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Journal of Chromatography A, 1033 (2004) 213–220
JOURNAL OF CHROMATOGRAPHY A
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Development and application of polymer-coated hollow fiber membrane microextraction to the determination of organochlorine pesticides in water

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Received 3 September 2003; received in revised form 2 December 2003; accepted 23 January 2004

Abstract

A novel extraction procedure coupled with gas chromatography–mass spectrometric detection for quantification of organochlorine pesticides (OCPs) in water is described. Amphiphilic polyhydroxylated polyparaphenylene (PH-PPP) was synthesized and coated on the surfaces of a porous polypropylene hollow fiber membrane (HFM). Due to the high porosity of the HFM, maximum active surface area to achieve high extraction efficiency is expected. The polymer-coated HFM was used for the extraction of 15 OCPs from water. The extraction efficiency was compared with emerging and established methods such as liquid-phase microextraction (LPME), solid-phase microextraction (SPME) and stir bar sorptive extraction (SBSE) techniques. We term the current procedure as polymer-coated hollow fiber microextraction (PC-HFME). PC-HFME showed good selectivity and sensitivity. Detection limits for OCPs were in the range of 0.001–0.008 $\mu g\,l^{-1}$. The sensitivity and selectivity of the coated HFM could be adjusted by changing the characteristics of the coated PH-PPP film.

Keywords: Water analysis; Hollow fiber membrane; Extraction methods; Pesticides; Organochlorine compounds

1. Introduction

Solid-phase microextraction (SPME), a solvent-free extraction procedure, possesses several advantages over conventional liquid–liquid extraction (LLE) due to its intrinsic simplicity [1–3]. It can achieve low detection limits and has acceptable reproducibility [4–7]. SPME is normally used in conjunction with gas chromatography [8] in which analytes are thermally desorbed in the heated injector of a gas chromatograph. SPME–liquid chromatography (LC) is also possible, provided a suitable interface that permits solvent elution of the analytes is available [9]. SPME is increasingly being used for pesticide residue analysis [10,11]. However, it has a few drawbacks, such as limited lifetime and linear range, fragility of the fibers, sample carryover and relatively expensive fibers and fiber assembly holder [12]. Recently, Sandra and co-workers developed a new extraction technique based on the same extraction principles as SPME [13] but the sorbent, which is polydimethylsiloxane (PDMS), is coated on a stir bar. This technique is known as stir bar sorptive extraction (SBSE) and the coated stir bars are commercialized under the name of Twister. However, in this technique, only PDMS-coated stir bars are available and the stirring bead is always placed at the bottom of the flask. Moreover, usage of the same coated stir bar in repeated experiments may also have potential sample carryover problems.

Solvent-minimized liquid-phase microextraction (LPME) is considered an emerging alternative to SPME or SBSE and, in some instances, incorporates the use of porous hollow fiber membrane (HFM) to support the solvent during extraction. Various organic compounds such as organochlorine pesticides (OCPs) [14], polycyclic hydrocarbons [15], drugs [16], polychlorinated biphenyls [17] and amino alcohols [18] can be extracted satisfactorily using HFM-supported LPME, in which a few microliters of the extracting organic solvent is protected inside the HFM. The detection limits of HFM-LPME for many compounds are comparable to those of SPME and superior to those of LLE [19].

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doi:10.1016/j.chroma.2004.01.050

We propose here a simple and inexpensive extraction technique which involves a coupling of HFM with SPME and SBSE technology. In this novel procedure, a short length of HFM (ca. 1.2 cm) is coated with a functional polymer, polyhydroxylated polyparaphenylene (PH-PPP) that represents the adsorbent and placed in an aqueous sample solution for extraction and enrichment of the analytes. In contrast to SPME or SBSE, the extraction device is free-moving and tumbles continuously throughout the stirred sample solution during extraction to enhance the extraction efficiency. The key features are the low cost and disposability of the coated fibers to remove sample carryover problems without compromising the extraction efficiency. We report here the development and optimization of the new procedure, named as polymer-coated hollow fiber microextraction (PC-HFME), and describe its application towards the extraction of OCPs from seawater.

