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# Determination of organic micropollutants in rainwater using hollow fiber membrane/liquid-phase microextraction combined with gas chromatography–mass spectrometry

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## Abstract

A simple and rapid liquid-phase microextraction (LPME) method using a hollow fiber membrane (HFM) in conjunction with gas chromatography–mass spectrometry (GC–MS) is presented for the quantitative determination of 16 polycyclic aromatic hydrocarbons (PAHs) and 12 organochlorine pesticides (OCPs) in rainwater samples. The LPME conditions were optimized for achieving high enrichment of the analytes from aqueous samples, in terms of hollow fiber exposure time, stirring rate, sample pH, and composition. Enrichment factors of more than 100 could be achieved within 35 min of extraction with relative standard deviations (R.S.D.s) 1.3–13.6% for PAHs and 1.7–13.8% for OCPs, respectively, over a wide range of analyte concentrations. Detection limits ranged from 0.002 to 0.047  $\mu\text{g l}^{-1}$  for PAHs, and from 0.013 to 0.059  $\mu\text{g l}^{-1}$  for OCPs, respectively. The newly developed LPME–GC–MS method has been validated for the analysis of PAHs and OCPs in rainwater samples. Extraction recoveries from spiked synthetic rainwater samples varied from 73 to 115% for PAHs and from 75 to 113% for OCPs, respectively. Real rainwater samples were analyzed using the optimized method. The concentrations of PAHs and OCPs in real rainwater samples were between 0.005–0.162, and 0.063  $\mu\text{g l}^{-1}$ , respectively.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) are important classes of persistent organic pollutants (POPs) that are commonly found in the environment. POPs are long-lived

organic compounds, and originate almost entirely from anthropogenic activities such as chemical industry, combustion, and agriculture [1]. Both PAHs and OCPs are of particular concern due to their environmental and health effects. These micro organic pollutants are semi-volatile at atmospheric conditions, and may occur both in the gas phase and as attached to particles depending on the vapor pressure of the compound [2]. The major removal mechanism of the semi-volatile organic compounds from the atmosphere is through

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deposition, which can take place either wet or dry deposition. Wet deposition of POPs to both aquatic and terrestrial ecosystems is particularly important in places that receive abundant rainfall like Singapore. However, wet deposition studies involve specific difficulties such as transport of equipment to the locations of study and limited sample sizes. Thus, large volume filtration/extraction methods such as liquid–liquid extraction (LLE) are not applicable to this type of studies and microextraction methods have to be developed prior to the chromatographic analysis of trace organic pollutants.

Currently, most microextraction is carried out by solid-phase microextraction (SPME). This technique allows a rapid and solvent-free extraction of organic compounds from aqueous samples by partitioning between the stationary phase and the aqueous medium [3]. The technique is commercially available, and is capable of extracting micropollutants in aqueous samples prior to GC analysis [4–6]. The main drawbacks of SPME are (i) increase in the cost of analysis per sample due to the use of dedicated and expensive apparatus, (ii) degradation of fibers with increased usage, and (iii) carryover between extractions [7]. In order to overcome these problems, a simple and inexpensive device for liquid-phase microextraction (LPME) based on disposable polypropylene hollow fiber membrane (HFM) has been recently introduced [8–11]. In LPME, analytes are extracted from a large volume of water samples through pores of a porous hollow fiber of polypropylene into a small volume of an organic solvent under magnet stirring. Compared to a solid-phase extraction column, the price of each extraction unit is low, and each extraction device is used only for a single extraction. As a result, carryover effects between extractions are eliminated.

We recently investigated, for the first time, the applicability of LPME combined with gas chromatography–mass spectrometry (GC–MS) to the determination of PAHs and OCPs in rainwater samples collected in Singapore. Different aspects of the extraction procedure such as the chemical nature of sample matrix, the extraction time, the magnetic stirring speed, and the extraction solvent were optimized to achieve high analyte recovery and enrichment in a short time. In addition, this method was validated for quantitative purposes and applied to rainwater samples collected at various locations in Singapore.

The principal objective of this paper is to outline and discuss the quantitative analysis of both PAHs and OCPs in rainwater based on LPME–HFM extraction.

