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Automated hollow fiber-protected dynamic liquid-phase microextraction of pesticides for gas chromatography–mass spectrometric analysis

Li Hou, Gang Shen, Hian Kee Lee*

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

Abstract

Dynamic liquid-phase microextraction (LPME) controlled by a programmable syringe pump was evaluated for extracting pesticides in water prior to GC–MS analysis. A conventional microsyringe with a 1.3-cm length of hollow fiber attached to its needle was connected to a syringe pump to perform the extraction. The microsyringe was used as both the microextraction device as well as the sample introduction device for GC–MS analysis. The attached hollow fiber served as the ‘‘holder’’ and ‘‘protector’’ of 3 μl of organic solvent. The solvent was repeatedly withdrawn into and discharged from the hollow fiber by the syringe pump. Pesticides were extracted from 4-ml water samples into the organic solvent impregnated in the hollow fiber. The effects of organic solvents, plunger movement pattern, agitation and extraction time were investigated. Good repeatabilities of extraction performance were obtained, with the RSD values ranging from 3.0% (alachlor) to 9.8% (4-chlorophenol) for the 14 pesticides; most RSD values were under 5.0%. The method provided a 490-fold preconcentration of the target pesticides. The limits of detection were in the range of 0.01–5.1 μg/l ($S/N=3$) in the GC–MS selected ion monitoring mode. In addition, sample clean-up was achieved during LPME because of the selectivity of the hollow fiber, which prevented undesirable large molecules from being extracted. A slurry sample (mixture of 40 mg soil/ml of water) containing seven pesticides was extracted using this method which also gave good linearity and precision (most RSDs<7.0%, $n=3$).
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Keywords: Liquid-phase microextraction; Extraction methods; Automation; Pesticides

1. Introduction

The determination of pesticides in the environment has received great attention not only because of their toxicity and persistence but also because of their universal usage [1,2]. These compounds represent risks to the environment in respect of human health and the well-being of non-target species. Hence, the trace analysis of pesticides, for example in aqueous samples, represents an important analytical necessity. In order to detect the low levels a preconcentration step is needed in general prior to instrumental determination.

Conventional liquid–liquid extraction (LLE) has been the main method for enrichment of organic pollutants from aqueous solutions. It is still being widely used. However, this method requires the use of large amounts of toxic organic solvents and can take considerable time to perform even when it is

*Corresponding author. Fax: +65-6779-1691.
E-mail address: chmleehk@nus.edu.sg (H.K. Lee).

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automated. Without automation, it is too labour-intensive. In recent years, many other techniques have been reported as alternatives to LLE such as flow injection extraction [3], micro-liquid extraction [4], solid-phase extraction [5], solid-phase microextraction (SPME) [6] and supported liquid membrane extraction [7]. On-capillary enrichment procedures for capillary electrophoretic analysis, such as field-amplified stacking injection [8] and analyte sweeping [9], have also been used. Among these approaches, liquid-phase microextraction (LPME) [4,10], which based on the use of small amounts (e.g. 8 μl or less) of organic solvent to extract analytes from moderate amounts of aqueous matrices, has attracted increasing attention. It has been shown to be a viable alternative sample preparation method to conventional LLE [11,12]. Liquid–liquid–liquid microextraction [13] or solvent microextraction with backextraction supported by a liquid membrane has also been developed [14]. Porous polypropylene hollow fiber with impregnated organic solvent was used as an interface between the donor and acceptor phase [15,16]. The hollow fiber with walls of 0.2-μm pore size provided a measure of sample clean-up because it prevented large molecules in donor phase from being extracted [16,17].

He and Lee [18,19] previously reported a novel liquid–liquid microextraction method in which a commonly used microsyringe was employed as a microseparatory funnel for extraction within the barrel, as well as a syringe for injection into a GC–MS system. The described dynamic LPME provided high preconcentration factors and was shown to be fast and highly efficient but was performed manually. In this procedure, although increasing sampling time is useful to increase the sensitivity, it is not convenient. In addition, this method is not suitable for ‘‘dirty’’ samples such as slurry and soil sample, etc., because the particles in such solutions will damage the syringe.