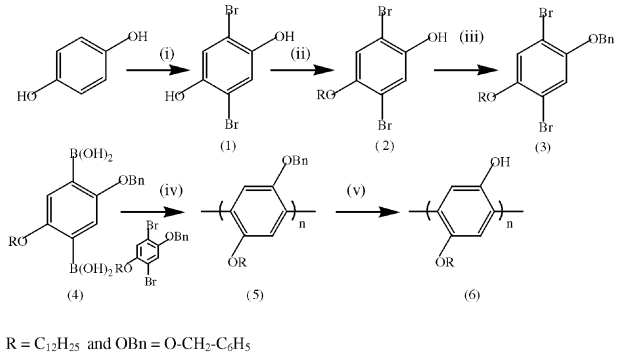
2. Experimental

2.1. Chemicals and reagents

All pesticides used were purchased from Polyscience (Niles, IL, USA). Phenanthrene-d10 and pyrene-d10, used as internal standards (I.S.), were obtained from Aldrich (Milwaukee, WI, USA). HPLC-grade solvents were purchased from BDH (Dorset, UK). The water used was purified using a Milli-Q (Millipore, Bedford, MA, USA) water purification system. Each pesticide was dissolved in hexane to obtain a standard stock solution at a concentration of $1\,g\,l^{-1}$ and they were stored at 4 °C. A fresh standard solution (containing $10.0\,mg\,l^{-1}$ of each of the 15 pesticides) were prepared in hexane every week and stored at 4 °C. Q3/2 Accurel polypropylene hollow fiber membrane was purchased from Membrana GmbH (Wuppertal, Germany). The specifications of the hollow fiber are as follows: inner diameter 600 μm, wall thickness 200 μm and pore size 0.2 μm. Length of HFM used for extraction was 1.2 cm. An artificial seawater sample using natural sea salt (Coral Reef Red Sea salt, obtained from Red Sea Fish Pharm (P), Eilat, Israel) dissolved in deionized water to a salinity of 3%, conductivity 49.8 mS and pH 8.25, was prepared for the matrix effect experiments. The SPME fiber holder and fiber assemblies for manual sampling were purchased from Supelco (Bellefonte, PA, USA) and used without modification. Polydimethylsiloxane–divinylbenzene (PDMS–DVB, 65 μm)-coated fibers from Supelco were used for OCP extraction in the comparative studies and Chrompack crimper vials (Palo Alto, CA USA) were used for chemical desorption by ultrasonication.

2.2. Instrumentation

Sample analyses were carried out using a Shimadzu (Tokyo, Japan) QP2010 gas chromatography–mass spectrometry (GC–MS) system equipped with a Shimadzu AOC-20i autosampler and a DB-5 fused silica capillary column 30 m × 0.32 mm i.d., film thickness 0.25 μm (J&W Scientific, Folsom, CA, USA). Helium was used as the carrier gas at a flow rate of $1.5\,ml\,min^{-1}$ and a split ratio of 20. Samples (2 μl) were injected in splitless mode with an injection time of 2 min. The injection temperature was set at 250 °C, and the interface temperature at 280 °C. The GC–MS temperature program used was as follows: initial temperature 50 °C, held for 2 min, then increased by $10\,°C\,min^{-1}$ to 300 °C and held for 3 min. OCP standards and samples were analyzed in selective ion monitoring (SIM) mode with a detector voltage of 1.5 kV and a scan range of *m*/*z* 50–500.



R = $C_{12}H_{25}$ and OBn = O-CH_2-C_6H_5

Scheme 1. Synthetic scheme for PH-PPP.

In all cases, control experiments were performed on organic-free water to assess the presence of any contamination occurring from reagents, coated polymers and fibers.

2.3. Synthetic strategy of the polyhydroxylated polyparaphenylene

The functional polymer was synthesized according to the reported procedure [20]. Scheme 1 describes the synthesis of the monomers and functionalized PPP. The polymerization between the monomers 3 and 4 were performed under optimized Suzuki coupling conditions [20]. The obtained polymer was treated with 10% Pd/C for debenzylation and the polymer 6 was purified by precipitation from methanol. The polymer was only soluble in tetrahydrofuran, chloroform, toluene, dichloromethane and dimethylformamide.

2.4. Preparation and characterization of the polyhydroxylated polyparaphenylene-coated HFM

The commercially available hollow fibers were cut into ∼1.2 cm lengths and soaked in the PH-PPP solution (toluene) within the concentration range of $0.25–1\,g\,l^{-1}$ and kept at room temperature for 1 day. The fibers were then removed and dried in air to evaporate the solvent completely. Compared with commercial SPME fibers, the porosity of the coated HFM affords a large surface area, allowing high extraction efficiency. In the attenuated total

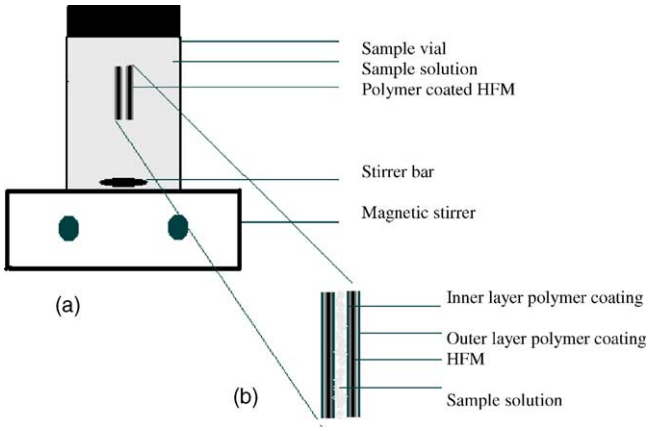


Fig. 1. Schematic diagram of PC-HFME (a) and enlarged view of HFM (b).