## 2. Materials and methods

### 2.1. Standard and reagents

All HPLC grade solvents were purchased from Merck (Darmstadt, Germany). Purified water was obtained from a Milli-Q-system (Millipore, Milford, MA, USA). All pesticides and PAHs used in this work were purchased from Poly Science (Niles, IL, USA) and Supelco (Bellefonte, PA, USA), respectively. A standard stock solution containing 12 OCPs (i.e.  $\alpha$ -BHC, Lindane,  $\beta$ -BHC, Heptachlor, Aldrin, Dieldrin, Endrin, Endosulfan, *p,p'*-DDD, *p,p'*-DDT, Endrin aldehyde and Methoxychlor) and 16 PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]fluoranthene, chrysene, benzo[*a*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[*a*]anthracene and benzo[*ghi*]perylene) were used in this study. Sodium phosphate tri-basic ( $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ ) crystals (93% pure, Mallinckrodt Inc., Paris, KY, USA) were used to prepare the buffer by dissolving 23.8 g of  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  into 250 ml of water; giving a final pH of 13. A Q3/2 Accural KM polypropylene hollow fiber membrane (Membrana GmbH, Wuppertal, Germany) with an inner diameter of 600  $\mu\text{m}$ , a wall thickness of 200  $\mu\text{m}$  and a pore size of 0.2  $\mu\text{m}$  was used for extraction.

### 2.2. Sample locations and sampling

Fresh rainwater samples (wet-only samples) were collected manually on a time and/or volume basis in pre-cleaned glass bottles with a glass funnel. Only few milliliter (5 ml) samples are required to analyze PAHs and OCPs. However, sufficient amounts of rainwater were collected to analyze other parameters for our routine rainwater characterization studies using well-established analytical methods [12,13]. Rainwater samples were analyzed on the same day of collection. The pH of the samples varied in the range of 3.9–4.7 and the conductivity, 30.5–84.5  $\mu\text{S cm}^{-1}$ . The concentration of dissolved organic carbon was 51  $\mu\text{M}$ . The average relative magnitude of ionic

species concentration followed the order:  $\text{SO}_4^{2-}$  ( $105 \mu\text{eq.l}^{-1}$ ),  $\text{H}^+$  ( $85 \mu\text{eq.l}^{-1}$ ),  $\text{Cl}^-$  ( $50 \mu\text{eq.l}^{-1}$ ),  $\text{Na}^+$  ( $40 \mu\text{eq.l}^{-1}$ ),  $\text{NO}_3^-$  ( $30 \mu\text{eq.l}^{-1}$ ),  $\text{NH}_4^+$  ( $22 \mu\text{eq.l}^{-1}$ ),  $\text{Ca}^{2+}$  ( $18 \mu\text{eq.l}^{-1}$ ),  $\text{Mg}^{2+}$  ( $8 \mu\text{eq.l}^{-1}$ ),  $\text{K}^+$  ( $7 \mu\text{eq.l}^{-1}$ ),  $\text{HCOO}^-$  ( $2 \mu\text{eq.l}^{-1}$ ) and  $\text{CH}_3\text{COO}^-$  ( $1 \mu\text{eq.l}^{-1}$ ). The ratio of the sum of cations to the sum of anions was generally in the range of 0.94–1.08, indicating that the major ions in rainwater have been identified and measured accurately.

### 2.3. LPME procedure

A schematic setup of LPME is shown in Fig. 1. LPME supported by a HFM was performed in a  $10 \mu\text{l}$  microsyringe, with a cone tip needle ( $0.47 \text{ mm o.d.}$ ) (Hamilton, Reno, NV, USA). Prior to each extraction, the syringe was rinsed with acetone and then toluene a total of ten times to avoid analyte carryover and air bubble formation. Finally,  $5 \mu\text{l}$  of toluene was drawn into the syringe. The syringe needle was then tightly fitted with a  $1.3 \text{ cm}$  length of HFM, which was then impregnated with toluene for  $10 \text{ s}$  to open membrane pores, prior to immersion  $5 \text{ mm}$  below the surface of a  $5 \text{ ml}$  unfiltered sample solution in a volumetric flask. The syringe plunger was depressed so that the HFM was completely filled with toluene. PAHs are extracted separately under the following conditions: sample pH 9; ionic strength 30% (NaCl); extraction time  $30 \text{ min}$ ; stirring speed  $700 \text{ rpm}$ , respectively. For OCP analysis, sample pH was not adjusted, and only ionic strength was increased to 30%. Extraction took place between

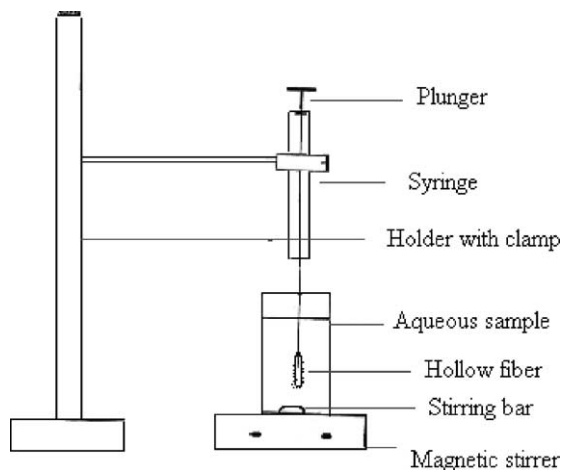


Fig. 1. Schematic setup of LPME with hollow fiber membrane.

the sample solution and the solvent in the HFM for  $30 \text{ min}$  at a magnetic rotation speed of  $700 \text{ rpm}$ . Following sample extraction, the stirrer was switched off and the solvent in the hollow fiber was retracted into the syringe. Then, the syringe with hollow fiber was removed from the sample solution and the fiber was detached. The extracted solvent volume was adjusted to  $2 \mu\text{l}$  position and injected into the GC–MS.

