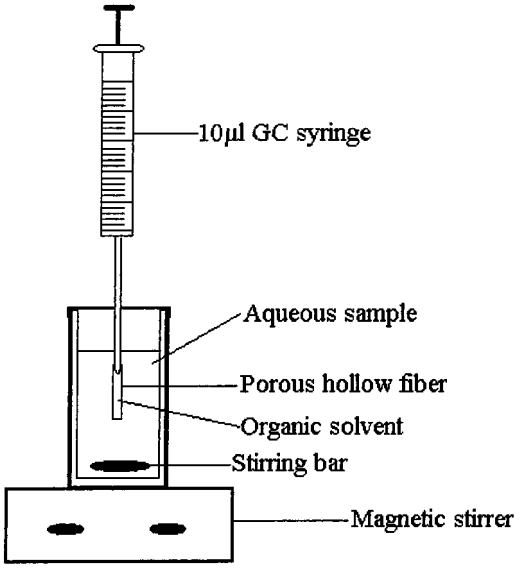

Figure 1. Schematic representation of LPME/HF. For clarity, the syringe pump to which the syringe is affixed is not shown.

A 10-μL GC microsyringe with a cone needle tip and 0.47-mm i.d. (SGE Scientific, Sydney, Australia) was used for the LPME experiments. A PHD 2000 programmable syringe pump, bought from Harvard Apparatus Inc. (Holliston, MA), was used to automate and control the movement of the syringe plunger.

Instrument. Analysis of PAH analytes was performed using a Shimadzu (Tokyo, Japan) QP-5000 GC/MS system equipped with a 30-m × 0.32-mm-i.d. fused-silica capillary column with a 0.5-μm DB-5 coating (J&W Scientific, Folsom, CA). Helium was used as the carrier gas at 1.2 mL/min. The GC conditions were as follows: injector temperature, 250 °C; initial oven temperature, 150 °C for 2 min, programmed to 300 °C at 10 °C/min, then maintained at 300 °C for 3min. Initially, full-scan mode (m/z 40−400) was used to obtain basic information, such as retention time, and the ions selected for identification and quantification. Subsequently, SIM (selected ion monitoring) mode was applied for quantification.

Extraction Process. Two modes of LPME/HF were investigated and compared in our experiments. The basic experimental apparatus is shown in Figure 1. A 3-mL aqueous sample was placed in a 4-mL sample vial. The sample vial was clamped to fix its position above the magnetic stirrer (Heidolph, Kelheim, Germany). A 10-μL GC syringe was used to introduce organic solvent into the hollow fiber, support the hollow fiber, and also to serve as a sample introduction device for the GC/MS. In static LPME/HF, the syringe was clamped on a retort stand; while in dynamic LPME/HF, the syringe was set on the syringe pump, and the plunger was clamped by the pusher block and retaining bracket.

A hollow fiber was cut to produce 1.5-cm segments. The approximate internal volume of this segment was ∼3.5 μL. The hollow fiber segments were sonicated for 2 min in HPLC-grade acetone to remove any contaminants in the fiber. After sonication, the fibers were removed from the acetone, and the solvent was allowed to evaporate completely. These hollow fiber segments were used for subsequent extractions.

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Static LPME/HF consisted of the following steps: 3 μL of 1-octanol was withdrawn into the syringe. The needle of the syringe was inserted into a hollow fiber segment. The hollow fiber was immersed into 1-octanol for 5 s for impregnation of its pores, and then it was filled with the same solvent from the syringe. Then, the fiber (together with the syringe needle) was placed into the aqueous sample, and the syringe was fixed on the retort stand. The magnetic stirrer was switched on to start the extraction. After a prescribed time, the solvent in the fiber was retracted into the syringe, and the syringe was removed from the sample. A 1-μL aliquot of extractant was injected into the GC/MS system for analysis.