We have previously reported hollow fiber-protected liquid-phase microextraction, also termed LPME/HF, for the analysis of two polycyclic aromatic hydrocarbons (PAHs) [2]. Owing to the porous property of the hollow fiber wall, the interfacial area between solvent and aqueous sample was increased, thus enhancing the extraction efficiency. Two modes of this technique (static LPME with HF and dynamic LPME with HF) were developed and compared. It was observed that dynamic LPME/HF that was automated by using a syringe pump could provide higher enrichment and better reproducibility. In order to investigate dynamic LPME/HF in more detail and evaluate this method for the extraction of ‘‘dirty’’ samples, the application of this procedure has been extended to the extraction and analysis of pesticides. A microsyringe with a 1.3-cm length of hollow fiber attached to its needle was connected to a syringe pump to perform automated extraction. Factors important to extractions, such as the most suitable organic solvent, plunger movement pattern, stirring rate and extraction time, were studied. To evaluate the procedure and to demonstrate the protection afforded by the hollow fiber, slurry samples were extracted and analysed.

2. Experimental

2.1. Standards and reagents

The Accurel Q 3/2 polypropylene hollow fiber membrane (600 μm I.D., 200-μm wall thickness, 0.2-μm pore size) was purchased from Membrana (Wuppertal, Germany). The pesticides were purchased from different suppliers. HPLC-grade methanol and toluene were from J.T. Baker (Phillipsburg, NJ, USA). 1-Octanol (>99.5%) and *n*-hexane were obtained from Merck (Darmstadt, Germany). Deionized water was produced on a Nanopure (Barnstead, Dubuque, IA, USA) water-purification system.

Stock solutions (0.1 mg/ml of analyte) were prepared separately in methanol. They were stored at 4 °C. A fresh standard sample was prepared by spiking deionized water with the 14 analytes at known concentrations (5–50 μg/l) every week during the study of extraction performance under different conditions, and stored at 4 °C.

The water samples (1.0 l) were collected from a pond situated in a golf course. The water samples were filtered through a Whatman (UK) filter paper and a 0.45-μm membrane (Millipore) to eliminate particulate matter and then kept at room temperature (25 °C, 24 h) for homogenization. The samples were filtered again prior to extractions.

2.2. GC–MS analysis

All analyses were performed on a Shimadzu (Tokyo, Japan) QP5000 GC–MS system. The GC system was fitted with a DB-5 column (30 m×0.32 mm I.D., 0.25-μm film thickness) from J&W Scientific (Folsom, CA, USA). Helium was used as the carrier gas at a flow rate of 1.5 ml/min. The following temperature programme was employed: initial temperature of 80 °C for 4 min; increase at 10 °C/min to 150 °C, held for 1 min; then another increase at 5 °C/min to 200 °C; yet another ramp at 30 °C/min to 290 °C, held for 5 min. The injector temperature was 250 °C and all injections were made in splitless mode. The detector was scanned over the range m/z 50–500 to confirm the retention times of the analytes. For determination of the pesticides, selected ion monitoring (SIM) was performed. To confirm pesticide ions tentatively identified by SIM, one characteristic fragment ion was monitored in addition to the molecular ion (Table 1). The interface temperature was 270 °C. The external standard method was used for quantitative analysis of spiked water samples whereas the pond and slurry samples were analyzed based on standard addition.

2.3. Apparatus

A 10-μl microsyringe with a cone needle tip (SGE, Sydney, Australia) was used for extraction. It was used together with a Harvard Apparatus (Holliston, MA, USA) PHD 2000 syringe pump. The hollow fiber was ultrasonically cleaned in acetone and dried before use. It was cut into 1.3-cm segments for extraction. The approximate internal volume of this segment was ~3 μl which was suitable for the amount of extraction solvent used in this work.

