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Dynamic hollow fiber-supported headspace liquid-phase microextraction

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Abstract

With the increasing concern over deteriorating environmental quality, the analysis of organic pollutants in air, water, and soil has become critically important. The development of simple, efficient, and inexpensive analytical sample pretreatment is crucial for monitoring and evaluating the environment. In this work, a dynamic hollow-fiber supported headspace liquid-phase microextraction (DHF-HS-LPME) approach was developed. In dynamic LPME, the extracting solvent is held within a hollow fiber, affixed to a syringe needle and immersed in the sample solution, and is moved to-and-fro by using a programmable syringe pump. The movement facilitates mass transfer from the sample to the solvent. Here, a similar approach was adopted, except that extraction was from the headspace rather than by direct immersion. Analysis of the extract was carried out by gas chromatography–mass spectrometry. The effect of sampling temperature, water, salt, dwelling time were investigated. Results indicated that this novel headspace microextraction method gave good analyte-enrichment factors, linear range, limits of detection and repeatability, all of which were evaluated by extracting PAHs from soil samples. This technique represents an inexpensive, convenient, fast and simple sample preparation of this class of semi-volatile organic compounds.

Keywords: Headspace liquid-phase microextraction; Environmental analysis; Programmable syringe pump; Polycyclic aromatic hydrocarbons

1. Introduction

Analyte extraction and pretreatment is the most challenging and time-consuming step in an analytical procedure. There are several approaches to accomplish this, including flow injection extraction [1,2], solid-phase extraction [3,4] and liquid–liquid extraction [5], headspace extraction [6], etc. Among these, direct headspace sampling has been widely used in environmental, food, fragrance, flavor, pharmaceutical and biological analyses [7–10] for many years. It can be used for volatile organic compounds (VOCs) without interference since there is no direct contact with the sample matrix. The classical headspace analysis is done by sealing the sample in a gas-tight vial with a septum. After a prescribed extraction time, the analyte vapor is sampled, generally with a gas-tight microsyringe. However, such a method is only suitable for highly volatile compounds and requires that the analyte possesses high Henry's Law constant [11]. Thus, its application is limited. Techniques such as purge and trap, headspace solid-phase microextraction, headspace liquid-phase microextraction have been developed to improve extraction efficiency and widen their applications in VOC and semi-VOC analysis.

Recently, miniaturization has become an important trend in the development of sample pretreatment techniques. Headspace solid-phase microextraction (HS-SPME) [12,13], developed by Pawliszyn, has wide applicability to VOC and semi-VOC analysis. The technique is a convenient and solvent-free extraction method that is suitable for headspace sampling. During the sampling, the SPME fiber is suspended in the headspace above an aqueous or soil sample. By doing so, interference problems due to the fact that the SPME fiber is not in direct contact with the sample matrix are eliminated. Headspace SPME has become very popular in recent years. An important feature of this technique is that extraction and injection are incorporated in the same device, thus minimizing analysis time. There is virtually no complex sample pretreatment involved. The main drawbacks are that these fibers are expensive and have a limited lifetime, as they tend

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to degrade with the number of samplings. In addition, the fused silica fiber is fragile and the polymer containing can be easily damaged. Furthermore, sometimes sample carryover is difficult or impossible to be eliminated.

Recently, headspace solvent microextraction or liquid-phase microextraction (LPME) has been shown be an inexpensive, convenient, and precise sample cleanup and preconcentration technique at trace levels. Liu and Dasgupta [14] were the first to report single-drop system where one drop of organic solvent was suspended in a larger aqueous drop to extract the analytes. After extraction, the extractants were analyzed using a light-emitting diode-based absorbance detector. More recently, Shen and Lee [15] reported a headspace LPME technique in which an organic solvent film was formed in a microsyringe barrel and used as the extraction interface. As compared with droplet solvent microextraction or LPME, the selection of extractant solvents in HS-LPME seems to be more flexible, since without any contact with the sample, the issue of possible solvent solubility in the sample does not arise.

However, there are some problems in the aforementioned techniques. For example, the surface area of the organic solvent is limited. For droplet HS-LPME, since there is no support for the organic solvent except for the tip of the microsyringe, the solvent volume cannot be too large; otherwise, the organic solvent will detach from the tip. For Shen and Lee's approach, the extraction contact interface between the headspace inside the syringe channel and organic solvent film is limited. This limited interfacial contact area between sample and solvent of HS-LPME may be the reason that the extraction efficiency for this technique is not very high.