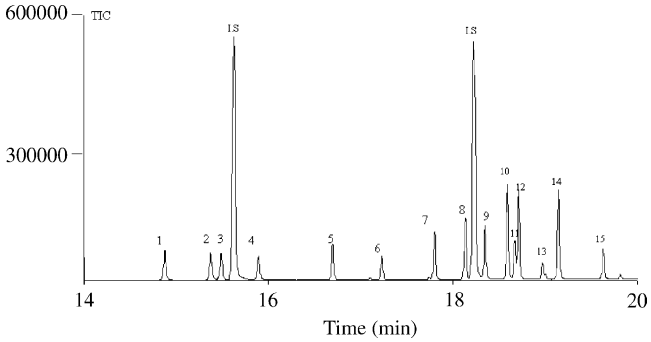


Fig. 2. Total ion chromatogram of OCPs after PC-HFME of spiked seawater. Sample spiked at 5 μg l^{-1} of each OCP and 50 μg l^{-1} of internal standard (I.S.). Peak identification: (1) α-HCH; (2) β-HCH; (3) γ-HCH; (4) δ-HCH; (I.S.) phenanthrene-d10; (5) heptachlor; (6) aldrin; (7) heptachlor epoxide; (8) α-chlordane; (I.S.) pyrene-d10; (9) β-chlordane; (10) *p,p′*-DDE; (11) dieldrin; (12) *p,p′*-DDD; (13) endrin; (14) *p,p′*-DDT; (15) endosulfan sulfate.

reflection Fourier transform infrared spectrum, appearance of a peak at 3378 cm^{-1} corresponds to the –OH stretching vibration of the PH-PPP, indicating the presence of a thin polymer coating on the fiber surface. By varying the polymer concentration in the coating solution, the thickness of the polymeric film on HFM could be controlled. Although not studied in the present work, it is possible to tune the selectivity of the active extraction medium by changing the functional groups on PH-PPP.

2.5. PC-HFME methodology

The PC-HFME experimental setup is shown in Fig. 1(a). A polymer-coated HFM was placed in a 4 ml sample vial containing analytes and the sample solution was agitated at (1000 rpm) for 30 min on a Vibramax 100 (Heidolph, Kelheim, Germany) magnetic stirrer. The agitation and the amphiphilic polymer coating aided the immersion and movement of the fiber in the aqueous sample solution. The fiber was then removed with a pair of tweezers. The extracted analytes on the fiber were desorbed in 100 μl of hexane (the coated polymer is insoluble in hexane) in a crimper vial via sonication for 10 min. The fiber was then removed and discarded, the hexane evaporated to dryness with a gentle stream of nitrogen gas and reconstituted to 20 μl with the same solvent. Finally, 2 μl of the reconstituted extract was injected into the GC–MS. A representative total ion chromatogram of an extract from spiked water (at 5 μg l^{-1} of each OCP) using PC-HFME is shown in Fig. 2.

3. Results and discussion

The disposable PC-HFME device is schematically illustrated in Fig. 1(b). PC-HFME is an equilibrium-based extraction procedure operating with the principle of partitioning organic analytes between the aqueous sample and the polymer coating on the fiber surface [13,21–23]. The large coated surface area of the highly porous HFM is expected to enhance the extraction efficiency. The analytical factors affecting extraction efficiency such as thickness of polymer coating, sample pH, ionic strength, selection of suitable desorption time and desorption solvent were optimized.

During desorption more than 90% of all OCPs were desorbed in the first attempt. Since the length (1.2 cm) of the HFM used is short and only a small amount of active polymer is needed for coating, the fiber can be considered disposable; little is gained from having to regenerate, recondition and reuse the fiber. The low cost of the fiber is another advantage. Thus, the extraction device is considered for single-use only and sample carryover effects are not an issue in this technique.

3.1. Extraction mechanism of OCPs using PH-PPP-coated HFM

The asymmetrically functionalized polymer used here has an amphiphilic character and electron rich backbone [20]. One side of the polymer backbone is incorporated with long alkyl chains (R = $C_{12}H_{25}$) and the other side with phenolic –OH groups. When the polymer is coated on the HFM, it is anticipated that alkyl chains of the polymer interact with the non-polar HFM surface through hydrophobic interactions. The high extraction efficiency for OCPs observed in our experiments may be due to the electrostatic interaction between the electron rich polymer backbone and the electron deficient OCPs.