2.4. Extraction procedures

The schematic of the extraction is illustrated in Fig. 1. The syringe pump was first programmed based on: (i) refill speed; (ii) sampling volume (the volume of organic solvent withdrawn into the hollow fiber); (iii) dwell time (length of time the organic plug remain in the hollow fiber); (iv) infusion speed; (v) sampling volume (the volume of organic solvent infused into the microsyringe); (vi) dwell time (length of time the aqueous plug remain in the hollow fiber; and (vii) restart. Briefly, automated dynamic LPME consists of the following sequence: (a) 3 μl of organic solvent (typically toluene) was manually withdrawn into the microsyringe followed by an equal volume of water. The needle tip was inserted into the hollow fiber and the assembly was immersed in the organic solvent for ~5 s to impregnate the pores of the hollow fiber with the organic solvent. Then, while the fiber remained

Table 1
Elution order, molecular mass and characteristic ions used for GC–MS-SIM analysis [23]

No.	Compound	Molecular mass	Solubility (mg/l)	Characteristic ions used for GC–MS-SIM analysis (m/z)
1	2,5-Dimethylphenol (DMP)	122.2	–	122, 107
2	4-Chlorophenol (CHL)	128.6	27 000	128, 136
3	2,3,5-Trimethylphenol (TMP)	136.2	762	136, 121
4	Allidochlor (ALL)	173	–	173, 138
5	1,2,4,5-Tetrachlorobenzene (TCB)	215.9	0.606	216, 214
6	Pentachlorobenzene (PCB)	250.3	0.562	250, 248
7	Molinate (MOL)	187.3	880	187, 126
8	Hexachlorobenzene (HCB)	284.8	0.005	284, 286
9	Lindane (LIN)	290.8	10	290, 181
10	Heptachlor (HEP)	374	0.056	374, 272
11	Alachlor (ALA)	269.8	242	269, 160
12	Aldrin (ALD)	365	0.025	363, 263
13	Chlorpyriphos (CPS)	350.6	2	349, 197
14	Dieldrin (DIE)	381	0.186	378, 263

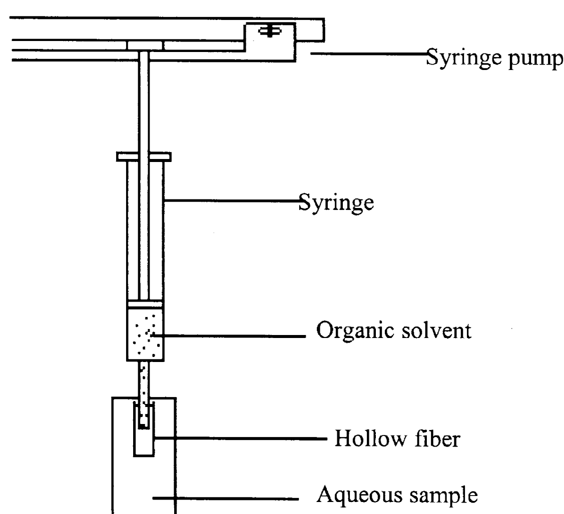

Fig. 1. Set-up of automated dynamic LPME using hollow fiber.

immersed in the organic solvent, the water in the syringe was injected to flush the hollow fiber in order to remove excess organic solvent from the inside of the fiber; (b) the fiber needle was removed from the organic solvent and subsequently immersed in 4 ml of aqueous sample. The organic solvent in the syringe was then injected completely into the hollow fiber; (c) the microsyringe was connected to the syringe pump and the pump programme was activated; (d) after extraction, the syringe containing the 3 μl analyte-enriched solvent was injected directly into the GC–MS for analysis. A fresh hollow fiber was used for each extraction.