To address the above-mentioned problems, in the present work, we developed a new approach to headspace analysis, that is, dynamic hollow fiber-supported headspace liquid-phase microextraction (DHF-HS-LPME) controlled by a programmable syringe pump. Polycyclic aromatic hydrocarbons (PAHs) were selected as model compounds since they are widespread environmental pollutants and hazardous to health. The newly developed technique was used to evaluate and monitor the trace levels of these compounds. In this technique, with the support of the hollow fiber, the surface area of the organic phase in contact with the headspace was increased dramatically. The results indicated that the procedure is an efficient, inexpensive, fast and convenient extraction technique to analyze PAHs in a complicated matrix as soil. This work provided an alternative to the present headspace microextraction techniques such as HS-SPME and HS-LPME.

2. Experimental

2.1. Reagents and materials

Six model PAHs (acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene) were purchased from Supelco (Bellefonte, PA, USA). HPLC-grade methanol and methylene chloride were bought from J.T. Baker (Phillipsburg, NJ, USA). Acetone (pesticide-grade) was from Fisher Scientific (Fair Lawn, NJ, USA). 1-Octanol (>99% purity) was obtained from Merck (Darmstadt, Germany). Ultrapure water was provided by a Milli-Q (Millipore, Bedford, MA, USA) water purification system.

Stock standard solutions (100 $\mu g\,ml^{-1}$ of each PAH) were prepared in methanol:methylene chloride (1:1). They were stored at $-10\,^{\circ}C$. Working solutions were prepared by dilution of stock standards with ultrapure water. These solutions were stored in the dark at 4 °C and were prepared weekly.

The Q3/2 Accurel polypropylene hollow fiber was bought from Membrana (Wuppertal, Germany). The inner diameter of the hollow fiber was 600 μm, the thickness of the wall was 200 μm, and the wall pore size was 0.2 μm.

2.2. Apparatus

A 10 μl microsyringe (SGE, Sydney, Australia) with a cone needle tip was used for extraction. A NE-1000 programmable syringe pump, purchased from New Era Pump Systems (Farmingdale, NY, USA), was used to automate and control the movement of the syringe plunger.

2.3. Preparation of soil sample

The soil samples (previously checked to be PAH-free) were pulverized, air-dried and sieved to a grain size of 2 mm. One hundred grams of soil was mixed with acetone until the soil was covered by the solvent to form a slurry. The standard mixtures of six PAHs were spiked into the slurry. The soil sample was dried and equilibrated overnight in a fume hood. The prepared sample was kept in the refrigerator at 4 °C until analysis.

2.4. GC–MS analysis

Chromatographic analysis was performed on a Hewlett-Packard (Palo Alto, CA, USA) series 6890 gas chromatograph equipped with HP5973 mass selective detector. The GC was fitted with a ZB-1 column (30 m × 0.25 mm I.D., 0.25 μm) from Phenomenex (Torrance, CA, USA). Helium was used as carrier gas with a flow rate of 1.8 $ml\,min^{-1}$. The gas chromatographic conditions were as follows: initial oven temperature 150 °C for 1 min, increased to 300 °C at the rate of 10 $^{\circ}C\,min^{-1}$, then held at 300 °C for 2 min; injector temperature was 280 °C. The total time for one GC–MS run was 18 min. All injections were used in splitless mode. The detector was scanned over the range of *m*/*z* 50–550 to confirm the retention times of the analytes. For determination of the PAHs, selected ion monitoring mode was performed. The target ions we used were molecular ions for the PAHs. The interface temperature was set at 280 °C.

