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Journal of Chromatography A, 976 (2002) 377–385

JOURNAL OF CHROMATOGRAPHY A

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# Application of static and dynamic liquid-phase microextraction in the determination of polycyclic aromatic hydrocarbons

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**Abstract**

Two modes of liquid-phase microextraction (LPME), static and semi-automated dynamic, have been developed for the HPLC analysis of polycyclic aromatic hydrocarbons. In static LPME, a small drop (3 μl) of organic solvent was held at the tip of a microsyringe needle and exposed to the sample containing the analytes, permitting extraction to occur. In semi-automated dynamic LPME, a syringe pump was used to automate the repetitive procedure of filling a microsyringe barrel that functioned as a microseparatory funnel, with fresh aliquots of sample, and expelling them after extraction. The factors influential to both techniques such as the type of organic solvent, extraction time, sampling volume, number of samplings, salt concentration and temperature were investigated. Static LPME provided high enrichment (60- to 180-fold) and simplicity. The analytical data exhibited a relative standard deviation range of 4.7–9.0%. Dynamic LPME provided higher (>280-fold) enrichment within nearly the same extraction time (≈20 min) and better precision (≤6.0%). Both methods allow the detection of polycyclic aromatic hydrocarbons at μg/l levels in water by HPLC. Water samples collected from two rivers were analyzed using the methods, respectively. The results demonstrated that both modes of LPME were fast, simple and accurate.


*Keywords:* Liquid-phase microextraction; Extraction methods; Water analysis; Environmental analysis; Polynuclear aromatic hydrocarbons

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental pollutants and many are suspected to be carcinogenic [1,2]. Because of this, the analysis of PAHs in environmental samples has become an important topic. Evaluation and monitoring of trace levels of these compounds from different environmental matrices are imperative. In order to determine trace levels of these pollutants, an extraction and pre-concentration step is usually necessary.

Current techniques for the extraction and concentration of PAHs from water are liquid–liquid extraction (LLE), solid-phase extraction (SPE) [3–5] and supercritical fluid extraction (SFE) [6]. LLE requires large amounts of toxic organic solvents, and is time-consuming. SFE and SPE use considerably less solvent, but cost more to operate. Recently, solid-phase microextraction (SPME) has been used for concentration of PAHs [7,8]. However, it is also expensive and sample carry-over can be a problem.

Recently, liquid phase microextraction was developed as a novel solvent-based pretreatment method, which is fast, simple, inexpensive, requires little solvent and produces little waste. Since only a few microliters of solvent is used, there is minimal

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0021-9673/02/$ – see front matter 
PII: S0021-9673(02)01152-4

exposure to toxic organic solvents when this method is used. Liquid-phase microextraction (LPME) only requires very simple and low cost devices and does not suffer from carry-over between extractions that may be experienced using SPME etc. This fairly new technique has been described in several papers [9–15].

He and Lee [9,10] introduced a novel liquid–liquid microextraction method in which the commonly used microsyringe was employed as a microseparatory funnel for extraction, as well as a syringe for injection into a GC. Static and dynamic modes were investigated. The dynamic mode of the procedure was shown to be fast and highly efficient but was performed manually. Furthermore, although increasing sampling time was useful to increase the sensitivity, it was experimentally impractical. This paper reports on the automation of dynamic LPME, in combination with HPLC for analysis of PAHs. A programmable syringe pump was used to automate the extraction. Static LPME was also applied to the analysis of PAHs as comparison. The factors influential to both modes of LPME were studied and optimized.

## 2. Experimental

### 2.1. Chemicals and sample

Fluoranthene was bought from Supelco (Bellefonte, PA, USA). Pyrene, chrysene, benzo[*b*]fluoranthene and benzo[*k*]fluoranthene were bought from Dr. Ehrenstorfer (Augsburg, Germany). Benzo[*a*]pyrene was bought from Aldrich (Milwaukee, WI, USA). Stock solutions (0.1 mg/ml) of each analyte were prepared in methanol. HPLC-grade methanol, acetonitrile, toluene, methylene chloride, chloroform and benzene were from J.T. Baker (Phillipsburg, NJ, USA). Deionized water was produced on a Nanopure ultrapure water system (Barnsted, Dubuque, IA, USA). Dichloromethylsilane was from Fluka (Buchs, Switzerland). Water samples were prepared by spiking deionized water with analytes at known concentrations (10–50 μg/l) to study extraction performance under different conditions.