3.2. Selection of PH-PPP coating concentrations

The selectivity of PC-HFME can be fine-tuned by using appropriate coatings on the porous HFM. Fig. 3 shows the effect of different concentrations of PPP solutions used for coating the HFM for OCP extractions. It is conceivable that more active polymer present on the porous membrane will facilitate better extraction. However, a thick film may

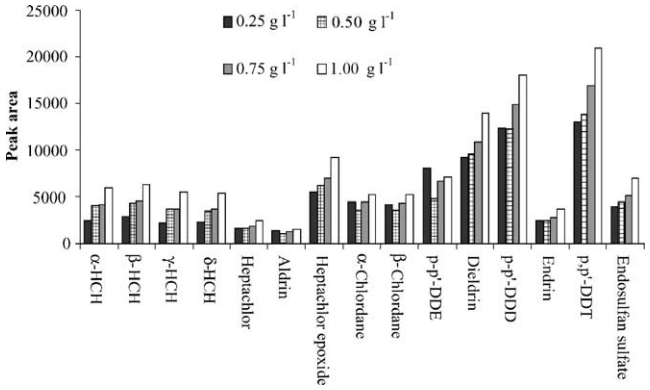


Fig. 3. Effect of different concentrations of PH-PPP solution used to coat HFM, on OCP extraction over 30 min extraction time.

reduce the extraction efficiency due to low diffusion rate of the analyte in the polymer membrane. Therefore, an optimum coating concentration (or thickness of the film) should be selected to provide higher extraction yields for the target analytes. From our experiments, all analytes were extracted efficiently when a polymeric solution at $1\,g\,l^{-1}$ concentration was used to coat the HFM. PH-PPP was not soluble in toluene at a concentration $>1\,g\,l^{-1}$.

3.3. Extraction time

As mentioned earlier, PC-HFME is an equilibrium extraction procedure. The amount of analyte extracted depends on the partition coefficient or the rate of mass transfer process at the interface of the aqueous phase (i.e. sample) and polymeric phase (i.e. coating). In our experiment, the extraction equilibrium was established within the range of 5–40 min at room temperature (23 °C) with constant stirring (1000 rpm). The amount of compounds extracted (area of GC signals) generally increased with extraction time up to 30 min (see Fig. 4) and no significant improvement thereafter. Thus, an optimum extraction time of 30 min was selected for all our experiments.

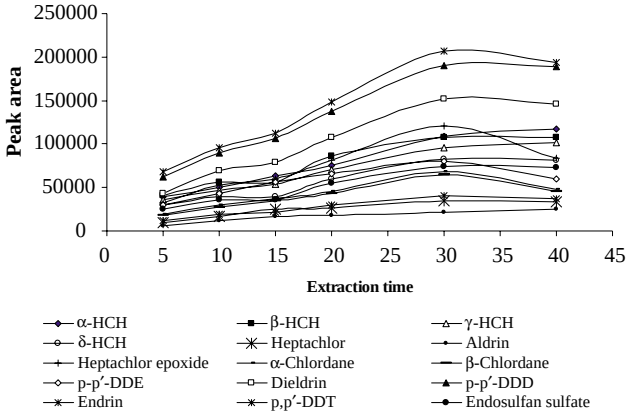


Fig. 4. Extraction time profile with respect to HFM coated with $1\,g\,l^{-1}$ of PPP solution.

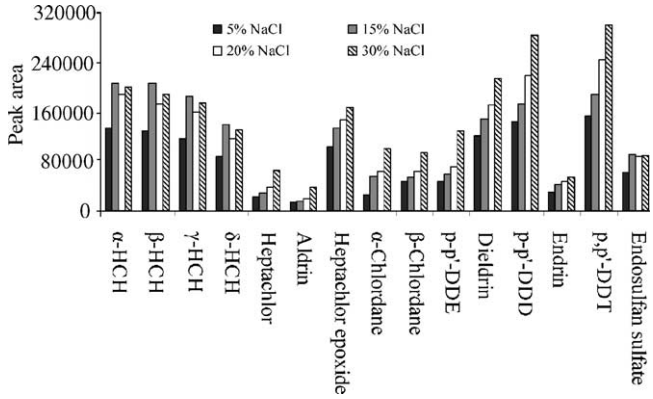


Fig. 5. Effect of NaCl in sample solution on PC-HFME.