3. Results and discussion

3.1. Automated dynamic LPME

Dynamic LPME [18,19] as previously described provides a fast, simple and highly efficient extraction approach. However, it has disadvantages arising from its manual operation and its preconcentration factor can still be improved. Moreover, the procedure appears to work well for clean matrices because particles in the sample affect the extraction by plugging the microsyringe being used as the microseparatory funnel and are potentially detrimental to the analytical instrument. This means that dynamic LPME falls short of being a clean-up procedure.

In this study, we automated the dynamic LPME by a syringe pump so that this method could be more accurate and more easily operated. Also, we connected a 1.3-cm length of hollow fiber on the needle of the microsyringe to replace the microsyringe as the microseparatory funnel. There are some advantages in using the hollow fiber as a microseparatory funnel. As described in the previous study [18,19], extraction takes place predominantly between the aqueous sample plug and the organic film that forms on the inner surface of the syringe when the plunger is withdrawn. With the use of the hollow fiber, although extraction also takes place between the organic film and aqueous sample plug, the organic film forms on both the inner surface and external surface of the hollow fiber when the plunger is withdrawn as a result of the porous property of the hollow fiber, and surface tension [2]. Thus, the organic film formed here is thicker than that which forms in the syringe barrel, as described in our previous study. By repeatedly manipulating the plunger in and out of the microsyringe barrel, the thicker organic film would be in contact with fresh aqueous sample having the initial analyte concentration. The hollow fiber also shows some selectivity because of the pores in its wall so that this technique can be used to extract "dirty" matrices such as slurry samples whilst preventing the co-extraction of extraneous materials.

3.2. Optimization of automated dynamic LPME

The different parameters that can affect the automated dynamic LPME process (organic solvent, extraction time, movement pattern of plunger and solution stirring rate) were optimized based on data obtained under SIM acquisition mode. Extraction performance was determined by the enrichment factor, the ratio of peak area of any single analyte attained with extraction and that without extraction.

The first parameter to be optimized was the organic solvent. The extraction solvent must be compatible with the fiber so that the pores in the wall of fiber can be filled completely. Also, the extraction solvent must be immiscible with water and have low volatility. Based on these considerations, 1-octanol,

n-hexane and toluene were investigated. In these experiments, 3-min extractions from 25-μg/l standard solutions with the fastest syringe speed (0.5 μl/s) and dwell time at 5 s were performed. *n*-Hexane gave low enrichment factor (EF) for target analytes (the highest was ~30). For most target analytes, 1-octanol gave similar EF as toluene, but its gas chromatographic behaviour was not satisfactory and there were too many unidentified peaks even in SIM mode. Possibly, the batch of 1-octanol we used was not sufficiently pure. Since toluene could enrich most target analytes ~100-fold, peaks were well resolved in SIM mode and it was easily immobilized in the fiber, it was chosen as the most suitable extraction solvent.

The next step was to optimize the number of samplings (extraction cycles). This study was carried out by varying the number of samplings in the range 5–45 (Table 2). The other experimental parameters were the same as for the optimization of the extraction solvent. Like SPME, dynamic LPME is a process dependent on equilibrium rather than exhaustive extraction. The amount of analyte extracted at a given time depends upon the mass transfer of analyte from the aqueous phase to the organic solvent phase. From the results obtained from studying the optimum number of samplings it can be seen that the effect of this parameter varies for the different pesticides. The number of samplings chosen in this study was ten since under these conditions the peak area of every pesticide had a maximum value and also precision was better than that under longer extraction times. The reason that analyte was lost with increasing extraction cycles is that some of the extraction solvent was lost as a result of dissolution when the hollow fiber with solvent was immersed in the water sample. Since only a small volume of organic solvent was used in our method, this effect of solvent depletion was more severe with increasing extraction cycles. After the optimum number of extraction cycles had been determined, the movement pattern of the plunger was 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 two pauses between (dwell time) withdrawing 3 μl of the organic solvent (which was inside the hollow fiber) into the syringe and discharging it into hollow fiber, with fresh aqueous sample going in and out of the hollow fiber, respectively, at the same time. The analytes were extracted rapidly from the aqueous sample to organic solvent (including toluene immobilized in the pores of the porous polypropylene hollow fiber) when the plunger moved. In this section, the effects of the plunger movement speed (sampling volume/withdrawal time = sampling volume/discharge time) and the dwell time between plunger movement on extraction efficiencies were studied. First, setting the plunger movement speed at 0.5 μl/s, the dwell time was varied. Results are shown in Table 3. For all the analytes except 4-chlorophenol and hexachlorobenzene, the extraction efficiency was best when dwell time was fixed at 4 s. With the dwelling time fixed at 4 s, we carried out separate experiments in which the plunger movement speed was varied. The results are