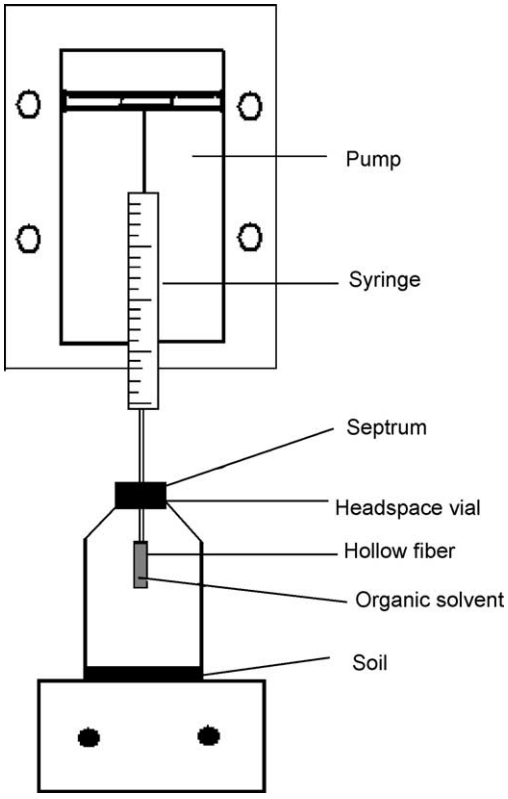

Fig. 1. Experimental setup of DHF-HS-LPME.

2.5. Dynamic hollow fiber-supported headspace liquid-phase microextraction (DHF-HS-LPME)

The experimental setup of DHF-HS-LPME is illustrated in Fig. 1. Briefly, headspace microextraction was carried out as follows: the hollow fiber was cut manually and carefully into 1.5 cm lengths. These segments were ultrasonically cleaned in acetone and dried in air before use. A 3.0 μl aliquot of 1-octanol was withdrawn into the microsyringe with a cone needle tip. A headspace sample vial septum cap was pierced by the microsyringe. The needle tip was inserted into the hollow fiber and then the fiber was immersed in 1-octanol for 20 s for impregnation of the porous wall. After impregnation, the fiber together with the syringe was fixed on the retort stand. To determine the effect of salt addition on the extraction, 0–0.3 g ml^{-1} sodium chloride solutions were prepared; 1 ml of each solution was then added, respectively, to the sample (in a 20-ml vial), and mixed well, before extraction. The vial was placed in position and capped such that the fiber-needle assembly was in the headspace region. Masking tape (Hi-Bond, Singapore) was used to wrap around the seal formed by the septum cap and the sample vial. Before extraction, the sample was preheated at 90 °C for 10 min, and then adjusted to 40 °C for extraction. The syringe pump was switched to start the extraction. The sample was stirred at 42 rad s^{-1} (400 rpm). The final movement of the plunger was to withdraw the extract into the syringe barrel. After extraction, the fiber-needle assembly was removed and the extract (2 μl) was then injected into the GC–MS for analysis. The used fiber was discarded and a fresh one was used for the next experiment.

3. Results and discussion

3.1. DHF-HS-LPME

DHF-HS-LPME consists of a three-phase system that includes sample matrix (condensed phase)/headspace/hollow fiber-supported organic phase. There are two interfaces: the condensed phase/headspace, and the headspace/extracting organic solvent. For the hollow-fiber supported organic phase, when the syringe plunger was withdrawn, a thin organic solvent film (OSF) along the hollow fiber was formed, as previously described for HS-LPME [16]. This film greatly increased the contact area between the extracting organic phase and the headspace. This is due to the fact that for the same volume the surface area of a sphere is the smallest [15]. The PAHs in the vapor partitioned between the OSF and the headspace. The OSF includes the outside and inside walls of the hollow fiber. When the plunger was depressed, the PAHs-enriched OSF was transferred to the bulk organic solvent. The next extraction cycle was then repeated.

During the extraction, the amount of extracted analyte in DHF-HS-LPME is expressed by the following equation, which is analogous to the equation described for headspace SPME by Pawliszyn and Górecki [17].

$$n = \frac{K_{\mathrm{osf-hs}} C_0 V_\mathrm{s} V_\mathrm{o}}{K_{\mathrm{osf-hs}} V_\mathrm{f} + K_{\mathrm{hs}} V_{\mathrm{hs}} + V_\mathrm{s}}$$

where n is the amount of analyte extracted by organic solvent at equilibrium. $K_{\mathrm{osf-hs}}$ is the equilibrium partition constant for the analyte between the OSF and the headspace and K_{hs} is the headspace-sample matrix partition coefficient. V_o V_h, and V_s are the volumes of extracting organic solvent, headspace, and sample matrix, respectively. C_0 is the initial concentration of the analyte in the sample. However, the above equation is only applicable for a steady mass transfer reaching partition equilibrium.

For non-equilibrium, Ai [18] proposed a theoretical model to deal with the adsorption process in SPME and indicated that the extracted amount of analytes showed excellent linearity with the initial concentration in the sample matrix within a extraction time which was much shorter than that required to reach equilibrium. This model also can be used for headspace solvent LPME [19].