Water samples were collected from a local river, and from a drain. Samples were filtered followed by storage at room temperature (25 °C, 24 h). They were filtered again prior to extractions.

### 2.2. Silanization of glassware

All glassware used was silanized as described by Potter [16] to prevent adsorption of PAHs.

### 2.3. Static liquid-phase microextraction

The experimental set-up of static LPME is illustrated in Fig. 1a. One 10-μl microsyringe with a 22 °C bevel needle tip (ITO, Fuji, Japan) was used for introducing organic solvent. Another 10-μl microsyringe with a flat-cut needle tip (glass barrel, I.D. 0.46 mm, needle I.D. 0.11 mm) (Hamilton, Reno, NV, USA) was for injecting extracts into the HPLC. Static LPME consists of the following steps: (1) The magnetic stirrer is switched on to agitate the aqueous sample solution; (2) the microsyringe is rinsed with organic solvent (e.g. toluene) for at least five times to ensure that no air bubble is left in the barrel and the needle; (3) a specified volume (e.g. 3 μl) of organic solvent is drawn into the syringe with the needle tip out of the solution, the plunger is depressed by 1 μl; (4) the needle is then inserted through the septum of the sample vial (3-ml capacity) and immersed in the aqueous sample. The distance between the tip and stirring should be kept consistently (ca. 1 cm) for all experiments to ensure good precision; (5) the plunger is depressed to expose the organic drop to the stirred aqueous solution for a period of time; (6) the drop is retracted into the microsyringe, which is retracted from the sample vial; (7) the organic solvent drop is trans-

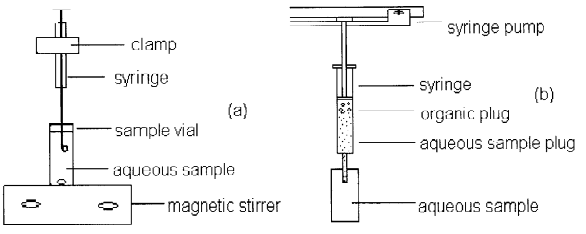


Fig. 1. (a) Schematic of static LPME (not to scale); (b) set-up of automation of dynamic LPME (not to scale).

ferred to a micro-vial (25-μl capacity) dried by a slow nitrogen flow, and redissolved in 10 μl methanol; (8) the extract (10 μl) is injected into the HPLC.

It must be noted that in this procedure, a little over 3 μl of toluene, for example 3.2 μl, is withdrawn into the syringe and then the volume is adjusted accurately to 3 μl before immersing the needle under the solution in order to prevent air bubble formation.

### 2.4. Dynamic liquid-phase microextraction

The experimental set up of dynamic LPME is illustrated in Fig. 1b. A Harvard Apparatus (Holliston, MA, USA) model PHD 2000 syringe pump was used for extraction. Two 25-μl microsyringes (Hamilton) with flat-cut needle tips were used, one for automated extraction controlled by the pump (placed vertically), and the other for HPLC injection. Dynamic LPME consists of the following steps: (1) The syringe pump was programmed as: (i) refill speed (e.g. 1.33 μl/s); (ii) sampling volume (e.g. 0.020 ml); (iii) dwell time (e.g. 2 s); (iv) infusion speed (e.g. 1.33 μl/s); (v) sampling volume (e.g. 0.020 ml); (vi) dwell time (e.g. 2 s); (vii) restart; (2) a specialized volume (e.g. 4 μl) of organic solvent was withdrawn into the 25-μl microsyringe; (3) the microsyringe was placed in the groove of the pump; (4) the needle of the microsyringe was inserted through the septum of sample vial (3-ml capacity) and its tip immersed in the aqueous sample; (5) the syringe extraction program was activated; (6) after extraction the needle containing the original volume of organic solvent was inserted into a micro-vial (25-μl capacity) dried by a slow nitrogen flow, and redissolved with 10 μl methanol; (8) the extract (10 μl) was injected into the HPLC.