3.4. Effect of ionic strength

For many analytes, aqueous solubility decreases with increasing ionic strength, and thus an enhancement of their extraction from the aqueous solution is observed [24]. The influence of salt on the extraction efficiency of pesticides using PC-HFME was investigated by adding various amounts of NaCl (ranging from 5 to 30% (w/v). Fig. 5 shows the extraction efficiency, with respect to the NaCl concentrations and reveals that the addition of NaCl increases the extraction efficiency of the OCPs. An optimum value of 30% salt concentration was used for all our extractions, based on the results given in this figure.

3.5. Effect of pH

The effect of sample pH was also evaluated and the results are shown in Fig. 6. The pH of the sample solution had a minor effect on the extraction efficiency. Better extraction of OCPs such as heptachlor (HCH), heptachlor epoxide, dieldrin, α-HCH and β-HCH was observed at pH 10. *p,p′*-DDT, *p,p′*-DDD, and endrin had lower responses beyond a pH value of 10. At pH higher than 7, it is expected that the polymeric –OH groups are ionized to the anionic form, thereby

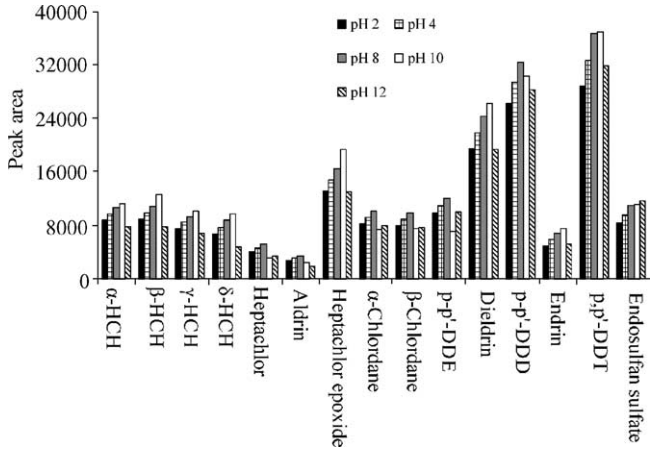


Fig. 6. Effect of sample solution pH on PC-HFME.

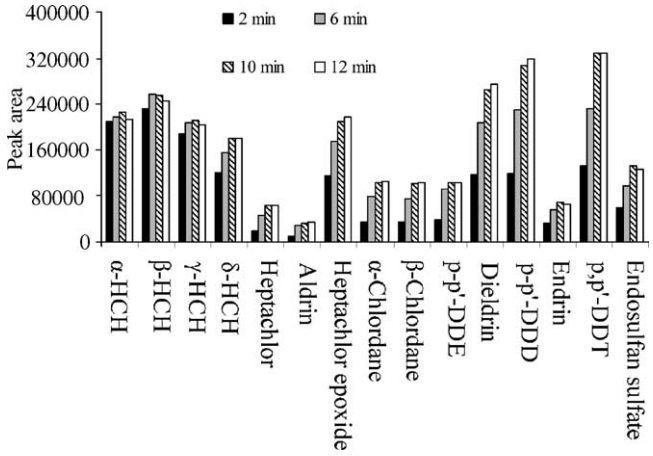


Fig. 7. Desorption profile of OCPs using different sonication times.

increasing the affinity towards the analytes. On the basis of these results, a sample pH of 10 was selected as optimum.

3.6. Desorption time

After the extraction was complete, the analyte-enriched HFM was sonicated in hexane. Sonication time was significantly shorter than the extraction time. Due to strong interaction between PH-PPP and HFM surface and the insolubility of PH-PPP in hexane, the polymer coating was not desorbed during the sonication step. The desorption time profile for all analytes was studied using sonication times from 1 to 12 min. Based on Fig. 7, which shows the profiles at different desorption times; 10 min desorption time appears to be optimum for all analytes.

3.7. Desorption solvent

Various organic solvents were investigated to desorbs the analytes from the coated HFM. In SBSE and SPME, when coupled with liquid-based analytical methods (e.g. LC), analytes are desorbed with organic solvents [25]. In PC-HFME, various organic solvents were tested to assess their suitability. In these experiments, the HFM was placed in a 0.15 ml conical insert of a crimp top vial filled with 100 μl of the organic solvent. Two factors should be considered while selecting a good solvent for desorption studies: (i) the polymeric layer must be insoluble in the solvent; and (ii) analytes should be soluble in the selected solvent. On the basis of these considerations, hexane, 2-propanol, nonane, methanol and acetone were investigated as potential desorption media. As Fig. 8 shows, hexane afforded a higher efficiency for most of the OCPs and was thus selected.

