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Determination of organochlorine pesticides and their metabolites in radish after headspace solid-phase microextraction using calix[4]arene fiber

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Abstract

A novel laboratory-made sol–gel calix[4]arene/hydroxy-terminated silicone oil coated fiber has been applied for headspace solid-phase microextraction (HS-SPME) combined with gas chromatography (GC) with electron capture detection (ECD) to determine 12 organochlorine pesticides (OCPs) and their metabolites in radish sample. The analytes in the study consisted of α-, β-, γ- and δ-hexachlorocyclohexane (BHC), 1,1,1-trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane (*o*,*p*′-DDT), 1,1,1-trichloro-2,2-*bis*(4-chlorophenyl)ethane (*p*,*p*′-DDT), 2,4-dichlorobenzophenone (*o*,*p*′-DBP), 4,4-dichlorobenzophenone (*p*,*p*′-DBP), 1,1-dichloro-2,2-*bis*(4-chlorophenyl)ethylene (*p*,*p*′-DDE), *bis*(4-chlorophenyl)methane (*p*,*p*′-DDM), 1,1-dichloro-2,2-*bis*(4-chlorophenyl)ethane (*p*,*p*′-DDD) and endrin. The following parameters were adjusted to optimize HS-SPME in order to obtain the maximum sensitivity: extraction temperature, extraction time, the addition of salt, desorption temperature and time. Especially, the effect of the complex radish matrix on quantitative extraction of pesticides was discussed in detail. Detection limits of the developed method for radish matrices were below 174 ng/kg for all pesticides. Relative standard deviations for quintuplicate analyses of radish samples fortified each analytes were not higher than 13.1%. The results demonstrate the suitability of the HS-SPME/GC–ECD approach for the analysis of multi-residue OCPs and metabolites in radish.

Keywords: Solid-phase microextraction; Calixarene; Organochlorine pesticides; Radish; Food analysis

1. Introduction

Organochlorine pesticides (OCPs) are known to be one of the most persistent organic micropollutants present in the environment and tend to accumulate in organisms [1]. At one time, they had been widely applied in agriculture, either directly to soil or sprayed over crop fields. The pesticides can enter the crop through the soil and water. Determination of pesticide residue amounts in foodstuff at trace levels, i.e. ng/g is difficult and extremely complex, since the OCPs have to be accurately separated from food. Traditionally the determination of OCPs in foodstuff usually comprises three steps: extraction, clean-up and chromatographic analysis, it is time consuming and labor intensive, and requires large volumes of sample and solvents (e.g. liquid–liquid extraction).

SPME is a solventless extraction procedure that does not require complex instrumentation, and allows the extraction and concentration to be focused in a single step. It consists in the immersion of a silica fiber coated with a stationary phase in the aqueous sample (for non-volatile compounds) or "headspace" located above the sample (for volatile compounds). In these extraction techniques, developed by Pawliszyn and co-workers [2], the analytes are sorbed directly from an aqueous or gaseous phase onto the fiber and later are thermally desorbed in the injector of the GC and transferred to the capillary column. SPME has been used for many applications, such as determinations of drugs in biological fluids,

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organic contaminants in soils, hydrocarbons in surface water and wastewater, caffeine in beverages and volatile organic compounds in water. Pesticides have also been determined by SPME in different matrices like wine [3], fruits [4,5], soils [6], honey [7,8], tea [9] and milk [10]. They often select, as specified by the manufacturer for chlorinated pesticides, an SPME fiber coated with a 100 μm polydimethylsiloxane (PDMS) layer for the analysis of chlorinated pesticides [11].

The sol–gel-coated 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxy-26,28-dihydroxycalix[4]arene/hydroxy-terminated silicone oil coated SPME fiber (C[4]/OH-TSO) was first prepared previously in our laboratory [12–14]. The new fiber shows high sensitivity and selectivity to benzene derivatives (BTEX), polycyclic aromatic hydrocarbons (PAHs), aromatic amines, phthalic acid esters (phthalates, PAEs) and chlorophenols. In addition, owing to the characteristics provided by sol–gel technology, the coating has high thermal stability (380 °C) and solvent stability (organic and inorganic) as well as a longer lifetime.