Dynamic LPME/HF consisted of the following steps: The first three steps as in static LPME/HF were repeated. The impregnated hollow fiber together with the needle was immersed into the aqueous sample, and the syringe was fixed on the syringe pump. The magnetic stirrer and the syringe pump were simultaneously switched on. The plunger was withdrawn at a speed of 1.9013 mL/hr (the maximum speed for the 0.47-mm i.d. syringe) to withdraw 3 μL of aqueous sample into the hollow fiber. A dwelling (waiting) time of 5 s was set, after which the plunger was then depressed at the same speed to refill 3 μL of the solvent into the fiber. The same dwelling time of 5 s followed this refill operation. The same process was then repeated for a prescribed period of time. Finally, the aqueous sample was expelled from the fiber, and the syringe pump and the stirrer were switched off. The syringe was removed from the sample solution, and a 1-μL aliquot of extractant was withdrawn into the syringe barrel for subsequent injection into the GC/MS for analysis.

RESULTS AND DISCUSSION

In this work, we investigated two modes of LPME/HF, that is, static and dynamic LPME/HF. These two modes were different from each other with respect to plunger movement and the mode of extraction. To evaluate and compare the performance of two modes simply and clearly, peak area and relative peak area percentage, which is the percentage ratio of the peak area of extractant by dynamic LPME/HF to that by static LPME/HF from the aqueous samples at the same concentrations, were used as the GC/MS signals and relative GC/MS signals, respectively.

Selection of Organic Solvent. The type of organic solvent used in LPME/HF was an essential consideration for successful experiments, especially for dynamic LPME/HF, since the solvent must be confined within the pores of the hollow fiber and a very thin organic film should be formed when the syringe plunger is retracted to withdraw the water sample. Generally speaking, there are several requirements for the organic solvent. First, it should be easily immobilized in the hollow fiber pores and be of low volatility. Since the hollow fiber used is made from polypropylene, the organic solvent should have good affinity for this material. This is to prevent solvent loss during extraction, especially in view of the frequent movement of the solvent plug in the hollow fiber during dynamic LPME/HF. Second, it should be immiscible with water, because a thin film should be formed during the dynamic LPME/HF procedure. And last, it should be compatible with GC/MS. On the basis of the above considerations, 1-octanol was selected for this work.[20−23]

Table 1. Comparison of Extraction Efficiencies at Various Organic Solvent Volumes[a]

	fluoranthene[b]		pyrene[b]	
solvent vol (μL)	static LPME/HF	dynamic LPME/HF	static LPME/HF	dynamic LPME/HF
1	100	163	100	152
2	157	263	158	234
3	280	337	305	309
4	336	343	307	309
5	348	359	329	330

[a] Relative GC/MS signals were employed to evaluate the performance of the two extraction modes (relative GC/MS signals is defined as the peak area percentage ratio of the extracts at different conditions to those under static LPME/HF with 1 μL of 1-octanol for 10 min). Water samples were spiked at a concentration of 100 μg/L of each compound. Extraction time was 10 min with a 10 s + 10 s dwelling time. [b] Results varied within 5% RSD (n = 6).

Static LPME/HF of PAHs. We have successfully applied static LPME/HF, also termed hollow-fiber-protected LPME,[24] to the analysis of triazine herbicides. In this technique, organic solvent impregnated in the hollow fiber segment was exposed as a solvent column in a stirred aqueous sample. Therefore, the configuration of the extraction solvent is rod-shaped rather than spherical. This rod-shaped configuration increases the solvent surface area, since for the same volume, the surface area of a sphere is the smallest. Since the hollow fiber was porous, the interfacial area included the longitudinal surface area and the exposed end area of the solvent column. The analytes in the aqueous sample were largely extracted through the hollow fiber into the solvent by diffusion. It was illustrated in our previous work that this configuration can increase the extraction efficiency in comparison with the performance of drop-based LPME.

In this work, static LPME/HF was investigated on the basis of several parameters, such as organic solvent volume, extraction time, reproducibility and linearity. In addition, we also compared the performance of static LPME/HF with that of dynamic LPME/HF.

(1) Organic Solvent Volume. The organic solvent volume for extraction was studied in the range of 1−5 μL. Table 1 shows that the analytical signals of fluoranthene and pyrene increase with the solvent volume in the range of 1−4 μL.