Table 2
Effect of varying number of samplings on peak areas of pesticides[a]

Compound[b]	Sampling number				
	$n=5$	$n=10$	$n=15$	$n=30$	$n=45$
TCB	100	745	138	53	127
PCB	100	650	131	54	108
HCB	100	677	130	66	71
HEP	100	1615	300	112	248
ALD	100	582	123	64	79
DIE	100	538	122	61	90

[a] Relative GC–MS signals were employed to evaluate the performance of varying number of samplings (relative GC–MS signals are defined as the peak area percentage ratios of the extracts at different sampling numbers to those when sampling number = 5). Water samples were spiked at a concentration of 15 μg/l.

[b] See Table 1 for explanation of abbreviations.

Table 3
Effect of dwell time on the extraction of pesticides[a]

Compound[b]	Dwell time					
	2 s	3 s	4 s	5 s	6 s	7 s
DMP	100	81	134	131	47	43
CHL	100	121	114	192	30	46
TMP	100	97	149	136	82	53
ALL	100	80	119	117	61	46
TCB	100	151	195	117	96	118
PCB	100	155	212	124	87	134
MOL	100	91	116	78	50	41
HCB	100	105	142	84	63	158
LIN	100	102	158	82	68	52
HEP	100	107	145	82	63	108
ALA	100	92	116	85	66	49
ALD	100	108	147	81	68	131
CPS	100	108	144	81	58	92
DIE	100	107	139	85	64	96

[a] Relative GC–MS signals were employed to evaluate the performance of different dwell times (relative GC–MS signals are defined as the peak area percentage ratios of the extracts at different dwell times to those when dwell time is 2 s). Water samples were spiked at a concentration of 15 μg/l.

[b] See Table 1 for explanation of abbreviations.

shown in Table 4. The GC–MS peak area decreased with the decrease of plunger movement speed. This can be explained by the theory reported previously [20]. The relation between the film thickness (d_f) and flow speed (μ) was:

$$d_f = \text{constant} \cdot R(\mu\eta/\tau)^K$$

where R is the inner diameter of the tube, η is the viscosity of the film-forming phase, τ is the surface tension, and K is an empirical constant equal to 1/2 or 2/3. So lowering the plunger movement speed would result in a thinner film.The thinner film becomes the limiting factor for the attainment of equilibrium between the organic film (OF) and aqueous sample plug (ASP). It is possible that more analyte would be extracted if the plunger movement speed could be improved further. In our experiments, 0.5 μl/s was the fastest speed at which the PHD 2000 syringe pump could operate automatically. On the basis of the above study, 0.5 μl/s was selected as the plunger movement speed and the dwell time was fixed at 4 s for subsequent work.

Finally, the agitation of aqueous sample was optimized. A faster stirring rate can be employed to both accelerate extraction and enhance the extraction efficiency since agitation permits the continuous exposure of the extraction surface to fresh aqueous sample. Although for dynamic LPME, exposure of

Table 4
Effect of syringe plunger speed on the extraction of pesticides[a]