### 2.4. Basic principles

In LPME, the principles of liquid–liquid extraction and the miniaturized nature of SPME are combined to realize the advantages of both techniques. Briefly, the analytes of interest are extracted from about  $5 \text{ ml}$  of aqueous environmental samples into smaller volumes (typically  $5 \mu\text{l}$ ) of water-immiscible organic solvents (acceptor solution) present inside the lumen of porous hollow fibers. Thus, LPME is an equilibrium process and can be very effective for analyte enrichment because of the increase in the volume ratio of donor solution and acceptor phase.

In addition to enrichment, substantial sample clean-up can also be achieved with the use of a suitable organic solvent. In the interest of using the same solvent for extraction of semi-polar (OCPs) and non-polar (PAHs), toluene was investigated along with several other organic solvents (hexane, dichloromethane, chloroform and isooctane). Toluene demonstrated good selectivity for all target analytes and showed no significant solvent loss during extraction [14]. Both hexane and isooctane displayed poor enrichment factor for target analytes, particularly for OCPs. Therefore, toluene was selected as the extraction solvent for this work in view of its higher selectivity, extraction efficiency, and insignificant loss during extraction compared to the other solvents. As a result of analyte enrichment and sample clean-up, the LPME extract does not require any further handling before the GC analysis.

### 2.5. Enrichment factor and recoveries

The enrichment factor  $E_f$  was calculated based on the following equation:

$$E_f = \frac{1}{(V_o/V_a + 1/K)}$$

where as  $K$  is the distribution coefficient,  $V_o$  the volume of organic solvent and  $V_a$  the volume of aqueous sample.  $K$  is calculated based on the two-phase equilibrium condition:

$$K = \frac{C_{o\text{eq.}}}{C_{a\text{eq.}}}$$

where  $C_{o\text{eq.}}$  is the concentration of analyte in the organic phase and the  $C_{a\text{eq.}}$  the concentration of analyte in the aqueous phase. The optimum conditions were applied to investigate the enrichment factors of analytes. The enrichment factors for PAHs ranged from 46 to 167 whereas for OCPs, the range was from 63 to 155.

Like SPME, LPME is also an equilibrium extraction procedure. Therefore, the relative recoveries of PAHs

and OCPs were calculated from the peak area ratio of each analyte in the rain water samples and spiked ultrapure water samples.

## 2.6. GC–MS conditions

Sample analysis was carried out using a Shimadzu QP5050 GC–MS (Tokyo, Japan) equipped with Shimadzu AOC-20i auto sampler and DB-5 fused silica capillary column (30 m × 0.32 mm i.d., film thickness 0.25 μm, J&W Scientific, Folsom, CA). Helium was used as carrier gas with 1.5 ml min<sup>-1</sup> flow rate. Two microliters of sample was injected in splitless mode with an injection time of 2 min. The injection temperature portion was set at 250 °C, and the interface temperature was 280 °C. The GC temperature program

Table 1  
LPME–GC–MS quantitation data of PAHs and OCPs: linearity range (0.5–100 ng ml<sup>-1</sup>), enrichment factor, limits of detection and precision