### 2.5. HPLC analysis

HPLC was performed on a Shimadzu (Tokyo, Japan) LC-6A pump equipped with a Shimadzu SPD-6A UV detector and a CR-3A integrator. A Whatman PartiSphere $C_{18}$ 110×4.7 mm I.D. column was used. The mobile phase was acetonitrile–water (65:35). A flow-rate 1.0 ml/min was applied, and the detection wavelength was 254 nm.

## 3. Results and discussion

### 3.1. Optimization of static and dynamic LPME

The initial objective was to optimize static and dynamic LPME sampling conditions for the extraction of PAHs from water samples. A univariate optimization approach was used in the current study. There were several parameters to optimize performance of static and dynamic LPME such as the type of extraction solvent, its volume, extraction time, salt concentration and temperature. For dynamic LPME, other important parameters affecting extraction efficiency such as the pattern of the plunger movement, sampling volume and number of samplings were also considered.

We used the enrichment factor to evaluate the extraction efficiency under different conditions. The enrichment factor, defined as the ratio of the peak area of a particular attained with extraction and that without extraction.

#### 3.1.1. Optimization of static LPME

We studied the extraction of four PAHs including pyrene, chrysene, benzo[*b*]fluoranthene and benzo[*a*]pyrene by static LPME. Initially, the experiments for the selection of extraction solvent were carried out. Methylene chloride, chloroform, hexane, cyclohexane, benzene and toluene were compared in the extraction of PAHs. Traditionally, methylene chloride and chloroform are often used to extract PAHs in LLE [17]. The main reason for the choice of these two solvents is the relatively higher solubilities of PAHs in them. However, they are not suitable for static LPME because of the difficulty of holding their respective microdrops at the tip of the microsyringe for a considerable time ($\geq$15 min). The extraction results of benzene and toluene were similar in terms of peak area and were better than hexane and cyclohexane (Table 1). Toluene provided lightly higher concentration factors than benzene and was more easily held at the tip of the microsyringe (drop stability was significantly higher). Thus, it was chosen as the organic solvent for extracting PAHs. Secondly, experiments were carried out to determine the optimum organic drop size. Generally, in LPME, an equilibrium of solute is developed between two immiscible liquid phases: the aqueous and the or-

Table 1
Extraction efficiency using different organic solvents[a]

| PAHs | Preconcentration (-fold) | | | |
|---|---|---|---|---|
| | Hexane | Cyclohexane | Benzene | Toluene |
| Pyrene | 20 | 30 | 35 | 40 |
| Chrysene | 40 | 40 | 60 | 80 |
| Benzo[*b*]fluoranthene | 20 | 20 | 40 | 50 |
| Benzo[*a*]pyrene | 8 | 8 | 25 | 30 |

[a] Extracting for 15 min from 3 ml spiked water sample (50 μg/l of each analyte using 2-μl drops, with stirring rate at 500 rpm). Data were obtained from mean values of three experiments.

ganic phases. In our study, a solute is extracted from an aqueous solution into an immiscible organic solvent. The amount of the analytes extracted into organic drop is given by [18]:

$$N = KV_{org,eq}C_{aq,ini} \quad (1)$$

where $N$ is the number of moles of analytes extracted by the organic drop; $K$ is the distribution coefficient of an analyte between the aqueous phase and the organic drop; $V_{org,eq}$ is the volume of organic drop at equilibrium; and $C_{aq,ini}$ is the initial concentration of the analyte in aqueous solution. As depicted by Eq. (1), the amount of analytes extracted by the organic drop is linearly proportional to the drop size at equilibrium, which is demonstrated by the linear increase of HPLC signals with the size of the toluene drop in the range of 1–4 μl (Fig. 2). Although a larger drop size should be used for greater enrichment, ≥4 μl dropsize are not preferred since they often detach from the needle tip and are lost. On this basis, 3 μl was used to study the performance of LPME. This gave the highest potential for good enrichment without sacrificing drop stability. Thirdly, the influence of agitation on the extraction of PAHs was investigated in Fig. 3. As stirring speed increased, the total extraction rate increased. Based on the film theory of convective–diffusive mass transfer [19], at steady state, the diffusion coefficient in the aqueous phase increases with increasing stirring rate because faster agitation can decrease the thickness of the diffusion film in the aqueous phase. This film theory was confirmed to be valid in the LPME method [13]. Thus, extraction efficiency increased with higher stirring speed. Our results support this observation. However, higher stirring speed gives rise to instability of the organic drop. The stability of an organic drop at the tip of the needle depends on the balance of three forces [9]. When the aqueous solution is stirred too vigorously, the equilibration exerted by the three forces is disturbed so that the attached organic drop is detached from the needle tip. It was found that a 3-μl toluene drop was unstable when stirring speed was over 700 rpm. On this basis, stirring speed was fixed