3.2. Selection of organic solvent for DHF-HS-LPME

It is essential to select a suitable organic solvent for DHF-HS-LPME. The following factors should be considered. Firstly, the solvent should be compatible with the hollow fiber. Secondly, the solvent should have a high boiling point and low vapor pressure so that it can stand under

Table 1
Effect of dwelling time on the DHF-HS-LPME of PAHs

Compound	Dwelling time			
	2 s	5 s	8 s	10 s
Acenaphthene	100 ± 4.1%	120.9 ± 5.2%	117.8 ± 3.8%	16.3 ± 4.6%
Fluorene	100 ± 3.8%	115.8 ± 5.3%	97.6 ± 4.6%	65.8 ± 5.3%
Phenanthrene	100 ± 5.7%	117.2 ± 6.7%	105.5 ± 4.3%	98.2 ± 5.8%
Anthracene	100 ± 10.1%	196.8 ± 12.1%	187.9 ± 10.1%	63.4 ± 9.8%
Fluoranthene	100 ± 8.2%	218.7 ± 6.7%	195.7 ± 7.6%	52.5 ± 9.5%
Pyrene	100 ± 10.1%	300.6 ± 13.8%	247.5 ± 9.7%	233.6 ± 8.9%

Extraction conditions: pre-extraction temperature, 90 °C; extraction temperature, 40 °C; extraction time, 10 min; dwell time, 5 s.

higher extraction temperature without apparent loss. Thirdly, according to the theory of "like attracts like", the extraction organic solvent should have high affinity with the analytes in the sample. Finally, the solvent should be compatible with GC–MS. Based on the above considerations and previous reported experience [14] with LPME, 1-octanol was chosen as extraction solvent for subsequent experiment, since it has a high boiling point (180 °C) and low vapor pressure (0.3 hPa at 20 °C).

3.3. Effect of dwelling time, extraction cycles and extraction time

In a sampling cycle, the dwelling time is defined as a waiting time after the complete flushing of solvent by the pump. The effect of the dwelling time was studied in the range of 2–10 s. For a certain extraction time, the plunger speed was set at its maximum speed (0.18 μl s^{-1}) and the dwelling time was varied. In addition, this dwelling time also represents the frequency of the plunger movement within a period of extraction time. As shown in Table 1, the extraction efficiency was optimum when the dwelling time was fixed at 5 s. For DHF-HS-LPME, during extraction, the diffusion coefficient in the gas phase is typically 10^4 times greater than in a condensed phase. The diffusion of analyte into 1-octanol is one of the slow steps in the overall mass transfer [14]. Therefore, the repeated plunger movement was beneficial to mass transfer during extraction. The dwelling time is an important factor for the repeated plunger movement: the shorter the dwelling time, the higher the frequency of the plunger movement. The higher frequency of the plunger movement allows a greater number of extraction cycles. A previous study [20] indicated that peak area signals increased with the number of extraction cycles. However, too short a dwelling time could cause less contact time between the headspace gas phase and the organic solvent film inside the hollow fiber. Thus, 5 s was selected for subsequent experiments.

For DHF-HS-LPME, the extraction does not attain equilibrium. It is due to the fact that it is not practicable to maintain an extraction time long enough for equilibrium to be established. In addition, the problem of solvent depletion should also be considered. The longer the extraction, the more likely the solvent will be depleted. Thus, a 10-min extraction time was deemed to be sufficient for subsequent experiments.

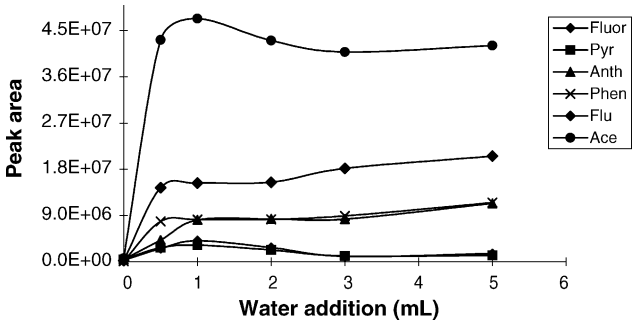

Fig. 2. Effect of water in sample on DHF-HS-LPME efficiency. *Abbreviations*: Ace, acenaphthene; Flu, fluorene; Phen, phenanthrene; Anth, anthracene; Fluor, fluoranthene; Pyr, pyrene. *Experimental conditions*: pre-extraction temperature, 90 °C; extraction temperature, 40 °C; extraction time, 10 min; dwell time, 5 s.