Analytes	Target ion ( <i>m/z</i> )	Confirmation ions ( <i>m/z</i> )	Correlation coefficient ( <i>r</i> <sup>2</sup> )	Enrichment factor	Detection limit (ng ml <sup>-1</sup> )	R.S.D. (%)
<b>PAHs</b>						
Naphthalene	128	129, 127	0.9382	160	0.003	4.22
Acenaphthylene	152	151, 153	0.9917	154	0.003	10.61
Acenaphthene	153	154, 152	0.9799	159	0.002	9.63
Fluorene	166	165, 167	0.9720	46	0.047	7.76
Phenanthrene	178	179, 177	0.9983	167	0.006	10.07
Anthracene	178	179, 177	0.9839	166	0.008	10.01
Fluoranthene	202	203, 101	0.9987	162	0.003	7.93
Pyrene	202	203, 101	0.9845	165	0.003	8.07
Benz[ <i>a</i> ]anthracene	228	226, 227	0.9952	108	0.010	7.16
Chrysene	228	226, 227	0.9924	109	0.006	7.37
Benzo[ <i>a</i> ]fluoranthene	252	253, 126	0.9954	64	0.003	8.82
Benzo[ <i>k</i> ] fluoranthene	252	253, 126	0.9968	67	0.011	5.87
Benzo[ <i>a</i> ]pyrene	253	252, 126	0.9920	64	0.018	8.02
Indenol[1,2,3- <i>cd</i> ]pyrene	276	275, 138	0.9958	138	0.040	7.30
Dibenz[ <i>a,h</i> ] anthracene	278	279, 275	0.9986	149	0.031	4.35
Benzo[ <i>ghi</i> ]perylene	276	138, 279	0.9970	146	0.040	5.60
<b>OCPs</b>						
α-BHC	181	183, 227	0.9997	139	0.017	13.72
Lindane	181	183, 219	0.9993	74	0.013	14.00
β-BHC	181	183, 219	0.9996	83	0.029	10.29
Heptachlor	227	181, 238	0.9991	113	0.030	1.90
Aldrin	272	274, 237	0.9996	105	0.059	2.01
Dieldrin	263	293, 265	0.9999	92	0.047	2.32
Endrin	235	246, 318	0.9999	98	0.033	1.93
Endosulfan	317	245, 263	0.9992	155	0.028	3.13
p,p'-DDD	207	195, 241	0.9989	67	0.028	2.28
p,p'-DDT	235	237, 165	0.9986	68	0.017	1.66
Endrin aldehyde	235	165, 176	0.9996	69	0.031	5.50
Methoxychlor	345	67, 281	0.9985	63	0.041	1.60

was as follows: initial temperature 50 °C, held for 2 min, then 10 °C min<sup>-1</sup> to 300 °C held for 3 min. PAHs and OCPs standards and samples were analyzed separately in selective ion monitoring (SIM) mode with a detector voltage of 1.5 kV. A scan range from 50 to 500 *m/z* was used. Ions were selected after injection of concentrated solution of compounds and recording the total ion chromatogram. The ions were divided into four groups that were recorded sequentially during the injection, on the basis of the retention times of the individual analytes. The highest abundant ion was selected as the quantitative ion; two other ions were used for confirmation of individual analytes (Table 1).

**Blank test:** Whole procedure blank tests were performed on organic-free water and for each analytical

method, to assess the presence of any contamination occurring from reagents and materials.

### 3. Results and discussion

#### 3.1. LPME method optimization

Parameters affecting the extraction efficiency (solvent selection, solvent size, phase ratio between donor solution and acceptor phase, extraction time, composition of donor and acceptor solutions) were investigated using Milli-Q water samples spiked with known concentrations of PAHs and OCPs. The goal was to optimize LPME experimental procedures so as to obtain high analyte recovery and enrichment factors. Both

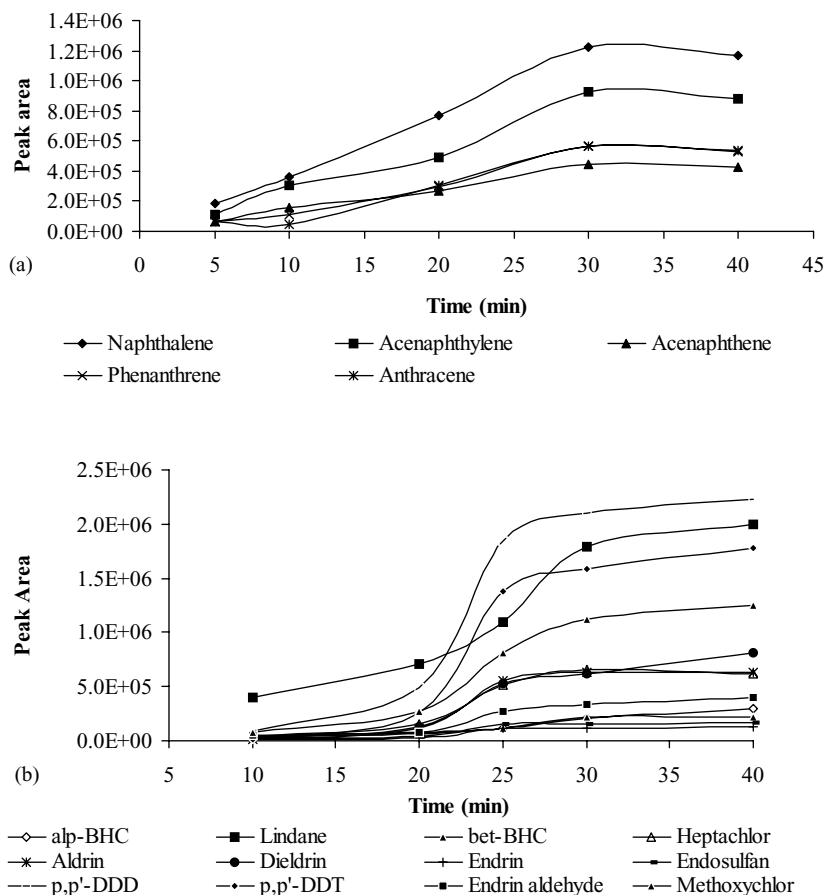


Fig. 2. Equilibrium profiles of (a) selected PAHs during liquid-phase microextraction at 80 ng ml<sup>-1</sup> of each analyte. The other PAHs behave similarly; (b) OCPs at 40 ng ml<sup>-1</sup> of each analyte.

enrichment factors and extraction recovery were determined by comparison of the GC response obtained from injection of acceptor solution after LPME and that from injection of standard solutions. Under the optimal extraction conditions, high extraction efficiency was achieved in a relatively short time as detailed in the following sections.