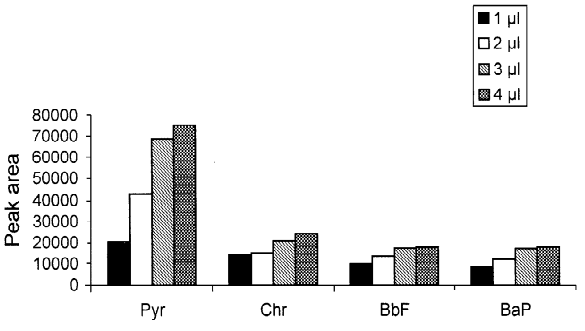


Fig. 2. Effect of different dropsize on the extraction efficiency of static LPME. Organic solvent: toluene; stirring rate: 500 rpm; extraction time: 15 min. Abbreviations: Pyr = pyrene, Chr = chrysene, BbF = benzo[*b*]fluoranthene, BaP = benzo[*a*]pyrene.

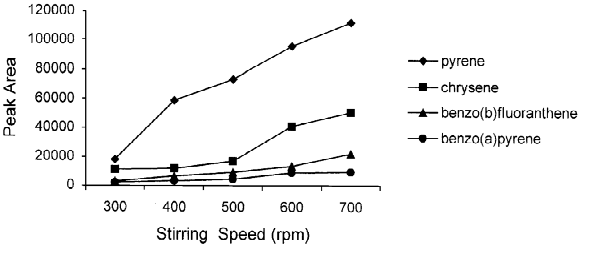


Fig. 3. Effect of extraction speed on the extraction of PAHs by static LPME. Organic solvent: toluene; dropsize: 3 μl; extraction time: 20 min.

at 600 rpm. Fourthly, the effect of extraction time on static LPME was investigated. In most SPME applications, the efficiency of extraction increased with extraction time. In our LPME work, from Fig. 4, we can see that the HPLC signals increased with extraction time up to about 20 min; subsequently the signals decreased in intensity. Like SME, static LPME is a process dependent on equilibrium rather than exhaustive extraction. A certain time is needed for equilibrium between organic drop and aqueous phase to be established. Generally, the amount of analyte extracted should increase with longer extraction time before equilibrium is established until a maximum is attained at equilibrium. However, in the case of toluene as extractant, its dissolution in the aqueous phase (0.052%, v/v) [20] is significant, especially under stirring, compared to the solubility of the adsorbent on an SPME fiber. The dissolution rate of toluene was 0.1 μl/8 min with 30-min extraction. It was observed that 3 μl of toluene was reduced to ca. 2.8 μl after exposure to a stirred (600 rpm) solution sample for 20 min. The extraction of analytes into the organic drop, and the dissolution of some of the organic drop into the aqueous solution govern the concentration in the microdrop. Thus the reason that at 20 min the highest extraction efficiency was attained could be due to a compromise amongst these factors that influenced LPME. So long as the extraction time consistently applied, quantitative analysis can be performed accurately.