Compound[b]	Syringe plunger speed			
	0.2 μl/s	0.3 μl/s	0.4 μl/s	0.5 μl/s
DMP	100 (4.2%)	74 (4.0%)	96 (3.2%)	112 (2.9%)
CHL	100 (5.7%)	80 (5.5%)	84 (4.1%)	359 (4.4%)
TMP	100 (3.0%)	73 (2.6%)	84 (2.0%)	110 (1.8%)
ALL	100 (3.3%)	71 (2.8%)	75 (2.5%)	107 (2.1%)
TCB	100 (2.8%)	71 (2.5%)	79 (1.9%)	121 (1.5%)
PCB	100 (2.6%)	74 (2.1%)	74 (1.6%)	123 (1.3%)
MOL	100 (3.5%)	68 (2.9%)	89 (2.0%)	110 (2.2%)
HCB	100 (4.0%)	120 (3.3%)	80 (2.1%)	205 (2.4%)
LIN	100 (6.4%)	64 (5.9%)	66 (5.0%)	123 (5.6%)
HEP	100 (6.9%)	107 (6.3%)	84 (5.5%)	125 (5.1%)
ALA	100 (3.1%)	73 (2.8%)	88 (2.2%)	117 (1.9%)
ALD	100 (7.5%)	151 (6.8%)	104 (5.9%)	174 (6.4%)
CPS	100 (3.8%)	65 (3.6%)	72 (3.0%)	105 (2.7%)
DIE	100 (4.3%)	67 (3.9%)	76 (3.2%)	110 (2.8%)

[a] Relative GC–MS signals were employed to evaluate the performance of different syringe plunger speeds (relative GC–MS signals are defined as the peak area percentage ratios of the extracts at different syringe plunger speeds to those when syringe plunger speed is 0.2 μl/s). Water samples were spiked at a concentration of 15 μg/l. The experiments were performed in triplicate.

[b] See Table 1 for explanation of abbreviations.

the extraction surface to fresh aqueous sample is mainly brought about by the repeated movement of the plunger, the agitation of aqueous sample also cannot be totally neglected. As seen from Table 5, extraction efficiency improved with the increase of stirring speed and most of the pesticides reached their highest peak areas at 1000 rpm. With extraction at 1250 rpm stirring, however, the peak area decreased, probably because air bubbles were generated and occupied the contact sites on the fiber surface so that the amount of analytes extracted into the organic solvent decreased. Thus, 1000 rpm was selected for subsequent experiments. Fig. 2 shows chromatograms obtained for a sample extract (spiked with 20 μg/l of each compound) obtained under the optimum conditions.

3.3. Method evaluation

Under optimum conditions, we investigated the performance of the method (Table 6). The maximum enrichment factor can reach as high as 490. The good linearity of response was in the range from 1 to 100 μg/l and the coefficients of variation, r^2, were higher than 0.9901. The limits of detection (LODs) calculated at $S/N=3$ under SIM, ranged between 0.01 to 5.1 μg/l. In comparison with literature values [21,22] relating to the SPME of pesticides in water, automated dynamic LPME provided relatively lower LODs except for heptachlor and chlorpyriphos. The reproducibility of the method was determined by performing six extractions for deionized water containing concentrations of 10 μg/l of each pesticide. The relative standard deviations (RSDs) of 14 pesticides were lower than 5.0% except for 4-chlorophenol (9.8%), lindane (8.7%), heptachlor (7.9%) and aldrin (9.0%). The good reproducibility could be explained by the automated extraction. The other reason for the good precision could be that the protection offered by the hollow fiber eliminated the effect of the matrix on the extraction.

3.4. Analysis of real samples

The performance of the method with real samples was tested for pond water and slurry samples. The sample of pond water was analysed after LPME and under SIM mode. Dieldrin was detected, and the result was confirmed by spiking the pesticide into the water which was reanalysed. The concentration of dieldrin was determined to be 0.2 μg/l by the standard addition method. Pond water was also spiked with the pesticides to assess matrix effects. The relative recoveries of all pesticides from the spiked sample were higher than 90%, as shown in Table 6. It is clear that this method is applicable to real world aqueous samples. In order to check the ability of the method to extract analytes from ‘‘dirty’’ samples, a slurry mixture of soil and water at 40 mg/ml containing the target pesticides was investigated. The experiment conditions were the