In this work we present an application of the HS-SPME/GC–ECD for the analysis of 12 OCPs and their metabolites residues in radish using C[4]/OH-TSO fiber, and investigated the radish matrix influence, addition of salt, as well as the effect of other important experimental parameters like adsorption–desorption temperature and time. Finally, we have checked the applicability of the proposed method to the analytical determination of these pesticides in radish samples and determined the detection limits and the reproducibility.

2. Experimental

2.1. Reagents and preparation of radish sample

The individual OCPs standards (1 mg/ml) were purchased from National Standard Material Center (Beijing, People's Republic of China). In the studies, the detector responses for these pesticides varied widely and the concentrations of the standard working solution mixture were adjusted accordingly. The standard working solution mixture was prepared in methanol from 12 organochlorine pesticides, including α-BHC, γ-BHC, *p*,*p*′-DDE (0.2 μg/ml); 2,4-dichlorobenzophenone (*o*,*p*′-DBP), 4,4-dichlorobenzophenone (*p*,*p*′-DBP), *p*,*p*′-DDD, *o*,*p*′-DDT, *p*,*p*′-DDT (0.4 μg/ml); δ-BHC, endrin (1.0 μg/ml); β-BHC (2.0 μg/ml); *bis*(4-chlorophenyl)methane (*p*,*p*′-DDM, 4.0 μg/ml); other chemical solvents are analytical-reagent grade.

OCPs are persistent organic micropollutants present in soil and water, and as a result, the tuber crops are chosen as the prior target matrix. Radishes are not only one of tuber crops, but also one of the most common and easily obtained foods in China, so they were chosen in this study. Sample of 100 g of radish was comminuted and homogenized with 100 ml of water. Homogenate of 25 g was further diluted to 100 ml with water.

2.2. Apparatus

A GC7890 II system (Techcomp, Shanghai, China) equipped with a split/splitless injector (0.75 mm ID glass liner, 2 min splitless time) and an electron capture detector (ECD, ^{63}Ni) was used. The data acquisition system SePu3000 was purchased from Puhucomp (Hangzhou, China). A laboratory-made SPME with C[4]/OH-TSO fiber (60 μm) syringe was used to transfer the extracted analytes to the GC injector for analysis. The commercially available polydimethylsiloxane (PDMS, 100 μm) fiber for comparison was obtained from Supelco (Bellefonte, PA, USA). A magnetic stirrer DF-101B (Gongyi, China) was used for stirring the samples during extraction.

2.3. GC conditions

The column used was a AT.SE-54 (30 m × 0.25 mm ID, 0.33 μm film thickness) obtained from Lanzhou Institute of Chemical-Physics Chinese Academy of Siences (Lanzhou, China). The temperature program was 80 °C held for 2 min, to 180 °C at 10 °C/min, 5 °C/min to 230 °C held for 2 min and then at 10 °C/min to 250 °C held for 10 min. The injector was at 270 °C. Ultrapure nitrogen (>99.999%) was used as the carrier gas and make-up gas. The pressure of the carrier gas was 80 kPa, the flow-rate of make-up gas was 20 ml/min, the flow-rate for the septum purge was 5 ml/min and the column flow-rate is 1 ml/min.

Hydrocarbon traps, oxygen traps and moisture traps, obtained from Dalian Institute of Chemical-Physics Chinese Academy of Sciences (Dalian, China), were used in-line. The fiber was injected in the splitless mode and the splitter was opened at the end of desorption period (delay time 2 min). The detector temperature was 300 °C.

2.4. HS-SPME procedure

The fiber was conditioned under nitrogen in the hot injector of the GC at 270 °C for 1 h prior to use. All extraction was performed with a 12 ml amber vial. In the vial, a 10 μl aliquot of the standard solution, 4 ml double-distilled water (or radish matrix solution) and 1.0 g K_2SO_4 were mixed, and a magnetic stirring bar was added. The vials were enclosed with butyl-rubber stoppers wrapped with Teflon sealing tape. First of all the fiber was withdrawn into the syringe needle and the needle penetrated the stopper of the vial; the fiber was then lowered into the headspace located above the sample solution by depressing the plunger. The solution was stirred at 70 °C for 30 min. When the absorption step was finished, the fiber was again withdrawn into the needle and the syringe was removed from the vial. The final step was thermal desorption of the analytes from the SPME fiber in the GC injector at 270 °C for 2 min.