The salting-out effect was also examined in this study by varying the amount of sodium chloride added (10–30%, w/v (i.e. saturated NaCl)) to the aqueous solution containing the target analytes. The obtained results reveal that there was a slight gain in extraction efficiency with an increase in the ionic strength of the medium (i.e. salt concentration). This decrease in the solubility of the organic analytes in the presence of

dissolved NaCl is expected and has been observed by other workers [17,18].

The effect of pH on the extraction efficiency of PAHs and OCPs were evaluated in the pH range of 2–12 by adding 6M HCl and 10% (w/v) NaOH to the samples. There was no considerable impact on the extraction yield of OCPs while varying the sample pH. Therefore, the pH of rainwater, which is typically about 4.2 for the Singapore rainfall, was not adjusted. On the other hand, the extraction yield of PAHs was observed to change over the pH range studied and had a maximum value at pH 9. As a result, the pH of the rainwater samples was maintained at pH 9 for maximizing the extraction yield of PAHs (data not shown).

Table 2

LPME–GC–MS of PAHs and OCPs in spiked rainwater: recoveries and precision of analytical data

POPs	50 ng ml <sup>-1</sup> spiked		80 ng ml <sup>-1</sup> spiked	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
<b>PAHs</b>				
Naphthalene	79.04	7.76	101.97	1.28
Acenaphthylene	70.51	6.82	103.04	11.93
Acenaphthene	102.97	4.80	104.19	8.65
Fluorene	105.70	7.54	101.26	3.64
Phenanthrene	72.75	8.11	113.25	10.64
Anthracene	100.67	5.00	94.67	7.18
Fluoranthene	106.15	9.02	83.25	11.89
Pyrene	107.09	9.58	87.59	12.59
Benz[ <i>a</i> ]anthracene	101.89	3.19	99.29	4.82
Chrysene	85.73	2.64	93.60	4.45
Benzo[ <i>a</i> ]fluoranthene	96.63	8.36	105.18	4.20
Benzo[ <i>k</i> ] fluoranthene	104.35	8.83	102.33	5.91
Benzo[ <i>a</i> ]pyrene	114.30	5.39	114.67	12.55
Indenol[1,2,3- <i>cd</i> ]pyrene	101.93	6.14	97.08	3.30
Dibenz[ <i>a,h</i> ] anthacene	81.31	8.31	110.13	13.68
Benzo[ <i>ghi</i> ]perylene	94.13	10.24	103.71	5.34
<b>OCPs</b>				
α-BHC	86.14	5.02	106.86	7.86
Lindane	93.44	4.36	112.60	10.87
β-BHC	87.42	9.12	111.58	7.18
Heptachlor	89.62	11.11	98.34	9.60
Aldrin	79.32	5.02	98.86	7.50
Dieldrin	74.94	1.74	87.28	12.40
Endrin	85.62	13.80	93.13	4.03
Endosulfan	79.42	6.84	90.07	12.31
p,p'-DDD	84.98	7.64	108.41	9.95
p,p'-DDT	81.60	8.88	97.62	7.75
Endrin aldehyde	82.90	8.32	102.18	10.30
Methoxychlor	97.18	3.26	102.55	11.66

### 3.2. Extraction time

LPME involves a dynamic partitioning of the target compounds between the hollow fiber and the sample solution. The extraction efficiency depends on the mass transfer of analyte from the aqueous phase to the organic solvent phase [15,16]. Since mass transfer is a time-dependent process, the function of extraction time was examined in this study. The sample was continuously stirred at room temperature (23 °C) with a magnetic stirrer to facilitate the mass transfer process and to decrease the time required for the equilibrium to be established. The stirring speed was fixed at 700 rpm. At higher stirring speed, the amount of extracted analytes decreased due to the generation of air bubbles in the hollow fiber and the loss of the organic solvent.