Since the solvent was confined in the hollow fiber, which served as its "holder" and "protector", the solvent column was so stable that it could tolerate very high stirring speeds (up to 1250 rpm). However, high agitation speed produced a large vortex in the sample solution, which led to a section of the hollow fiber being exposed to the atmosphere. High stirring speed also resulted in loss of the solvent by evaporation during the extraction procedure. For the above reasons, the stirring speed was set at 1000rpm. This was still much higher than the stirring speed normally applied to drop-based LPME.[17] In addition, the higher speed also allowed a larger solvent volume for extraction without any problem, although in the present context, it was unnecessary to use a large volume, since the typical GC injection volume was 1 μL. Therefore, 3-μL of solvent volume was selected for subsequent experiments.

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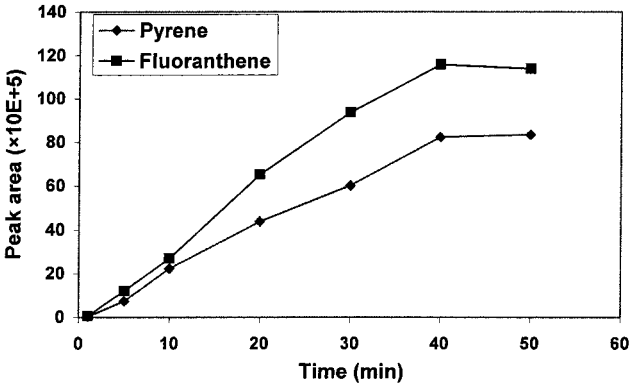

Figure 2. Extraction time profiles for fluoranthene and pyrene by static LPME/HF. Spiked concentration of each compound, 100 μg/L.

(2) Extraction Time and Reproducibility. The extraction time was investigated in the range of 1−50 min. Figure 2 shows that the analytical signals increase quickly with the extraction time until 40 min; after 40 min, no dramatic increase was obtained with additional extraction time. LPME is a process dependent on equilibrium rather than exhaustive extraction[11,15−17]. It requires a period of time for equilibrium to be established. Normally, the time for establishing equilibrium is selected as the extraction time. However, it is not normally considered practicable to maintain extraction time long enough for equilibrium to be established. This is apart from the problem of solvent depletion, as mentioned previously. A 10-min estraction time was deemed to be sufficient for subsequent experiments.

The reproducibility of the peak area was studied on six replicate experiments for a sample containing 100 μg/L of each of PAH. It should be noted that the reproducibility was much better than that of drop-based LPME. The relative standard deviations (RSD) of fluoranthene and pyrene were 3.98 and 4.54%, and the RSD values of previous LPME or SME were found to be 10% or even higher[11,15−17]. Precise timing was, however, essential in LPME/HF for good reproducibility, since the partition equilibrium was not established at the time extraction was stopped.

(3) Linearity and Enrichment Factor. Calibration curves of fluoranthene and pyrene were calculated using six spiking levels in the concentration range 10−400 μg/L. For each spiking level, three replicate analyses were performed. Each solution was subjected to extraction with 3 μL of 1-octanol for 10 min, and the measured GC/MS signals were plotted against the initial aqueous concentration of the PAHs. Coefficients of correlation (r^2) were 0.9993 and 0.9987 for fluoranthene and pyrene, respectively.

It should be noted that a >40-fold enrichment of PAHs was achieved when the solvent was exposed to the sample for only 10 min. Although static LPME/HF provided satisfactory extraction efficiency and good precision within a short time, it was clear to us that if the interfacial area between the solvent and aqueous sample could be increased further, higher extraction efficiency would be obtained.[11,12] With such consideration, dynamic LPME/HF was devised and evaluated.