3.4. Water effect on DHF-HS-LPME

The partitioning of VOCs between soil and headspace is usually very low. Thus, the water is used to promote the release of volatiles and has been used in headspace solid-phase microextraction (HS-SPME) [21] and HS-LPME [15]. In our present study, the effect of water was investigated by varying the amount of water between 0.5 and 5 ml added to 1 g of soil. As shown in Fig. 2, without addition of water, the extraction response obtained was the lowest. With 0.5 ml water, the extraction efficiency improved significantly (up to 80 times). The best results were obtained for most of the PAH when 1 ml water was added. However, the responses obtained between 1 and 5 ml of water were not dramatically different. One interpretation of the results would be that the water molecules helped to dislodge the PAHs from the soil. The active sites in soil are usually polar functional groups, such as –Si–O–, which have more affinity for polar molecules such as water. Thus, the addition of water could displace some active sites that were occupied by PAH molecules which then partitioned into the headspace. This result is consistent with the observation in HS-SPME and HS-LPME that water addition decreased the solubility of the analytes in the soil slurry and facilitated their partition into the headspace [15,21].

3.5. Temperature effect on DHF-HS-LPME

For headspace analysis of semi-volatile compounds, another important parameter is temperature. Temperature has

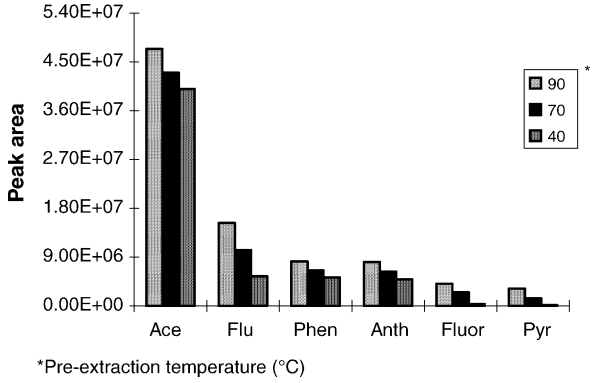

Fig. 3. Effect of pre-extraction temperature on DHF-HS-LPME.

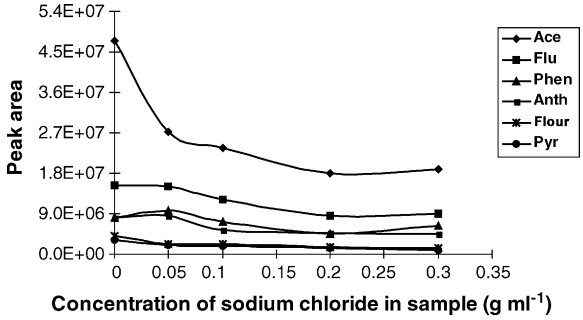

Fig. 4. Effect of addition of sodium chloride on DHF-HS-LPME.

a significant effect on both the kinetics and thermodynamics of the extraction process. Temperature affects the kinetics of sorption in the extracting organic solvent by determining the vapor pressures of analytes and diffusion coefficient values in the three phases [22]: sample matrix/headspace/hollow fiber-supported organic phase. The effects of temperature are of two aspects: pre-extraction temperature and extraction temperature. The extraction temperature was set at 40 °C. The pre-extraction temperature was evaluated from 40 to 90 °C. As seen in Fig. 3, for most volatile PAH compounds except acenaphthene, peak area responses at 40 °C were much lower than those at 90 °C. This is most probably related to the lower molecular weight, PAHs being much less volatile and are thus more easily released into the headspace. Thus, 90 °C was selected as the optimum pre-extraction temperature.

For the extraction temperature, because the process of analyte absorption in the hollow fiber-supported organic solvent is exothermic, the amount of analytes partitioned increase when the extraction temperature is reduced. Nevertheless, too low an extraction temperature can decrease extraction rate, because for higher boiling compounds, the distribution constants between the headspace and sample matrix should be large enough to enable sufficient amount of analytes to be extracted [21]. However, when the extraction temperature was set at higher temperature (60 °C), there was difficulty in ensuring that the solvent remained intact for extraction to be carried out satisfactorily. In view of that, the extraction temperature was set to be 40 °C.