3.8. Optimized extraction conditions

The goal was to optimize PC-HFME experimental procedures so as to obtain high analyte recovery and low detection limits. Under the optimum extraction conditions, high extraction efficiency was achieved in a relatively short time. On the basis of the experiments discussed earlier, the PC-HFME conditions include 1.2 cm of HFM coated with 1 g l^{-1} of PH-PPP in toluene used for 30 min extraction at room temperature (23 °C) in 30% NaCl, and at pH 10. Extracted OCPs in HFM was desorbed via sonication in 100 μl of hexane for 10 min. Hexane was preconcentrated with nitrogen gas and reconstituted to 20 μl.

3.9. Linearity, limits of detection, and repeatability

To evaluate PC-HFME, OCPs from aqueous standard solutions at a concentration range of 1–750 μg l^{-1} were extracted. All OCPs exhibited good linearity with correlation coefficients (r) of 0.9793–0.9990 (Table 1). This allowed the quantification of these compounds by the method of external standardization. Limits of detection (LODs) of the OCPs, calculated based on the signal to noise (S/N) ratio of 3 in GC–MS–SIM measurements, were in the range of

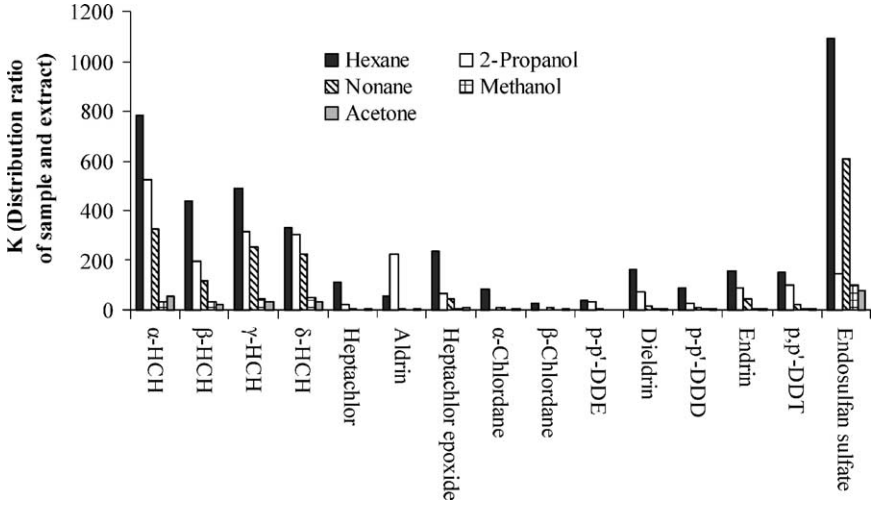


Fig. 8. Desorption profile of OCP at different solvents.

Table 1
PC-HFME: linearity range, limits of detection and precision

OCP	Linearity range ($\mu g\,l^{-1}$)	Coefficient of correlation (r)	Calibration curve	R.S.D. (%, $n = 4$)	Limit of detection ($\mu g\,l^{-1}$)
α-HCH	1–750	0.9883	$y = 384.98x + 4820.7$	6.6	0.001
β-HCH	1–750	0.9984	$y = 569.02x - 5325.2$	5.5	0.005
γ-HCH	1–750	0.9972	$y = 413.01x + 425.21$	6.5	0.003
δ-HCH	1–750	0.9972	$y = 458.73x - 6168.8$	5.5	0.002
Heptachlor	1–750	0.9981	$y = 211.92x - 1895.4$	7.4	0.007
Aldrin	1–750	0.9990	$y = 115.23x + 649.5$	8.6	0.006
Heptachlor epoxide	1–750	0.9981	$y = 420.22x + 7326.3$	5.1	0.002
α-Chlordane	1–750	0.9793	$y = 1329.3x - 45605$	7.2	0.002
β-Chlordane	1–750	0.9856	$y = 346.61x + 3612.8$	7.0	0.003
p,p′-DDE	1–750	0.9947	$y = 509.42x + 564.31$	10.6	0.001
Dieldrin	1–750	0.9974	$y = 653.6x + 8013.4$	5.7	0.001
p,p′-DDD	1–750	0.9956	$y = 842.64x + 19875$	7.4	0.001
Endrin	1–750	0.9973	$y = 155.56x + 3538.2$	4.7	0.008
p,p′-DDT	1–750	0.9929	$y = 1373.9x - 557.12$	7.4	0.001
Endosulfan sulfate	1–750	0.9955	$y = 447.53x - 5275.9$	5.0	0.003

0.001–0.008 $\mu g\,l^{-1}$. We obtained superior LODs for these OCPs than those values of the US Environmental Protection Agency Methods 508 and 625 [26,27]. These are also comparable to the LODs obtained for similar compounds in our previous SPME study [29]. The reproducibility studies were performed by extracting aqueous sample spiked at 10 $\mu g\,l^{-1}$ of each compound (four replicates). The relative standard deviations (R.S.D.) were in the range of 4.7–10.6%.