Dynamic LPME/HF of PAHs. In general, liquid−liquid extraction involves the distribution of the solute between two immiscible liquid phases. A solute is extracted from an aqueous phase into an organic solvent phase. In his work on LPME, Cantwell[10] investigated the kinetics of the extraction procedure

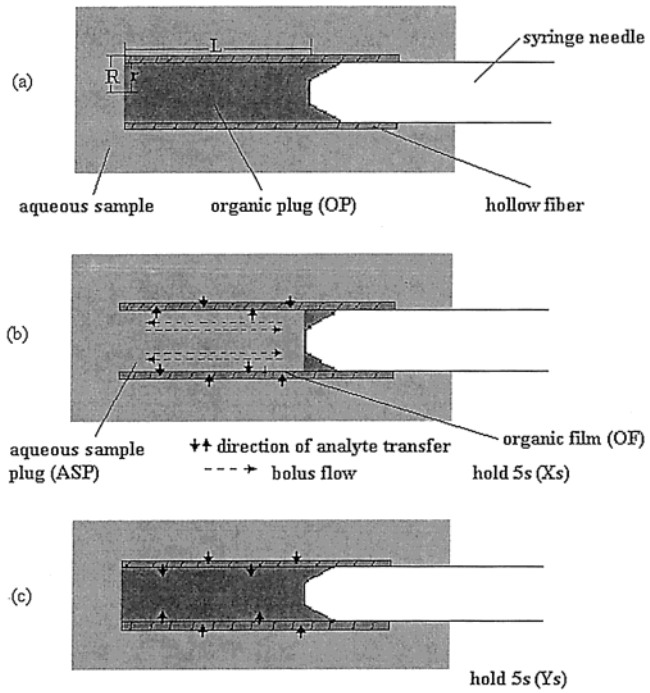

Figure 3. Expanded view of dynamic LPME/HF within the hollow fiber. For clarity, the organic solvent in the syringe needle in step b is not shown. *R* and *r* are radii of the hollow fiber with respect to the outer and inner walls.

and found that the extraction rate curves could be described by a first-order rate equation. The extraction rate is mainly affected by the first-order rate constant *k*, which is related to both the volume of aqueous sample and the solvent, V_{aq} and V_o, respectively, the interfacial area of contact between two phases A_i, the overall mass-transfer coefficient β_0 and the distribution coefficient κ:[10,11]

$$k = A_i\beta_0\left(\frac{\kappa}{V_{aq}} + \frac{1}{V_o}\right) \quad (1)$$

It is obvious that fast extraction requires A_i to be maximized and V_{aq} and V_o to be minimized. This point was tested in our previous dynamic LPME study.[11,12] In that work, a renewable microfilm within a microsyringe was formed by the repeated movement of the syringe plunger. When the plunger was withdrawn to develop the microfilm, the interfacial area of contact between two phases was increased significantly, and the volumes of organic solvent and aqueous sample were decreased. In this situation, the rate constant was increased. When the plunger was depressed, it allowed the mass transfer of analyte between the microfilm solvent and solvent plug. However, since the microfilm was formed within the microsyringe, the microfilm could only contact with the aqueous sample on its inner surface; the external surface was in contact with only the glass barrel. In our present work, the use of the hollow fiber means that the microfilm of the solvent could now be held outside the syringe, and the interfacial area of contact was significantly increased, because the external surface of the microfilm was also in contact with the aqueous phase via the wall of the hollow fiber. Figure 3 shows an expanded view of the extraction procedure in the hollow fiber segment.

Because of the porosity of the hollow fiber, a very thin organic film (OF in Figure 3b) was entrapped in the pores when the organic solvent was withdrawn into the syringe, followed by the aqueous sample solution. When the hollow fiber was immersed into 1-octanol for impregnation of its pores, the solvent would cover the surface of the hollow fiber (both external and internal surfaces) as a result of surface tension. Therefore, the interfacial area of contact was on both the external and inner surfaces of the OF. If we assume that the thickness of the OF was the same as the thickness of hollow fiber, then the interfacial area could be calculated as: $S = 2\pi(R + r)L$. Using this equation, the interfacial area was estimated to be 48 mm^2. On the contrary, the volume of organic film was much less than the value calculated from $\pi(R^2 - r^2)L$, since much of it was occupied by the hollow fiber wall. Therefore, the interfacial area was increased, but the solvent volume was decreased. According to eq 1, in this case, the extraction equilibrium between the aqueous sample and the solvent microfilm can be established quickly. In addition, as previously described for dynamic LPME,[11,12] bolus flow was also generated in the organic plug (OP) and aqueous sample plug (ASP) during the movement of the plunger, which also increases the mass transfer of analytes through the contacted end surface of the organic plug. After a dwelling time of several seconds to achieve equilibrium, the aqueous sample was expelled from the hollow fiber.