An increase in the extraction time resulted in the higher enrichment of both PAHs and OCPs as shown in Fig. 2a and b. The improvement of extraction

efficiency was most significant from 10 to 25 min; further prolongation of extraction led to a smaller rise of recovery. The influence of extraction time was most significant for OCPs, which apparently permeated more slowly through the membrane than PAHs. No correlation was established between recovery and water solubility or the octanol/water coefficient. Most of the target compounds including four ring PAHs and OCPs attained equilibrium at about 30 min. However, acenaphthene, indeno[1,2,3-*cd*]pyrene, benzo[*k*]fluoranthene and dieldrin reached equilibrium after 30 min. On the basis of the results obtained, an extraction time of 35 min was selected for the extraction of PAHs and OCPs from real rainwater samples. At this extraction time, the plateau of equilibrium is reached, providing stability and constant extraction conditions for the samples. Although the extraction time was relatively long, a large number of samples may be extracted simultaneously due to the simplicity and the low cost of the hollow fiber.

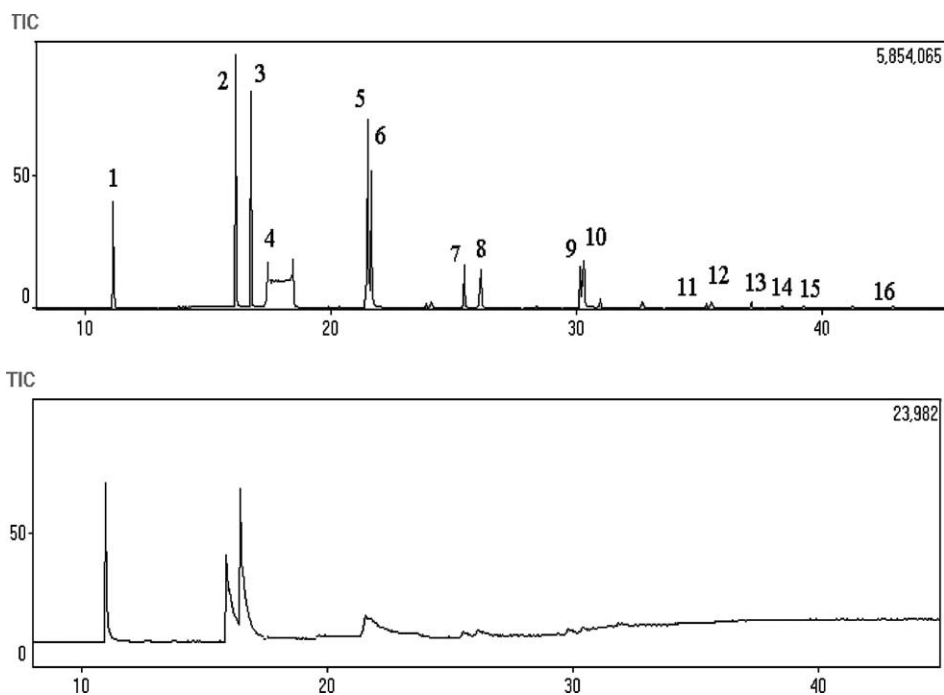


Fig. 3. Chromatogram of PAHs in (a) rainwater spiked with 80 ng ml<sup>-1</sup> of each analyte; (b) unspiked rainwater sample, after liquid-phase microextraction. (1) Naphthalene, (2) acenaphthylene, (3) acenaphthene, (4) fluorene, (5) phenanthrene, (6) anthracene, (7) fluoranthene, (8) pyrene, (9) benz[*a*]fluoranthene, (10) chrysene, (11) benzo[*a*]fluoranthene, (12) benzo[*k*]fluoranthene, (13) benzo[*a*]pyrene, (14) indeno[1,2,3-*cd*]pyrene, (15) dibenz[*a*]anthracene, (16) benzo[*ghi*]perylene.

### 3.3. Validation of the method

On the basis of the experiments discussed above, the optimal LPME conditions were toluene as the extraction solvent, an extraction time of 35 min at room temperature (23 °C), a stirring speed of 700 rpm, 30% NaCl, and pH 9 for PAHs (no pH adjustment for OCPs).

In order to evaluate the practical applicability of the LPME technique, ultrapure water samples (organics-free) were spiked with the PAHs and OCPs to give final sample concentrations of ranged between 0.5 and 100  $\mu\text{g l}^{-1}$ . Linearity, reproducibility, and the limits of detection under the optimal extraction conditions were investigated. Results of this series of experiments are summarized in Table 1. The GC peak area counts were plotted against the respective concentrations of PAHs and OCPs to generate calibration curves. The calibration gave a high level of linearity with a correlation coefficient ( $r^2$ ) between 0.9845

and 0.9999 for all analytes, except for naphthalene (0.9382). The excellent linearity obtained over an extended concentration range indicates that there were no capacity problems due to the acceptor phase saturation during LPME in this new set up. It should be noted that more than a 46-fold enrichment of organic micropollutants was achieved under the optimal extraction conditions, except for fluorene; enrichment is the ratio of the concentration of analytes in the sample extract to that in the original sample. Some analytes could be preconcentrated nearly 166-fold. The precision of the method was determined by performing five consecutive extractions under the same operating conditions. Overall, the reproducibility expressed as relative standard deviation (R.S.D.) was found to be satisfactory (ranging from 1.6 to 14% with a mean value of 7%). The limits of detection (LODs) for all target analytes at a signal-to-noise ratio of 3 using LPME were determined. The LODs ranged from 0.002 to 0.047  $\mu\text{g l}^{-1}$ . While determining the LOD,