### *3.1.2. Optimization of dynamic LPME*

In dynamic LPME, six PAHs including fluoranthene, pyrene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*a*]pyrene were investigated. Methylene chloride, chloroform, toluene and benzene were compared in the extraction of six PAHs. Although the chloroform drop was unstable in static LPME mode (see above discussion), this solvent was well protected by the syringe in dynamic LPME mode and gave the best results for dynamic LPME. This is probably because the solubility of PAHs is relatively higher in chloroform. Next, the volume of extraction solvent was investigated. In this experiment, a range of 1–7 μl of organic solvent was tested. HPLC signals generally increased with the size of the extraction solvent. The HPLC signals increased marginally for drop size beyond 5 μl. This suggests that when 5 μl was used the amount of analytes extracted was near the maximum. The effect of the syringe plunger movement on extraction was then investigated. In the dynamic LPME process, the extraction was performed by automatically manipulating the plunger repeatedly in and out of the microsyringe barrel. Each cycle of the extraction includes withdrawing and discharging of aqueous sample and two pauses in-between (dwell time). The analytes were extracted rapidly from the aqueous sample to the organic solvent when the plunger was in motion. The plunger movement speed (sampling volume/withdrawal time = sampling volume/discharge time), and the dwell time between plunger movement on extraction efficiencies were studied. With using a 10-μl sampling volume (i.e. volume of aqueous sample), and setting the plunger movement speed at 1.33 μl/s (that is, the fastest speed the instrument could operate automatically), we carried out separate experiments in which the dwell time was varied. For all the six PAHs, it is clear that increase of the dwelling time from 1 to 5 s had no significant influence on improving extraction efficiency. This result is in agreement with that observed previously (when the plunger was operated manually [10]. With the dwelling time fixed at 1s, we carried out separate experiments in which the plunger movement speed was varied. The results are shown in Fig. 5. The HPLC peak area decreased (for fluoranthene and pyrene) or showed no variation (for chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*a*]pyrene) along with the decrease in plunger movement speed. It is possible that more of the analytes would be extracted if the plunger movement speed could be improved further. As mentioned above, 1.33 μl/s was the fastest speed at

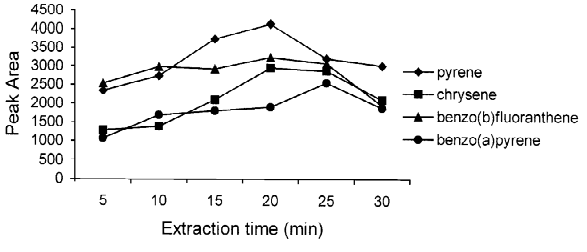


Fig. 4. Effect of extraction time on the extraction of PAHs by static LPME.

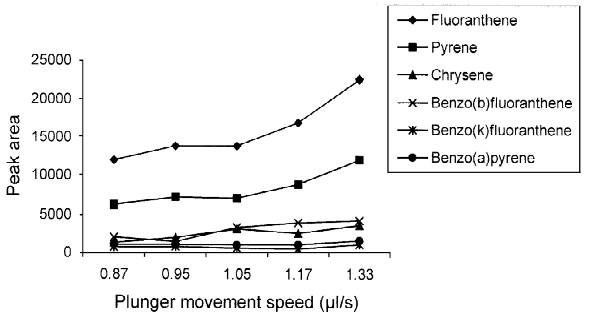


Fig. 5. Effect of plunger movement speed on extraction efficiency (dynamic LPME). Sampling volume: 10 μl; dwell time: 1s.

which the instrument could be operated automatically. We therefore selected 1.33 μl/s as plunger movement speed and a dwell time of 1 s for subsequent work. Next, the effect of sampling volume on dynamic LPME was investigated. The sampling volume refers to the volume of the aqueous sample plug ($V_{asp}$) that is drawn into the microsyringe in each cycle. The influence of $V_{asp}$ on extraction was studied by varying the sampling volumes for the extraction of chrysene from 4 to 20 μl. The peak area increased linearly with $V_{asp}$. All other compounds showed the same trend. Since 20 μl was the maximum capacity of the syringe, it was selected as the sampling volume. The effect of the number of samplings in dynamic LPME was then studied. It has been previously [9] shown that there is a linear relationship between analyte concentration in the organic plug and number of samplings ($n$) when $n$ is relatively small. In this work, similar linear relationships were observed between the peak area of the analytes and the number of samplings ($n=5$–40). In dynamic LPME, the repeated movement of the plunger resulted in the constant renewal of the organic film and aqueous sample plug. With an increased number of samplings, more of the analytes are ultimately extracted into the organic plug in the microsyringe. It was straightforward to sample many times automatically, in contrast to the manual method used previously [10], this led to selecting a sampling number of 40. Although extraction time will increase to about 20 min, it is acceptable due to the great enhancement in the enrichment factor. The effect of salt on the extraction was the next parameter to be studied. The experiments were carried out by varying the concentration of NaCl in the sample solution in the range of 20–250 mg/ml. No enhancement of extraction was found across this concentration range. On the contrary, for fluoranthene and pyrene, the extraction efficiency remained nearly constant at low concentrations of NaCl (~20 mg/ml). When more salt was added into the sample (>50 mg/ml), a decrease in extraction was observed (Fig. 6). For the other four analytes, the extraction efficiency remained nearly constant at all investigated concentrations. Conflicting reports of the influence of salt on both SPME and other modes of LPME have also been reported previously. Temperature as an extraction parameter has been exploited for conventional LLE [21]. In our study, experiments were carried out with sample solutions at 25 °C (room temperature), 40 °C and 60 °C (Fig. 7). The extraction efficiency was improved at 40 °C. This may be because high temperature increases solvent strength, accelerates the mass transfer between the OF and ASF and therefore improves extraction efficiency. Experiments were also performed at 60 °C. However, no significant improvement of extraction efficiency was observed at this temperature compared to that at 40 °C. This may be because the extraction solvent (chloroform) has a boiling point of 61 °C and it was beginning to suffer evaporative losses at 60 °C. Also, the solubility of