When the OP was being pushed back into the hollow fiber, (Figure 3c), the OF recombined with the bulk solvent and mass transfer of analytes occurred between the OF and the OP through the inner surface of the OF. As the analytes were transported from the OF to the OP, the previous equilibrium of analytes set up between the OF and the aqueous phase was broken, and the OF was refreshed. At the same time, the ASP was also renewed during this procedure as a result of the agitation of the bulk aqueous sample. Therefore, both OF and ASP were refreshed in the next cycle, and a new equilibrium would be established. At the same time, the mass transfer of analytes between the organic solvent and aqueous sample continued through the external surface of the hollow fiber throughout the extraction process. The repeated process of refilling the hollow fiber with the aqueous sample and then expelling it ensured that the OF and the ASP were periodically renewed; equilibrium was being repeatedly established and broken in this dynamic process. During this procedure, analytes were transported from aqueous sample to the organic solvent in the hollow fiber through the OF when ASP was refilled in the hollow fiber, as well as the external surface of the hollow fiber throughout the whole procedure. The end result was the enrichment of the analytes in the organic solvent impregnated in the hollow fiber.

To investigate the performance of dynamic LPME/HF, the following parameters were studied: sampling volume, dwelling time between ASP withdrawal and expulsion, extraction time, reproducibility, linearity, and enrichment.

(1) Sampling Volume. The sampling volume is the volume of solvent impregnated in the hollow fiber for extraction, that is, the volume of the OP, since the volume of the OF is so small that it can be neglected. When the plunger of the syringe was retracted each time, the same volume of aqueous sample was drawn into the hollow fiber. The influence of various V_o (OP volume) values was studied by measuring the GC/MS responses. We investigated V_o values in the range of 1−5 μL. Table 1 shows that the GC/MS signals increase with V_o values in the range 1−3 μL, after which there is no significant increase in signal intensities with further increase of organic volume.

One sampling cycle consisted of four steps, withdrawal and discharge of the OP in the syringe, and two pauses (dwelling times) between. When the OP was withdrawn into the syringe, the OF was generated within the wall of hollow porous fiber. Since this film was in contact with the aqueous sample both inside and outside the hollow fiber, analytes were extracted into the OF from both directions. When the OP was returned to the hollow fiber, the analytes were transferred to the OP by virtue of the recombination of the OF and the OP. It is likely that the extraction of analytes from the aqueous sample continued through the outside of the hollow fiber throughout the whole procedure. Therefore, the total extraction was a combination of these two extraction modes. Conversely, in static LPME/HF, the interfacial area involved only the exterior of the hollow fiber, since the solvent was confined in it during the extraction. The larger interfacial area of dynamic LPME/HF thus contributes to its higher extraction efficiency. Table 1 shows the GC/MS signals of static LPME/HF and dynamic LPME/HF using equal solvent volumes for extraction over the same extraction time.

It can be seen that the difference between the two modes decreases with the increase in solvent volume. Since the speed of plunger movement was limited to 1.9013 mL/h by the syringe pump, when the solvent volume was increased, the time required for withdrawing the solvent and expelling it was also increased. This gave rise to fewer extraction cycles over a given period of extraction time. Hence, the extraction efficiency of dynamic LPME/HF with larger solvent volumes was limited by this restriction. This also means that there were small or even no differences in performance efficiency between static and dynamic LPME at solvent volumes ≥3 μL.