3.6. Salt effect on DHF-HS-LPME

The effect of the addition of salt to the samples was also investigated. For SPME and LPME in aqueous solution, the addition of salt can decrease the solubility of analytes and enhance their partitioning onto the fiber (for SPME) and organic phase (LPME). The salt effect in SPME and LPME has been widely discussed, and there have been conflicting results [22]. It was reported that the salting-out effect was not apparent in SPME, while in LPME/HF this reduced extraction efficiency [16]. In our study, as shown in Fig. 4, no increase in extraction was observed after the addition of the sodium chloride. On the contrary, the extraction efficiencies were highest without addition of the sodium chloride, and subsequently decreased as more was added. This is due to the fact that the addition of salt to aqueous sample is usually used to enhance the response of headspace analysis of polar compounds while for nonpolar or weakly polar compounds, this effect is not significant. The PAHs studied in this work have low polarity. Furthermore, it is possible that the addition of salt to the soil slurry does not facilitate the desorption of the PAHs from the soil particles. This observation merits further study.

3.7. Quantitative analysis of DHF-HS-LPME

The spiked soil sample after being prepared was employed to investigate the repeatability, linearity, the square of correlation coefficient and limits of detection under the optimized extraction procedure. To determine the repeatability, six replicate experiments were carried out under the optimal

Table 2
Quantitative results of DHF-HS-LPME

Analytes	Linearity ($\mu g\,g^{-1}$)	Correlation coefficient	Limit of detection ($\mu g\,g^{-1}$)	RSD (%)
Acenaphthene	0.5–50	0.9972	0.047	6.30
Fluorene	0.5–50	0.9821	0.050	5.40
Phenanthrene	0.5–50	0.9653	0.0059	9.81
Anthracene	0.5–50	0.9980	0.0086	14.60
Fluoranthene	0.5–50	0.9745	0.073	6.60
Pyrene	0.5–50	0.9874	0.076	13.80

conditions. The results are shown in Table 2. The relative standard deviations (RSDs) were from 5.4 to 14.6%. Calibration curves for the PAH compounds were obtained by plotting peak areas versus the spiked soil sample concentration. The linearity of all the compounds was in the range of 0.5–50 $\mu g\,g^{-1}$. The limits of detection, defined at a signal-to-noise ratio (S/N = 3), ranged from 0.0059 to 0.076 $\mu g\,g^{-1}$. Compared with previously reported data by using solvent microextraction (or drop-based LPME) (LODs from 0.13 to 0.36 $\mu g\,g^{-1}$) [23], DHF-HS-LPME provided better detection limits.

4. Conclusions

This paper has demonstrated the successful application of dynamic hollow-fiber supported headspace liquid-phase microextraction (DHF-HS-LPME) to the analysis of semi-volatile compounds from soil. With a programmable syringe pump, an organic solvent film is formed within the hollow fiber and used as the extraction interface. Some factors, such as the addition of water, extraction temperature, pre-extraction temperature, addition of sodium chloride and syringe plunger speed were investigated and optimized. The optimized procedures were used to extract polycyclic aromatic hydrocarbons from soil.

DHF-HS-LPME provides an alterative to HS-LPME and HS-SPME for the analysis of semi-volatile compounds. DHF-HS-LPME can tolerate a relatively larger amount of organic solvent than drop-based HS-LPME. The extraction interface that facilitated more efficient mass transfer is increased by the supporting hollow fiber. Solvent loss is also insignificant because some of it is withdrawn into the syringe barrel with the automated movement of the plunger during extraction. Furthermore, in comparison with HS-SPME, this method is inexpensive, fast and requires only small volumes of organic solvent as extractant. The hollow fiber can be discarded after each extraction so that carryover and cross-contamination is avoided altogether. From the results of our experiments, we have shown that the DHF-HS-LPME combined with GC–MS is an effective method for the qualitative and quantitative analysis of PAHs in soil. The extraction process itself is automated, but more work needs to be carried out with respect to automation of the setup of the hollow fiber assembly for extraction, and before analysis of the extract. A possible limitation of this technique is that the extraction organic solvent should have a relatively high boiling point with low vapor pressure, limiting the choice of solvents. Further studies will address this drawback.

Acknowledgements

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