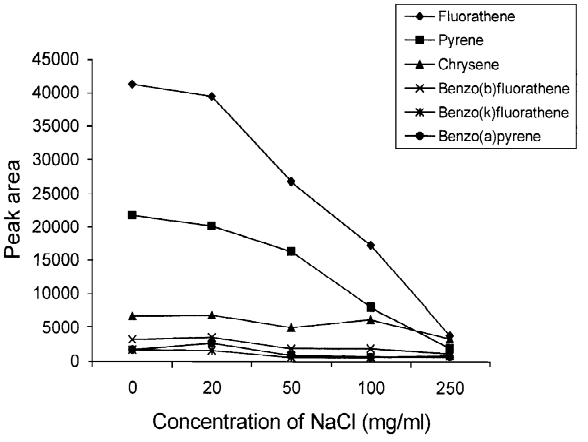


Fig. 6. Effect of salt strength on the extraction of PAHs by dynamic LPME.

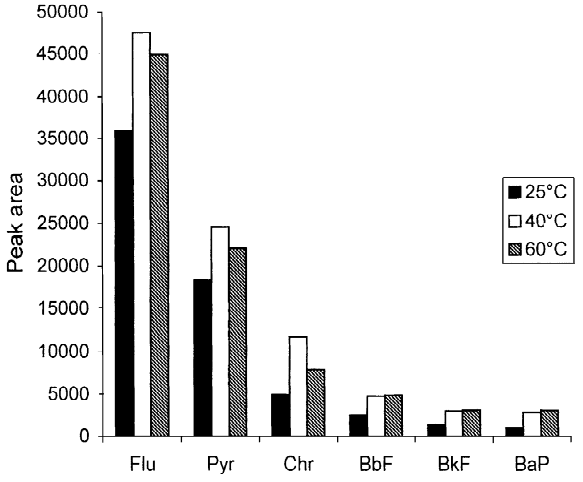


Fig. 7. Effect of temperature on the extraction efficiency for PAHs (dynamic LPME). Abbreviations: Flu = fluoranthene, Pyr = pyrene, Chr = chrysene, BbF = benzo[*b*]fluoranthene, BkF = benzo[*k*]fluoranthene, BaP = benzo[*a*]pyrene.

the analytes in water increases with increasing temperature, leading to a decrease in the extraction efficiency.

### 3.2. Quantitative consideration

The linearity of calibration plots was studied over a concentration range of 2–100 μg/l for static LPME and 1.2–85 μg/l for dynamic LPME. All the PAHs exhibited good linearities, with correlation coefficient ranging from 0.9878 to 0.9921 for static LPME and 0.9908–0.9981 for dynamic LPME. The study of reproducibility for both modes of LPME was carried out by extracting a spiked water sample containing 10–50 μg/l of the PAHs. The relative standard deviations (RSDs) were between 4.7 and 9.0% for the static mode and between 4.4 and 6.0% for the dynamic mode. The limits of detection (signal-to-noise ratio = 3) obtained ranged from 1 to 3.5 μg/l for static LPME and 0.35 to 0.60 μg/l for dynamic LPME. All these results are shown in Table 2.