(2) Dwelling Time and Extraction Time. Dwelling time is described as the time between refilling and infusing of the aqueous sample in one sample cycle. In other words, it is the time that the ASP remains within the hollow fiber in one cycle; it is also the time that the OP remains within the hollow fiber in one cycle. To depict dwelling time, we use the convention X s + Y s where X indicates the length of time in seconds (s) the ASP remains in the hollow fiber after being drawn in, and Y is the length of time the OP is resident in the hollow fiber after this ASP is expelled and before the next ASP is drawn in. This dwelling time also represents the frequency of plunger movement within a period of extraction time, and the shorter the dwelling time, the higher the frequency of plunger movement. In dynamic LPME/HF, repeated to-and-fro movement of the plunger is essential to the success of the extraction. As the OP was repeatedly moved along the hollow fiber during extraction, the OF was periodically refreshed, and more and more analytes were extracted from the bulk aqueous sample into the organic phase. If extraction time is defined as the total time that the organic phase is in contact with the aqueous phase, for a certain extraction period, the shorter the dwelling time, the greater the number of sampling cycles. In our previous study of dynamic LPME,[11,12] GC signals increased with the number of samplings. The results of the present work,

Table 2. Comparison of Extraction Efficiencies with Various Dwelling Times for Dynamic LPME/HF[a]

dwelling time[b]	extraction cycles	fluoranthene[c]	pyrene[c]
5 s + 5 s	30	212	164
10 s + 10 s	22	166	140
15 s + 15 s	16	129	97
static	1	100	100

[a] Water samples at a concentration of 100 μg/L of each compound. A 3-μL portion of 1-octanol was used to extract analytes from aqueous samples for 10 min. Results varied within 5% RSD ($n = 6$). [b] The first figure is the dwelling time of ASP in the hollow fiber, and the second figure is the dwelling time of OP in the hollow fiber. [c] Relative GC/MS responses are normalized to static LPME/HF data at 100 μg/L.

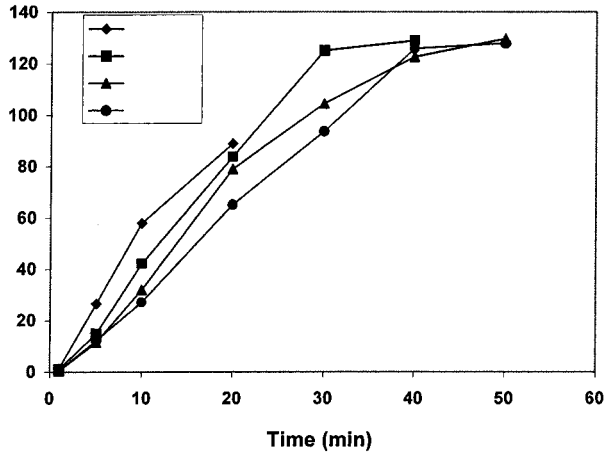

Figure 4. Extraction-time profiles for fluoranthene at various dwelling times by dynamic LPME/HF. Spiked concentration of fluoranthene, 100 μg/L.

shown in Table 2, also indicated that the extraction efficiency could be improved by increasing the number of samplings in the same period of extraction time.

As with LPME, dynamic LPME/HF is an equilibrium, rather than an exhaustive, extraction procedure. Hence, a certain time was needed to establish equilibrium. During extraction, the equilibrium of analytes between the OF and the aqueous phase was established and broken during the repeated sampling cycles until the final extraction equilibrium of analytes between aqueous sample and organic phase was reached. Therefore, the repeated establishment and breakdown of equilibrium between the OF and the aqueous sample were beneficial to the attainment of the final extraction equilibrium. We selected fluoranthene as a representative analyte and depict results of its extraction in Figure 4.

Based on 10 s + 10 s and 15 s + 15 s dwelling times in the figure, it appears that since, for a particular extraction time, shorter dwelling times allow for a greater number of sampling cycles, the faster the final extraction equilibrium is reached; that is, the plot for a 10 s + 10 s dwelling time flattens out sooner than that for a 15 s + 15 s dwelling time. (The figure also shows that dynamic LPME/HF attains equilibrium faster than static LPME/HF.) When the solvent was immersed into water, some of it was lost as a result of dissolution. Although it can be neglected in conventional LLE, this effect of solvent depletion cannot be entirely ignored in LPME, since only a small volume of organic solvent is used for extraction.[25] The solvent depletion effect is worsened in dynamic LPME by the repeated process of refilling the hollow fiber with