3. Results and discussion

The HS-SPME conditions were optimized in order to obtain the maximum sensitivity. The conditions for HS-SPME were tested using standard solutions of 12 OCPs and metabolites, and the following parameters were adjusted to optimize extraction: extraction temperature, extraction time, the addition of salt, the diluted multiple of radish sample, desorption temperature and time. The samples were continuously stirred at a constant speed (600 rpm).

3.1. Effect of extraction temperature

The extraction temperature and time required for the analytes to reach equilibrium between the aqueous and the stationary phase are interactional. The temperature has a double influence. Higher temperatures can decrease the diffusion coefficient of analytes in water and shorten the extraction time. But it can also decrease the distribution coefficient of SPME fibers between stationary phase and analytes, subsequently shifting the sorption equilibrium.

In order to study the effect of temperature on the extraction process, vials were immersed in a water bath heated by the magnetic stirring unit. A thermometer was used to monitor the water temperature. The study was carried out by varying the temperature in the range from 40 to 90 °C for 30 min with continuous stirring. The pH of the sample was not adjusted and salt was not added.

Fig. 1 illustrates the effect of extraction temperature on extraction efficiency. It shows that the extraction efficiency for most of the compounds increased by increasing the temperature up to 70 °C but decreased above 70 °C. Therefore, a working temperature of 70 °C was selected for further experiments.

3.2. Effect of extraction time

The extraction time may be influenced by both temperature and the stirring speed. So this parameter was determined by maintaining the extraction temperature of 70 °C and the stirring speed of 600 rpm. Other experimental parameters were the same as in Fig. 1. All the extractions were carried out in the range from 10 to 60 min.

Fig. 2 illustrates the extraction time profiles for 12 analytes. According to the left-hand graph in Fig. 2, the responses of four of the six analytes described became roughly constant (equilibrium was achieved); according to the right-hand graph in Fig. 2, equilibrium was achieved for all of the six analytes reported after 30 min. Hence, a 30 min extraction time was then chosen to carry out the following experiments.

3.3. Desorption temperature and time

The analyte can be desorbed effectively under a higher temperature in a shorter time, but the stability and the lifetime of the fiber will be affected and the analyte may be decomposed if the desorption temperature is too high. Fig. 3 showed the amount of all analytes desorbed with increasing temperature. As can be seen, a desorption temperature of 270 °C showed no carryover effect under that condition.

Another important parameter is the desorption time of the analytes from the SPME fiber in the injection part of GC. There are many factors that affect the desorption behavior, such as the boiling point as well as the partition constant of the analyte, the thickness of the stationary phase and the desorption temperature. After having experimented several desorption time (between 10 and 600 s) as shown in Fig. 4, we concluded like several authors [15,16] that 2 min are sufficient to allow the complete desorption of the analytes from the fiber which can be reused for another extraction.

3.4. Effect of dilution on sample extraction

Literatures [11,17,18] demonstrated the feasibility of extracting some OCPs from aqueous samples. In this paper, the application of HS-SPME for extraction of 12 OCPs and their metabolites in radish sample was studied. It was found that extraction efficiency were lower in radish sample than that in