### 3.3. Genuine water analysis

River water and tap water from our laboratory were analyzed by static LPME–HPLC. Drain water and the identical tap water as above were analyzed by using dynamic LPME–HPLC. The results for tap water analyzed by both static mode and dynamic mode showed that it was free of PAH contamination. In the river water sample analyzed by static LPME, chrysene and benzo[*b*]fluoranthene were detected (Fig. 8A) and their presence was confirmed by spiking the PAHs in the river water and reanalyzing it (Fig. 8B). The standard addition method was used for quantification. The concentration of chrysene and benzo[*b*]fluoranthene in the river water were determined to be 2.42 and 2.18 μg/l, respectively. In the drain water analyzed by dynamic LPME, fluoranthene, pyrene, chrysene, benzo[*b*]fluoranthene were detected (Fig. 9A). Using the same quantification method as for static LPME, their concentrations in the drain water were determined to be 0.56, 1.12, 2.38 and 1.07 μg/l, respectively. Fig. 9B shows the chromatogram of the spiked drain water obtained by dynamic LPME.

Table 2
Analytical data for static LPME and dynamic LPME

| Analyte | Enrichment (-fold) | | RSD (%) | | Linearity range (μg/l) | | $r^2$ | | Limit of detection | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Static | Dynamic | Static | Dynamic | Static | Dynamic | Static | Dynamic | Static | Dynamic |
| Fluoranthene | – | 280 | – | 5.0 | – | 2.2–22 | – | 0.9943 | – | 0.45 |
| Pyrene | 78 | 156 | 5.5 | 6.0 | 2–100 | 1.2–12 | 0.9916 | 0.9952 | 1 | 0.60 |
| Chrysene | 180 | 192 | 4.7 | 4.5 | 4–100 | 1.7–85 | 0.9903 | 0.9939 | 2 | 0.40 |
| Benzo[*b*]fluoranthene | 66 | 98 | 8.9 | 4.9 | 4–100 | 5.0–50 | 0.9878 | 0.9908 | 2 | 0.35 |
| Benzo[*k*]fluoranthene | – | 60 | – | 4.4 | – | 2.7–45 | – | 0.9927 | – | 0.45 |
| Benzo[*a*]pyrene | 60 | 88 | 9.0 | 5.6 | 8–100 | 3.0–50 | 0.9921 | 0.9981 | 3.5 | 0.50 |

$n = 3$.

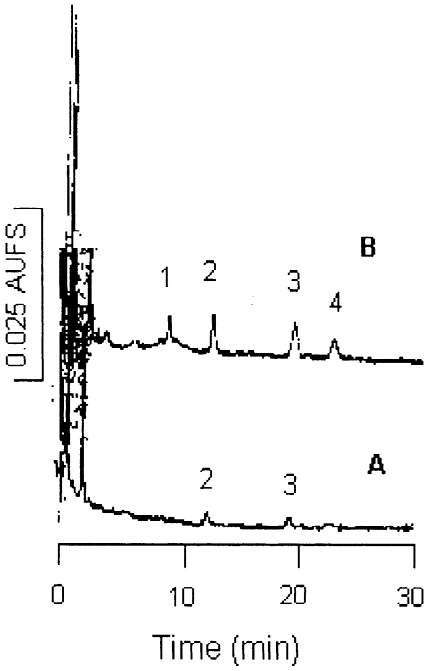


Fig. 8. Extraction of river water sample by static LPME under optimized conditions (A) River sample. (B) Standard addition of 0.5 ml 2.0 μg/ml standard solution to 50 ml river sample. Peaks: 1=pyrene, 2=chrysene, 3=benzo[*b*]fluoranthene, 4=benzo[*a*]pyrene.