Table 5
Effect of stirring speed on the extraction of pesticides[a]

Compound[b]	Stirring speed					
	0 rpm	300 rpm	500 rpm	700 rpm	1000 rpm	1250 rpm
DMP	100	800	1671	1784	2636	1587
TCB	100	673	1002	1161	1627	1531
PCB	100	836	1228	1587	1969	1936
MOL	100	1345	3683	4068	6529	5739
HCB	100	641	1065	1359	9298	1509
HEP	100	947	1133	1994	1499	1620
ALD	100	1141	849	1749	900	1075
DIE	100	877	761	1478	1148	1191

[a] Relative GC–MS signals were employed to evaluate the performance of different stirring speeds (relative GC–MS signals are defined as the peak area percentage ratios of the extracts at different stirring speeds to those when stirring speed is 0 rpm). Water samples were spiked at a concentration of 15 μg/l.

[b] See Table 1 for explanation of abbreviations.

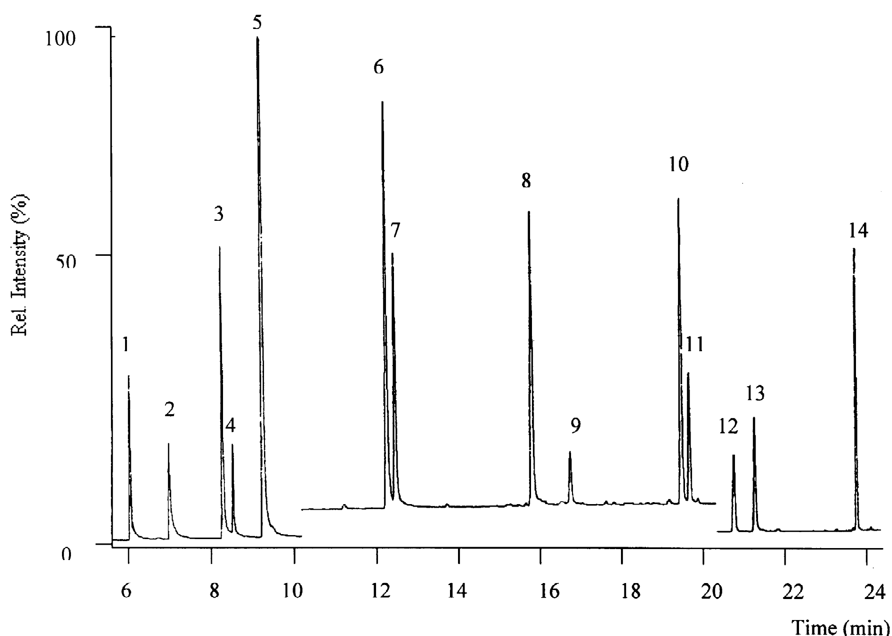

Fig. 2. Extraction of deionized water sample (spiked with 20 μg/l of each compound) by automated hollow fiber-protected dynamic LPME with GC–MS analysis. Only dieldrin (peak 14) was detected in pond water. The height of peak 5 is taken as 100% relative intensity. Other peak identities: (1) 2,5-dimethylphenol; (2) 4-chlorophenol; (3) 2,3,5-trimethylphenol; (4) allidochlor; (5) 1,2,4,5-tetrachlorobenzene; (6) pentachlorobenzene; (7) molinate; (8) hexachlorobenzene; (9) lindane; (10) heptachlor; (11) alachlor; (12) aldrin; (13) chlorpyriphos. For GC–MS conditions, see Experimental section.