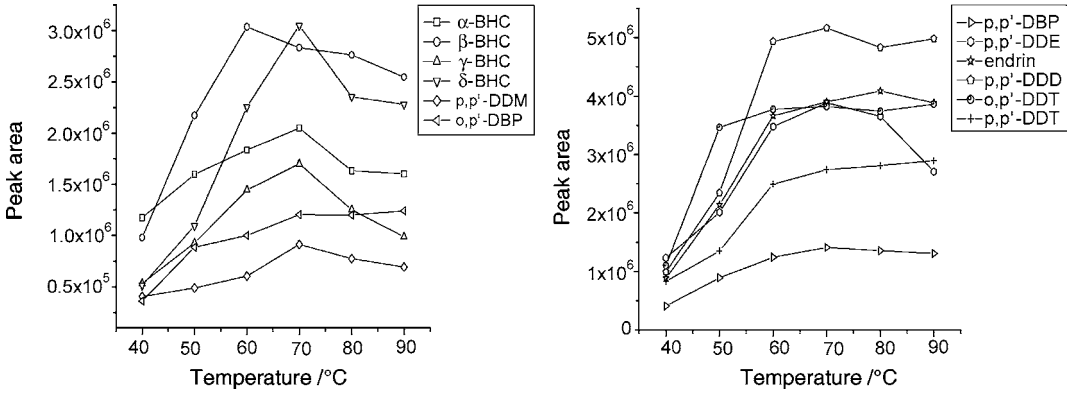

Fig. 1. Extraction temperature profile of standard solutions mixture (10 μl) of 12 OCPs and metabolites in 4 ml water. Injection temperature, 270 °C; ECD temperature, 300 °C; extraction time, 30 min; desorption time, 2 min; no salt. In the standard solutions mixture, the concentrations of α-BHC, β-BHC, γ-BHC, δ-BHC, *p,p′*-DDM, *o,p′*-DBP, *p,p′*-DBP, *p,p′*-DDE, Endrin, *p,p′*-DDD, *o,p′*-DDT and *p,p′*-DDT were 0.1, 1.0, 0.1, 0.5, 2.0, 0.2, 0.2, 0.1, 0.5, 0.2, 0.2, 0.2 μg/ml, respectively.

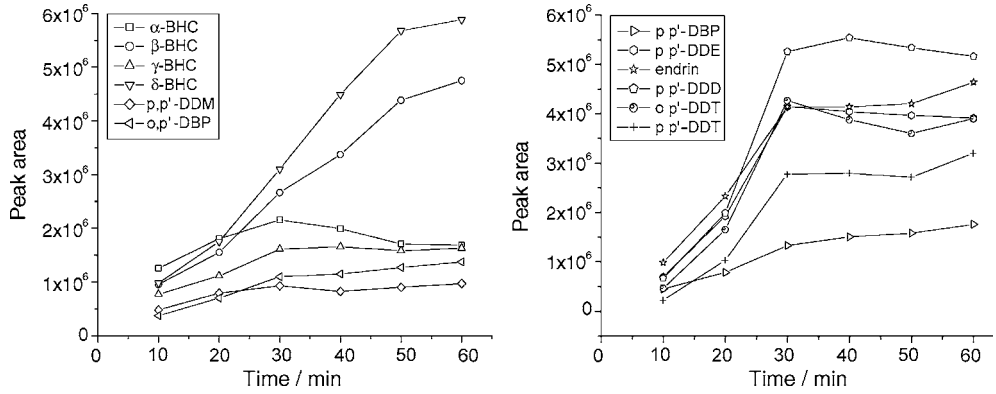

Fig. 2. Extraction time profile of 12 OCPs and metabolites in water. Injection temperature, 270 °C; ECD temperature, 300 °C; extraction temperature, 70 °C; desorption time, 2 min; no salt; concentrations and other conditions as in Fig. 1.