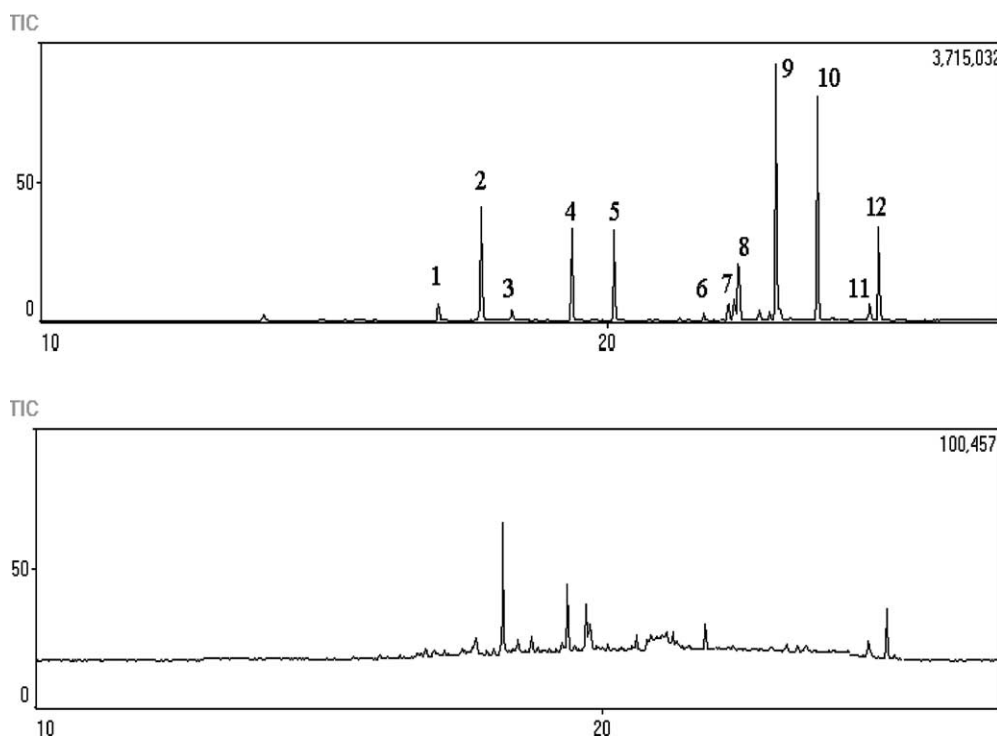


Fig. 4. Chromatogram of OCPs in (a) rainwater spiked with 40  $\text{ng ml}^{-1}$ ; (b) unspiked rainwater sample, after liquid-phase microextraction. (1)  $\alpha$ -BHC, (2) lindane, (3)  $\beta$ -BHC, (4) heptachlor, (5) aldrin, (6) dieldrin, (7) endrin, (8) endosulfan, (9) p,p'-DDD, (10) p,p'-DDT, (11) endrin aldehyde, (12) methoxychlor.



syringe blanks were carried out to confirm that no sample carryover occurred. The results show clearly that, under the present experimental conditions, LPME is a more sensitive technique than LLE [19].

Furthermore, the effect of concentration of PAHs and OCPs in the sample on recovery was studied. Since these organic pollutants are usually in the sub-ppb level concentration range in rainwater, the LPME method needs to be validated with a series of experiments at trace levels of the analytes. Extraction recoveries for the LPME procedures were evaluated using the standard addition method by analyzing test solutions prepared by spiking aliquots of real rainwater at the following two concentrations of PAHs and OCPs: 50 and 80  $\mu\text{g l}^{-1}$ . The results were

compared with extracts of ultrapure water spiked at the same concentrations. The recovery data are reported in Table 2 together with the relative standard deviations. No significant changes in recovery were observed over the concentration range. This means that, in the present context, the matrix has little effect on the analysis of samples. In other words, there was negligible irreversible adsorption or contamination during sample preparation. The R.S.D.s were calculated by analyzing five consecutive standard solutions at a fixed concentration for both classes of contaminants. The R.S.D.s of the recovery values usually increased with decreasing concentrations because of the increasing uncertainty of quantitative analysis in the sub-ppb range.