Table 6
Performance of automated dynamic LPME

Compound[a]	Enrichment (-fold)	Linearity range (μg/l)	Correlation coefficient (r^2)	RSD (%) ($n=6$)	Recovery[b] (%)	LOD[c] (μg/l)	LOD (μg/l)
DMP	80	1–50	0.9925	4.0	91.5	0.6	–[d]
CHL	30	1–50	0.9917	9.8	92.3	3.2	–[d]
TMP	200	1–50	0.9909	3.1	91.9	0.7	–[d]
ALL	80	10–100	0.9954	4.2	90.8	5.1	–[d]
TCB	180	1–50	0.9991	3.1	94.9	0.02	–[d]
PCB	186	2–100	0.9987	3.0	93.6	1.4	–[d]
MOL	200	2–50	0.9992	4.6	92.8	1.2	–[d]
HCB	190	2–100	0.9984	4.9	95.4	0.8	–[d]
LIN	294	5–100	0.9996	8.7	96.7	1.5	200[e]
HEP	270	10–50	0.9901	7.9	92.7	5.1	3.8[e]
ALA	340	2–50	0.9992	3.0	91.5	0.01	0.02[f]
ALD	212	10–100	0.9913	9.0	94.2	2.2	4.5[e]
CPS	490	5–100	0.9997	5.0	95.6	1.4	0.04[f]
DIE	320	1–50	0.9996	4.7	NC[g]	0.02	0.06[e]

[a] See Table 1 for explanation of abbreviations.
[b] Water samples containing 10 μg/l of each analyte.
[c] LODs of automated dynamic LPME calculated from $S/N=3$.
[d] Not available.
[e] LODs of SPME with 100-μm PDMS fiber of water sample [21].
[f] LODs of SPME with 100-μm PA fiber of water sample [22].
[g] Not considered since it was detected in pond water.

Table 7
Results of dynamic LPME of pesticides from slurry samples

Compound[a]	Linearity range (mg/g)	Correlation coefficient (r^2)	RSD (%)
DMP	0.1–0.5	0.9936	3.3
TMP	0.1–0.5	0.9807	9.0
TCB	0.5–1.5	0.9914	11.9
PCB	0.3–1.0	0.9923	6.3
HCB	0.2–0.8	0.9998	3.9
ALD	0.2–0.6	0.9935	4.0
DIE	0.5–1.5	0.9975	6.8

[a] See Table 1 for explanation of abbreviations.

same as the above optimum conditions except that a lower stirring speed (700 rpm) was used. Although it was sometimes possible for the extraction solvent to be contaminated by a small amount of particles possibly due to the stirring and to the fact that aqueous sample was being directly withdrawn into the fiber through its relatively wide-bore (600 μm) end, this problem could be largely solved by careful conduction of the experiment. As seen from Table 7, our method gave good linearity, with all the values higher than 0.9914 except for 2,3,5-trimethylphenol (0.9807). The precision was also satisfactory. The RSDs for the seven pesticides were lower than 7.0% except for 2,3,5-trimethylphenol (9.0%) and 1,2,4,5-tetrachlorobenzene (11.9%). The good precision obtained was as a result of a new fiber and fresh solvent being used for each extraction which eliminated carry-over errors. This clean-up technique is rapid and easy to use for the analysis of slurry samples.

4. Conclusion

We have combined the automation of hollow fiber-protected dynamic LPME with GC–MS to extract 14 pesticides. Good linearity, sensitivity and relative recoveries were obtained. The LODs for the 14 pesticides studied ranged from 0.01 to 5.1 μg/l; most LOD values were under 2.0 μg/l. Compared to manual dynamic LPME reported previously [19], our automation of dynamic LPME is easier to operate and can yield better precision. Up to 490-fold enrichment factor can be achieved. In addition, because of the selectivity of the porous hollow fiber, this method could be used to extract pesticides from ‘‘dirty’’ matrices. The extraction of a slurry sample by this method showed that it was not only a good preconcentration technique, but also an excellent sample clean-up procedure. Automated dynamic LPME is conveniently compatible to GC without the need for evaporation of solvent and reconstitution of analytes before injection. Also, it can be easily applied to real analysis of small volume (e.g. 4 ml) of aqueous samples. Accordingly, further investigations are now under the way to extend the procedure to biological samples such as blood or urine, etc.

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