Table 3. Comparison of Quantitative Extraction Efficiencies for the Two Target Compounds[a]

	fluoranthene		pyrene	
	static LPME/HF	dynamic LPME/HF	static LPME/HF	dynamic LPME/HF
R.S.D (100 μg/L) ($n = 6$)	3.98%	3.14%	4.54%	2.88%
r^{2}[b]	0.9993	0.9976	0.9987	0.9968
enrichment factor (mean)	45	75	42	63

[a] A 3-μL portion of 1-octanol was used to extract analytes from aqueous samples for 10 min with a 5 s + 5 s dwelling time. [b] Data were obtained from mean values of three determinations in the linearity range of 10−400 μg/L.

the aqueous sample and then expelling it and it was more severe for a shorter dwelling time and longer extraction time. Therefore, for a 5 s + 5 s dwelling time (representing a higher frequency of plunger movement than 10 s + 10 s and 15 s + 15 s dwelling times), it can be seen that equilibrium cannot be reached, because severe solvent depletion was experienced beyond the 20-min extraction time. There was insufficient extract left in the fiber after >20 min to permit us to analyze it accurately and meaningfully, and thus, no analytical data could be generated. Nevertheless, it was not necessary for equilibrium to be established, since if extraction operations were consistently applied, quantitative analysis was not compromised. For a reasonable extraction time of 10 min, satisfactory extraction efficiency was achieved with a 5 s + 5 s dwelling time (see Table 3). Thus, these two parameters were used for subsequent experiments.

(3) Reproducibility, Linearity, and Enrichment Factor. The reproducibility of GC/MS signals was studied for six replicate experiments for an aqueous sample spiked at 100 μg/L of the two PAHs extracted by 3 μL of 1-octanol. Linearity was obtained over the range of 10−400 μg/L and the coefficient of correlation (r^2) ranged from 0.9968 to 0.9993. The enrichment factor, defined as the ratio of GC/MS signals after extraction and that before extraction, was used to evaluate the extraction efficiency. It should be noticed that >40-fold enrichment for static LPME/HF and >60-fold for dynamic LPME/HF were achieved in only 10 min. The relative standard deviations (RSD) of two modes were lower than 4.54%. The results, together with the results of static LPME/HF, are listed in Table 3 for comparison.

As with the RSDs of static LPME/HF, those of dynamic LPME/HF are much better than those of the previous LPME procedure[11−12,15−17]. They are also better than those of static LPME/HF. This is a dramatic enhancement for LPME or SME. There are several reasons for this. First, the organic solvent was confined within the hollow fiber, resulting in increased stability of solvent. Second, the movement of the plunger was automatically controlled by use of the syringe pump. Therefore, the dwelling time and the speed of the plunger movement were more precise than those of manual dynamic LPME. Third, in static LPME, the plunger movement was controlled on the basis of only visual inspection when the organic solvent was withdrawn into syringe after extraction. In dynamic LPME/HF, the plunger was controlled by the syringe pump in every cycle; thus, a more precise solvent

(25) Zhao, L.; Lee, H. K. *J. Chromatogr. A.* **2001**, *919*, 381−388.

volume was attained for analysis. The enrichment achievable by dynamic LPME/HF was also higher than that of static LPME/HF, showing that it was a more attractive proposition to enhance extraction efficiency.

CONCLUSION

This paper described an improvement of drop-based LPME by using a hollow fiber, termed as liquid-phase microextraction combined with hollow fiber (LPME/HF) in conjunction with semiautomation for the dynamic mode. A comparison of static LPME/HF with dynamic LPME/HF shows that the stability of the microliter volume organic solvent of the extractant and the precision of the technique were improved significantly as a result of the protection afforded by the hollow fiber.

Both static and dynamic LPME/HF provided good extraction efficiency within a short period of time, especially for the latter, which could achieve higher enrichment factors than the former. The reproducibility of semi-automated LPME/HF was much better than that of manually operated LPME procedure reported previously. A very basic apparatus is required for extraction, in general. Hence, both of the LPME/HF modes reported here can serve as rapid screening techniques for environmental analysis.

The disadvantage of dynamic LPME/HF was that the operational speed was limited by the syringe pump used in this work; thus, the number of samplings was reduced over a particular extraction time period. A syringe pump that allows faster syringe manipulation would be desirable.

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