Table 3  
Concentrations ( $\mu\text{g l}^{-1}$ ) of PAHs and OCPs detected in rainwater samples using LPME–GC–MS

Analytes	Site 1 (19 October 2001)	Site 2 (29 October 2001)	Site 3 (19 November 2001)	Site 4 (30 November 2001)	Site 5 (27 December 2001)	Site 6 (09 January 2002)
<b>PAHs</b>						
Naphthalene	0.022	0.061	0.162	0.008	0.067	0.041
Acenaphthylene	0.044	0.005	0.007	0.014	0.005	0.005
Acenaphthene	0.022	0.008	0.029	0.004	0.007	0.024
Fluorene	0.080	0.057	0.054	0.068	0.064	0.059
Phenanthrene	0.021	0.013	0.012	0.006	0.013	0.006
Anthracene	0.041	0.009	0.013	0.012	0.012	0.011
Fluoranthene	0.027	0.005	0.005	0.010	0.014	0.026
Pyrene	0.049	0.008	0.008	0.017	0.006	0.005
Benz[ <i>a</i> ]anthracene	0.029	0.013	0.023	0.038	0.037	0.044
Chrysene	0.033	0.009	0.009	0.014	0.013	0.007
Benzo[ <i>a</i> ]fluoranthene	0.050	0.026	0.012	0.036	0.006	0.025
Benzo[ <i>k</i> ]fluoranthene	0.033	0.022	0.055	0.039	0.028	0.043
Benzo[ <i>a</i> ]pyrene	0.066	0.021	0.080	0.051	0.040	0.165
Indenol[1,2,3- <i>cd</i> ]pyrene	0.071	0.063	0.051	0.088	0.042	0.052
Dibenz[ <i>a,h</i> ]anthracene	0.036	0.039	0.055	0.036	0.044	0.039
Benzo[ <i>ghi</i> ]perylene	0.049	0.055	0.041	0.048	0.042	0.052
<b>OCPs</b>						
$\alpha$ -BHC	0.027	0.029	0.019	0.018	0.021	0.023
Lindane	nd	0.016	0.033	0.025	0.022	0.015
$\beta$ -BHC	0.030	0.031	0.054	0.032	0.029	0.060
Heptachlor	0.038	0.038	0.036	0.030	0.039	0.037
Aldrin	0.061	0.062	nd	0.060	0.063	nd
Dieldrin	0.055	0.049	0.050	0.053	0.057	0.049
Endrin	0.037	0.036	0.046	0.038	0.036	0.038
Endosulfan	0.041	0.031	nd	0.029	0.031	0.033
p,p'-DDD	nd	0.029	nd	0.035	nd	0.030
p,p'-DDT	0.022	0.032	0.019	0.021	0.033	0.021
Endrin aldehyde	nd	0.038	nd	0.039	0.043	nd
Methoxychlor	nd	nd	nd	0.050	0.045	nd

### 3.4. Application of the LPME method to real rainwater samples

The optimized LPME method was applied to the extraction of PAHs and OCPs in real rainwater samples collected in Singapore and the extracts analyzed by GC–MS.

Figs. 3 and 4 show typical chromatograms obtained from the analysis of real rainwater samples. The results obtained from the analysis are summarized in Table 3. The concentration of PAHs varied between 0.005 and 0.165  $\mu\text{g l}^{-1}$  and that of OCPs between non-detected and 0.063  $\mu\text{g l}^{-1}$ , respectively. Higher molecular weight PAHs (those with five and six benzene rings) are present in rainwater in relatively larger amounts (see Table 3), and this could be due to persistent nature of these compounds. In addition, these PAHs have relatively higher Henry's law constants (or low octanol–water coefficients) than the lighter ones and tend to be efficiently scavenged with high efficiency by cloud or rain droplets [20,21]. The PAHs are probably emitted from local sources involving incomplete combustion of fossil fuels such as urban vehicular traffic, chemical industries, and power plants. The pesticides measured in this study have been phased out in Singapore several years ago, and therefore, appear to have originated from long-range transport.

## 4. Conclusions

The potential of liquid-phase microextraction (LPME) has been demonstrated as a sample preparation technique prior to the GC–MS analysis of PAHs and OCPs in rainwater. LPME provided extracts with highly enriched analytes and excellent clean-up of micro organic pollutants. Good linearity, reproducibilities, and relative recoveries were also obtained. The use of disposable porous polypropylene hollow fibers as extraction units eliminated the possibility of carryover and the need of regeneration of the fiber. One disadvantage is that the extraction procedure cannot be easily automated. Nevertheless, the method is simple and cost-effective, and requires minimal solvent consumption. The rainwater samples analyzed

in this study contained significant amounts of PAHs and some OCPs. In view of the above-mentioned advantages over conventional analytical methods, the LPME in conjunction with the GC–MS analysis can be used as a routine tool for the assessment of organic micropollutants such as PAHs and OCPs in rainwater. Work is in progress to further develop and use LPME in combination with GC–MS, HPLC, and CE for other classes of organic pollutants present in atmospheric water droplets at trace levels.

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