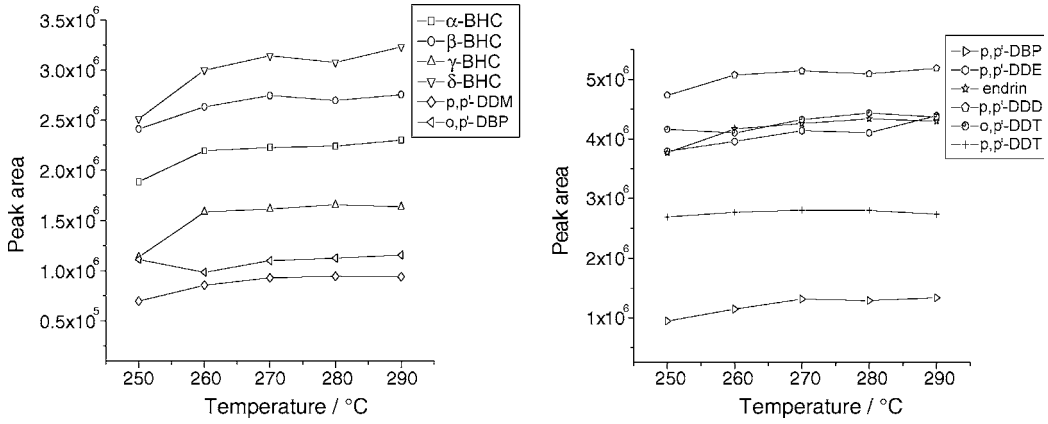

Fig. 3. Desorption temperature profile of 12 OCPs and metabolites in water. ECD temperature, 300 °C; extraction temperature, 70 °C; extraction time, 30 min; desorption time, 2 min; no salt; concentrations and other conditions as in Fig. 1.

aqueous samples. Low extraction efficiencies achieved when extracting complex matrices have also been reported by several authors when extracting pesticides in a variety of sample matrices as food samples (e.g. honey, fruits and fruit juices) [4,5,8].

Assuming the pesticide distributed in the sample between a "free" form and a "bound" form with matrix components, a sample dilution should increase the extraction efficiencies as a consequence of the displacement of the equilibrium towards the free form of the pesticide due to a reduced matrix effect. In attempt to reduce the matrix effect, the radish matrix was diluted with water. Fig. 5 shows peak areas of which the matrices were diluted covering a range of 2–32 times. Without doubt, the above hypothesis is supported by data re-

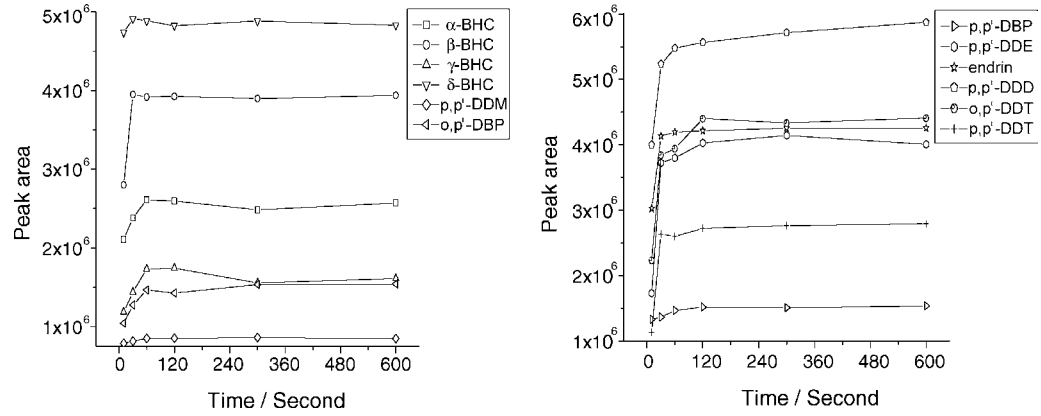

Fig. 4. Desorption time profile of 12 OCPs and metabolites in water. Injector temperature, 270 °C; ECD temperature, 300 °C; extraction temperature, 70 °C; extraction time, 30 min; no salt; concentrations and other conditions as in Fig. 1.