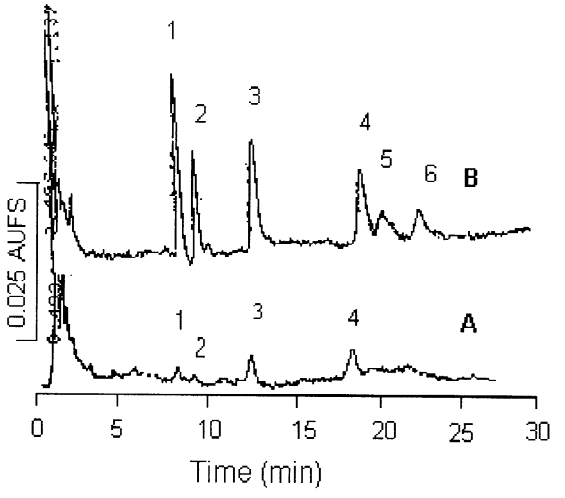


Fig. 9. Extraction of drain water sample by dynamic LPME under optimized conditions. (A) River sample. (B) Standard addition of 0.5 ml 2.0 μg/ml standard solution to 50 ml river sample. Peaks: 1=fluoranthene, 2=pyrene, 3=chrysene, 4=benzo[*b*]fluoranthene, 5=benzo[*k*]fluoranthene, 6=benzo[*a*]pyrene.

Both types of water were spiked with PAH standards at various concentration to assess matrix effects. Because LPME is a non-exhaustive extraction procedure like SPME, relative recoveries, defined as the ratio of HPLC peak areas of the respective spiked water (tap water, river water and drain water) extracts to spiked Milli-Q water extract, were calculated to evaluate their effects. The experiments were repeated three times. Results of relative recoveries and RSDs of tap water, river water and drain water are shown in Table 3. The data showed that for most target PAHs (in static mode), the relative recoveries were higher than 90% except for benzo[*b*]fluoranthene (88.7%) in tap water. This means that the tap and river water matrices had little effect on static LPME. This result is also as reported before [22]. The relative recoveries for all target PAHs (under dynamic LPME mode) were higher than 90%. This means that the matrix also had little effect on dynamic LPME.

## 4. Conclusion

We have investigated several important factors that influence the extraction efficiency of static LPME and automated dynamic LPME. Both methods need only several microlitres of solvent and 3 ml of aqueous samples. The detection limits were determined to be 1–3.5 μg/l for static mode and 0.35–0.60 μg/l for dynamic mode. Thus, quantifying trace levels of PAHs in water samples using either mode of LPME with HPLC is possible. Good linearity, sensitivity and relative recoveries were obtained by both LPME modes.

Automated dynamic LPME provided higher (>280-fold) enrichment within nearly the same extraction time (≈20 min) and better precision (≤6.0%) than static LPME. Compared to the manual dynamic LPME [10], automated dynamic LPME is easier to be operated and can yield better precision. Also, the enrichment factor is also greatly improved.

Both modes of LPME could be applied to real world analysis of aqueous samples. Since only 3 ml of samples are needed for extraction, this work can potentially be extended to biological samples, for example, blood and urine etc., although the possible

Table 3
Summary of results of analysis of PAHs in spiked samples after static LPME and dynamic LPME

| Compounds | Tap water | | | | River water[a] (static) | | Drain water[b] (dynamic) | |
|---|---|---|---|---|---|---|---|---|
| | Relative recovery[c] | | RSD[c] (%) | | Relative[c] recovery (%) | RSD[c] (%) | Relative[c] recovery (%) | RSD[c] (%) |
| | Static[a] | Dynamic[d] | Static[a] | Dynamic[d] | | | | |
| Fluoranthene | – | 98.9 | – | 5.0 | – | – | NC[e] | 5.8 |
| Pyrene | 97.9 | 99.5 | 6.4 | 6.0 | 95.8 | 7.8 | NC[e] | 6.4 |
| Chrysene | 92.8 | 99.6 | 5.8 | 4.5 | NC[e] | 6.3 | NC[e] | 4.7 |
| Benzo[*b*]fluoranthene | 88.7 | 99.8 | 9.3 | 4.9 | NC[e] | 9.9 | NC[e] | 5.3 |
| Benzo[*k*]fluoranthene | – | 98.8 | – | 4.4 | – | – | 95.3 | 5.0 |
| Benzo[*a*]pyrene | 101.9 | 98.8 | 9.9 | 5.6 | 96.7 | 11.7 | 94.9 | 5.9 |

[a] Water samples containing 100 μg/l of each analyte.
[b] Drain water samples containing 20 μg/l of each analyte.
[c] $n=3$.
[d] Water samples containing 10 μg/l of each analyte.
[e] Not considered since they were detected in river water or drain water.

problems posed by these more complex matrices need to be addressed as well.

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