3.9.1. Comparison between PC-HFME, SPME and LPME

PC-HFME was used to extract OCPs from seawater samples, using the previously determined optimum extraction conditions. Artificial seawater samples were fortified with pesticide standards at 5 and 20 $\mu g\,l^{-1}$ to assess matrix effects. Since PC-HFME is a non-exhaustive extraction procedure, the relative recovery, which is defined as the ratio of GC peak areas for the analytes in the spiked seawater extracts to the spiked ultrapure water extract, was considered [28]. Artificial seawater samples (at spiking concentrations of 20 $\mu g\,l^{-1}$ of each OCP) were employed for performing SPME and LPME supported by HFM for comparison of relative recoveries and precision. The optimum extraction conditions of these methods have already been described in our previous studies [29,14]. It should be noted that all these procedures involved stirring of the sample solutions at the respective optimum rates determined in these studies. As seen from Table 2, PC-HFME and SPME gave comparable precision, with R.S.D. ranging from 1.9 to 11.6% for 30 min extractions. They gave better results than LPME supported by HFM. These results demonstrate that artificial seawater matrices had little effect on the efficiency of PC-HFME. The distribution ratio (K_D) of OCPs in the sample and the respective extracts after PC-HFME, SPME and LPME were also calculated. Fig. 9 shows the high K_D of PC-HFME over SPME and LPME.

Table 2
Relative recoveries and precision of PC-HFME, SPME and LPME

OCP	PC-HFME				SPME		LPME	
	Recovery (%, 5 $\mu g\,l^{-1}$)	R.S.D. (%)	Recovery (%, 20 $\mu g\,l^{-1}$)	R.S.D. (%)	Recovery (%, 20 $\mu g\,l^{-1}$)	R.S.D. (%)	Recovery (%, 20 $\mu g\,l^{-1}$)	R.S.D. (%)
α-HCH	106.3	11.5	85.0	5.2	89.1	7.6	89.0	7.5
β-HCH	101.1	1.9	100.5	4.4	87.0	8.7	76.1	12.0
γ-HCH	108.3	7.4	90.0	5.1	88.8	7.5	71.8	13.4
δ-HCH	105.4	3.5	107.5	4.5	87.4	8.1	81.0	15.9
Heptachlor	104.9	9.2	83.2	5.4	93.4	9.0	81.0	8.4
Aldrin	94.9	8.4	84.3	6.9	103.4	8.7	91.0	10.7
Heptachlor epoxide	95.5	9.2	97.6	4.1	90.4	10.6	88.6	16.8
α-Chlordane	95.6	11.6	109.0	6.2	96.6	10.5	103.2	15.9
β-Chlordane	94.8	10.8	99.5	5.8	97.6	9.5	102.3	9.5
p,p′-DDE	94.3	3.3	107.1	8.5	108.1	11.3	95.3	11.5
Dieldrin	85.3	10.5	101.4	4.3	91.6	9.4	97.1	12.8
p,p′-DDD	89.1	10.7	104.3	6.1	97.0	7.4	109.1	9.1
Endrin	92.2	6.1	105.5	5.0	85.9	8.5	95.5	7.2
p,p'-DDT	91.9	9.5	106.4	6.1	97.8	6.7	110.4	11.4
Endosulfan sulfate	92.3	4.8	115.5	5.2	90.0	6.6	102.2	8.9

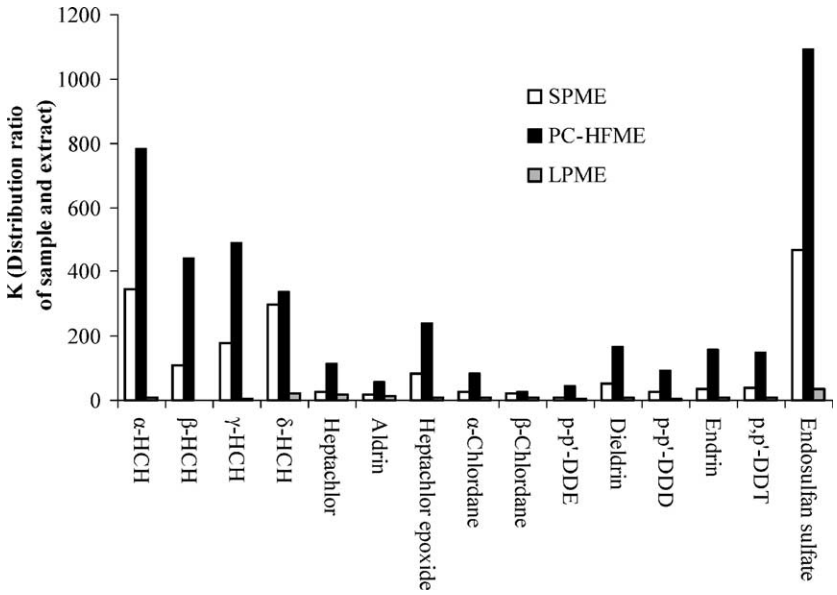


Fig. 9. Comparison between PC-HFME, SPME and LPME.