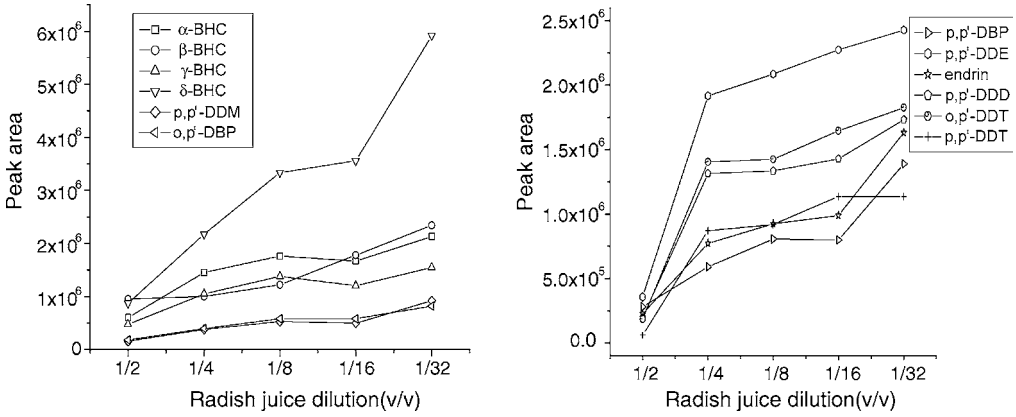

Fig. 5. Effect of dilution of radish matrix. Injector temperature, 270 °C; ECD temperature, 300 °C; extraction temperature, 70 °C; extraction time, 30 min; desorption time, 2 min; no salt; concentrations and other conditions as in Fig. 1.

ported in Fig. 5: the more the dilution factor, the higher the extraction efficiency; which leads to higher limits of quantification for samples. But such excess dilution of samples was inconvenient for a trace analysis. Since the OCPs and the metabolites is persistent organic pollutants and tend to accumulate in living organisms [1], and the limits of quantification for samples should be low, it is necessary to choose a feasible dilution factor. In this study, an eight-fold dilution was chosen as good compromise between increased extraction efficiency and loss of sensitivity, and was then adopted for further experiments on radish samples.

3.5. Effect of salt

Our studies showed that the addition of salt was not significant for most of the analytes (except δ-BHC) extracted from water, but it affects the extraction efficiency in radish matrix. Fig. 6 illustrates the response of 12 analytes in the diluting solutions of the samples containing different amount of potassium sulfate. It was evaluated by analyzing the amount of pesticides extracted from 4 ml eight-fold diluting solutions of radish matrix containing 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 g K_2SO_4, respectively. As is shown in the figure, the extraction of most of the analytes obtained higher sensitivities for K_2SO_4 1.0 g. A 1.0 g K_2SO_4 was selected in this study.

3.6. Comparison with commercial PDMS fiber

Fig. 7 illustrates the response of GC–ECD obtained when extracting OCPs standard solutions of the same concentration with C[4]/OH-TSO fiber and commercial PDMS fiber. These results demonstrated that C[4]/OH-TSO fiber shows higher extraction efficiency by contrast with PDMS fiber for the analytes except *p,p′*-DDT and *o,p′*-DDT. The high extraction efficiency of C[4]/OH-TSO fiber to these compounds is due to three points: firstly, the high extraction efficiency of C[4]/OH-TSO fiber to these compounds is due to the π–π interaction, hydrophobic interactions and cavity-shaped cyclic molecular structure [12,14]; secondly, it exhibits special selectivity to chloro-contained aromatics and as the number of chlorine substituents on the aromatic ring increases, so does the compounds' affinity to the fiber [13]; thirdly, the sol–gel technology provides higher surface area for the fiber

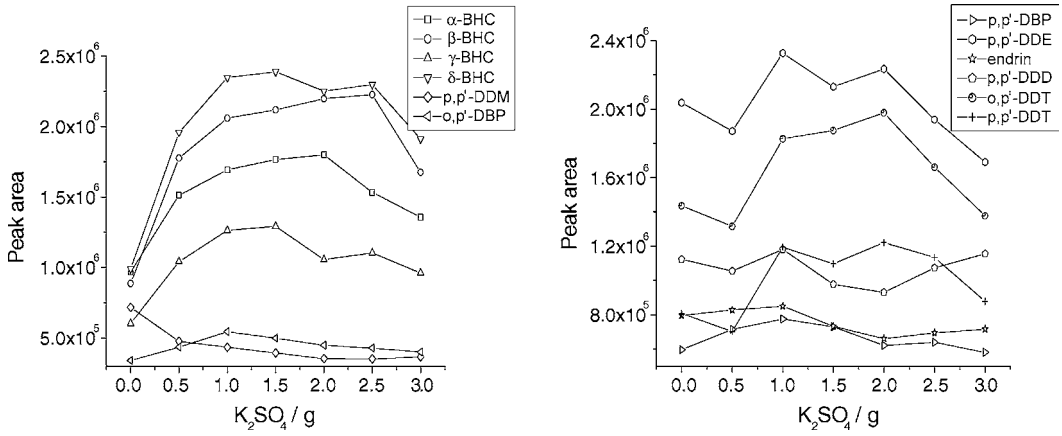

Fig. 6. Effect of salt in eight-fold diluting solutions of radish matrix. Injector temperature, 270 °C; ECD temperature, 300 °C; extraction temperature, 70 °C; extraction time, 30 min; desorption time, 2 min; concentrations and other conditions as in Fig. 1.

Table 1
Linearity, LOD, LOD' and R.S.D.

No.	Pesticides	Linear range (ng/l)	*R*	LOD (ng/l)	LOD' (ng/kg)	R.S.D. (%) ($n = 5$)
1	α-BHC	1.0–500	0.9938	0.185	1.48	7.63
2	β-BHC	10–5000	0.9932	1.86	14.9	12.3
3	γ-BHC	1.0–500	0.9952	0.292	2.34	9.80
4	δ-BHC	5–1250	0.9947	1.15	9.20	11.8
5	*p,p′*-DDM	40–10000	0.9922	21.7	174	9.58
6	*o,p′*-DBP	4–1000	0.9938	1.69	13.5	6.83
7	*p,p′*-DBP	2–1000	0.9965	1.13	10.2	7.40
8	*p,p′*-DDE	1.0–125	0.9976	0.159	1.27	13.0
9	Endrin	5–625	0.9935	2.47	19.8	8.94
10	*p,p′*-DDD	2–500	0. 9967	0.573	4.58	7.61
11	*o,p′*-DDT	2–250	0.9937	0.410	3.28	10.2
12	*p,p′*-DDT	2–500	0.9949	0.825	6.60	13.1

and hence results in an enhanced extraction efficiency in SPME.

3.7. Linearity, detection limits and precision

Linearity experiments were carried out in the radish matrix solutions of eight-fold dilution, spiked with the standard solutions of 12 OCPs mentioned before in certain concentration range.

The calculations of the limits of detection (LOD) was based on a three N/m ratio, where N is the background noise and m is the slope of the respective calibration equation. Since sample was diluted eight times before analysis, the limits of detection for radishes (LOD') were about eight times higher than LOD.

With the aim of testing the precision of this method, the relative standard deviation (R.S.D.) was determined by performing five consecutive extractions under the selected conditions.

Table 1 shows the LOD, LOD', correlation coefficients (*R*), linear range and precision obtained for each pesticide using C[4]/OH-TSO fiber. The LOD are lower than those mentioned in the literatures [10,19–21]. The linearity were good and the correlation coefficients were better than 0.992 in all cases. The precision are satisfying, with the R.S.D. less than 13.1% for all pesticides. The proposed method, with HS-SPME using C[4]/OH-TSO fiber, shows good advantages to the determination of the OCPs at trace amount level.

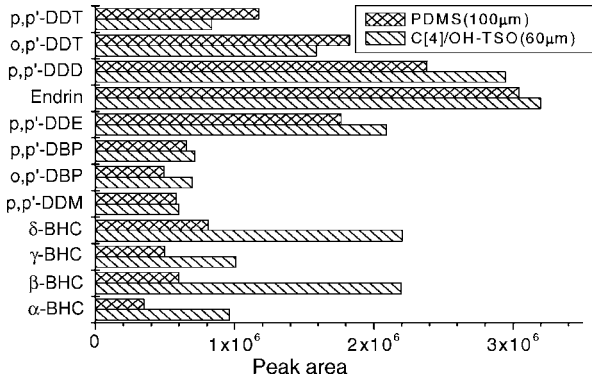

Fig. 7. Comparison of the extraction capability in water with C[4]/OH-TSO fiber and commercial PDMS fiber. Injector temperature, 270 °C; ECD temperature, 300 °C; extraction temperature, 70 °C; extraction time, 30 min; desorption time, 2 min; K_2SO_4 1.0 g; concentrations, half as in Fig. 1.