3.9.2. Real water analysis

As an example of the applicability of PC-HFME, coastal seawater samples collected from selected sites along the Straits of Singapore were analyzed. Concentrations of OCPs extracted from various samples using PC-HFME are given in Table 3. The pesticides measured in this study have been phased out in Singapore several years ago, and therefore appear to have originated from long-range atmospheric transport and agricultural runoff from neighboring countries. Fig. 10 shows a typical chromatogram generated from seawater sample after extraction by PC-HFME followed by GC–MS analysis.

Table 3
Concentration of OCPs in Singapore coastal seawater after analysis using PC-HFME and GC–MS

OCP	Mean concentration of OCPs in $\mu g\,l^{-1}$ ($n = 3$)			
	World Trade Center	Jurong Island	East Coast Park	West Coast Park
α-HCH	0.02	0.05	0.03	0.09
β-HCH	–[a]	2.01	0.01	0.02
γ-HCH	0.01	0.18	0.04	0.19
δ-HCH	0.01	0.05	0.04	0.03
Heptachlor	0.02	0.07	0.01	0.04
Aldrin	–	0.01	0.01	0.02
Heptachlor epoxide	–	–	0.01	–
α-Chlordane	–	–	0.01	–
β-Chlordane	–	–	0.01	–
p,p′-DDE	–	–	–	–
Dieldrin	0.04	0.04	0.01	0.10
p,p′-DDD	–	–	–	0.01
Endrin	0.14	0.46	0.21	1.66
p,p′-DDT	–	–	0.01	0.01
Endosulfan sulfate	0.02	0.03	0.03	0.02

[a] Below limit of quantification.

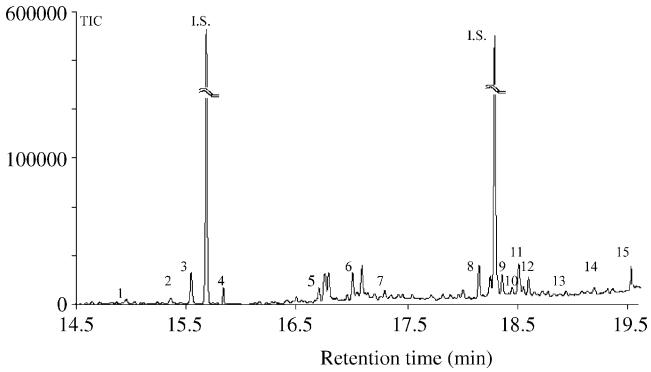


Fig. 10. GC–MS analysis of extract of typical real water sample after PC-HFME (peak identification as in Fig. 4).

4. Conclusion

This paper demonstrates the successful development and application of a novel extraction method named polymer-coated hollow fiber microextraction in combination with GC–MS analysis, for the analysis of OCPs from aqueous samples. The method exhibits good precision, reproducibility and linear response over a wide concentration range. The extraction device involves a hollow fiber membrane (1.2 cm in length) coated with a functionalized polyhydroxylated polyparaphenylene. It is allowed to tumble freely in the sample solution to enhance the extraction efficiency. Compared with SPME, higher enrichment factors were obtained under optimized extraction conditions determined in the present study. The newly developed microextraction procedure can achieve LODs in the range of 0.001–0.008 $\mu g\,l^{-1}$, exceeding the requirement for the analysis of OCPs in aqueous samples. One disadvantage is that the extraction procedure cannot be easily automated.

The need to evaporate the extract to dryness and then reconstituting it to ensure quantitative accuracy and precision may also be considered a drawback, especially when more volatile analytes are involved. Nevertheless, the method is rapid and easy to use for the qualitative and quantitative determination of OCPs. PC-HFME is compatible with established analytical techniques such as liquid chromatography and, possibly, capillary electrophoresis, and can potentially be tailored to any class of analytes of interest by selecting suitable functional polymers for coating the hollow fiber membrane. Unlike commercially available adsorbents, which are limited in variety, functional polymers used as coatings can be specially designed and synthesized in-house. It should be noted that PH-PPP is amphiphilic; we are currently studying the possibility of using it as an adsorbent to extract more polar compounds by PC-HFME.

Acknowledgements

The authors gratefully acknowledge the financial support of this research by the Agency for Science, Technology and Research of Singapore and the National University of Singapore.

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