Table 2
Recoveries

Pesticides	Added (ng/l)	Result (ng/l)	Recovery (%)
α-BHC	500	489.16	97.83
	250	273.75	109.5
	125	105.2	84.16
β-BHC	5000	4639.56	92.79
	2500	2982.29	119.3
	1250	1147.3	91.78
γ-BHC	500	501.97	100.4
	250	271.06	108.4
	125	97.99	78.39
δ-BHC	1250	1038.12	83.05
	625	702.9	112.5
p,p′-DDM	10000	8134.4	81.34
	5000	5552.7	111.1
	2500	2678	107.1
o,p′-DBP	1000	838.1	83.81
	500	459.45	91.89
	250	252.56	101.0
p,p′-DBP	1000	798.5	79.85
	500	459.3	91.86
	250	273.75	109.5
p,p′-DDE	125	110.91	88.73
Endrin	625	665.59	106.5
p,p′-DDD	500	422.71	84.54
	250	250.64	100.3
o,p′-DDT	250	231.92	92.77
	500	434.20	86.84
	250	212.46	84.98

3.8. Recoveries

Recovery tests were performed in order to study accuracy. These tests were based on the addition of known amounts of pesticides to radish matrix. The OCPs were added to the radish matrix as follows: the high spiked level is that a 10 μl standard working solution mixture was added to 4 ml diluting solution of radish matrix; the medium spiked level and

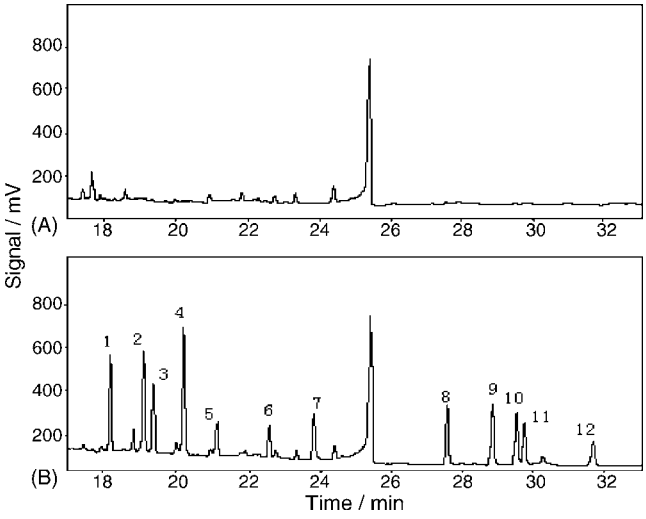

Fig. 8. HS-SPME/GC–ECD chromatograms of (A) 4 ml eight-fold diluting solutions of radish matrix blank and (B) 4 ml eight-fold diluting solutions of radish matrix spiked with 10 μl standard solution mixture (concentrations as in Fig. 1); K_2SO_4 1.0 g; other conditions as in Fig. 5. The numbers of the analytes are as listed in Table 1.

the low spiked level is 1/2 and 1/4 of the high spike level, respectively. The results obtained when these samples were analyzed were compared with the known amounts of standard OCPs added to radish matrix. Recoveries obtained in the analysis of fortified radish samples are above 78.4% and below 119.3% for each pesticide with different concentration, indicating the method accuracy (Table 2).

The HS-SPME/GC–ECD chromatograms of eight-fold diluting solution of radish matrix blank and spiked 12 OCPs and their metabolites in eight-fold diluting solution of radish matrix are shown in Fig. 8. No significant interferences with the studied analytes were observed, since the unspiked samples did not show any peak in the retention time of these compounds.

4. Conclusions

SPME has demonstrated to be a fast, simple, solvent-free method for extracting pesticides from water samples. Owing to many special characteristics of C[4]/OH-TSO fiber, it shows far higher extraction efficiency to most of the tested analytes than the commercially available PDMS fiber and the LOD are lower than those mentioned in the literatures. The complexity of the radish matrix makes it difficult to obtain a quantitative extraction of pesticides, but the decrease in concentration of the interfering components by a simple dilution of the sample makes possible the quantification of pesticides. Apparently dilution of samples may be inconvenient for a trace analysis, so an eight-fold dilution was chosen as good compromise between increased extraction efficiency and loss of sensitivity. The results tested showed that the proposed analytical method is adequate to determine OCPs in complex matrix at ultra trace levels.

Acknowledgments

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