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Journal of Chromatography A, 918 (2001) 177–188

JOURNAL OF CHROMATOGRAPHY A

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Determination of organochlorine pesticides and their metabolites in soil samples using headspace solid-phase microextraction

Ruey-An Doong*, Pei-Lin Liao

Department of Atomic Science, National Tsing Hua University, 101 Section 2, Kuang-Fu Road, Hsinchu 30013, Taiwan

Received 16 October 2000; received in revised form 5 March 2001; accepted 7 March 2001

Abstract

An analytical procedure was developed using headspace solid-phase microextraction (HS-SPME) for the determination of organochlorine pesticides (OCPs) and their metabolites in sandy soil samples. The developed procedures involving fiber selection, temperature effect, absorption time, soil matrix and the addition of solvents of different polarity were optimized. Also, the results were compared to those achieved using Soxhlet extraction standard method. The 100-μm polydimethylsiloxane (PDMS) and 65-μm PDMS–divinylbenzene showed good extraction efficiency for 18 organochlorine pesticides. An increase in the extraction efficiency of organochlorine pesticides and the metabolites was observed when the temperature increased, and an optimum temperature of 70°C for extracting OCPs was obtained. The application of other hydrophilic solvents had different effects on the extraction of organochlorine pesticides and the metabolites. Higher responses of OCPs were obtained when 5 ml of water was added to the soil. Good linearity of OCPs between 0.2 and 4 ng/g soil was observed. The relative standard deviation was found to be lower than 25%. Also the limits of detection were between 0.06 and 0.65 ng/g, which were lower than those obtained using Soxhlet extraction. Moreover, the optimized HS-SPME procedure was applied to the analysis of OCPs in certified reference material (CRM) 804-050 soil and compared with Soxhlet extraction procedure. Results obtained in this study were in good agreement with those obtained using Soxhlet extraction. The mean values obtained using HS-SPME technique were in the range of 16.5 to 1459.6 mg/kg, which corresponds to the recoveries of 68% to 127% of the certified values of CRM soil.

Keywords: Extraction methods; Headspace analysis; Soil; Environmental analysis; Organochlorine compounds; Pesticides

1. Introduction

Solid-phase microextraction (SPME) is a newly developed solvent-free analytical technology, which has the advantage of simplicity, lower detection limits and good reproducibility [1–4]. This method now is widely accepted as a reliable technique for the quantitative determination of volatile organic compounds [5,6], polycyclic aromatic hydrocarbons (PAHs) [7,8] and some organometallic compounds [9] in water samples. Also, SPME is of increasing interest in the field of pesticide residue analysis, as mentioned in several reviews [10,11]. It has been applied to the determination of several organophosphorus, organochlorine, or triazine compounds in aqueous solutions [12–15]. Also, an interlaboratory

*Corresponding author. Tel.: +886-3-5726-785; fax: +886-3-5718-649.

E-mail address: radoong@mx.nthu.edu.tw (R.-A. Doong).

0021-9673/01/$ – see front matter
PII: S0021-9673(01)00740-3

study on pesticides analysis by SPME was carried out with participation of 11 laboratories [16]. Results of the analysis showed that SPME was an accurate and fast method for sample preparation and analysis in aqueous solutions. However, the determination of pesticides in soil samples by SPME has received only limited attention.

Only a few references on the application of SPME for the determination of organophosphorus pesticides [17] and herbicides [18–20] in soil samples can be found. Most applications are based on the preparation of mixture of the soil with distilled water and analyze target compounds by directly dipping the SPME fibers into the slurry. However several disadvantages related to fiber stability and sensitivity have been pointed out [13,19]. Recently, headspace SPME (HS-SPME) has also been used to determine pesticide compounds in water samples and biological fluid samples [13,17,21]. Sampling in the headspace presents a significant advantage in terms of selectivity because only volatile and semivolatile organic compounds can be released into the headspace. Since the fiber is not in contact with the sample, background adsorption and matrix effects can be reduced, which also enhances the life expectancy of SPME fibers.

Although direct immersion SPME has been used for the determination of herbicides, chlorobenzene and chlorophenols in soils, few applications of HS-SPME for the analysis of organochlorine pesticides (OCPs) in soil environment have been documented. Therefore, the aim of the present study is to investigate the applicability of HS-SPME to the determination of organochlorine pesticide in soil samples. The variables involving fiber selection, temperature effect, absorption time, soil matrix and the addition of solvents of different polarity were optimized. Eighteen OCPs and their metabolites, three different classes, hexachlorocyclohexane (α-BHC, β-BHC, γ-BHC and δ-BHC), cyclodiene (aldrin, dieldrin, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, endosulfan I, endosulfan II and endosulfan sulfate) and diphenyl aliphatic (*p,p′*-DDT, *p,p′*-DDD, *p,p′*-DDE and methoxychlor) pesticides, were selected as the model compounds because the residues of these compounds are most often detected in soil and sediment environments. The results obtained are compared to those achieved using the Soxhlet extraction standard method.

2. Experimental

2.1. Reagents and materials

Standard mixtures of 18 OCPs at a concentration of 2000 μg/ml in toluene–hexane (1:1, v/v) were purchased from Supelco (Bellefonte, PA, USA). These standards were stored at 4°C and were used for the preparation of working standard solutions (20 μg/ml in acetone). Deionized water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Methanol, dichloromethane, acetone, and *n*-hexane were obtained from Mallinckrodt (Phillipsburg, NJ, USA). Light petroleum (boiling point 40–60°C) and diethyl ether were purchased from Riedel-de Haën (Seelze, Germany).

Six kinds of SPME fibers, a 100-, 30- and 7-μm poly(dimethylsiloxane) (PDMS), 75-μm carboxen (CAR)–PDMS, 85-μm polyacrylate (PA) and 65-μm PDMS–divinylbenzene (DVB) fibers, were also obtained from Supelco. All fibers were conditioned in the hot injector part of the gas chromatograph for 0.5–2 h and at 250~320°C, according to instructions provided by the manufacturer.

A sandy soil obtained from Taichung County, Taiwan was used in this study. Soils were air-dried and sieved with a 20 mesh sieve to remove coarse particles and debris. The water content, pH value and organic content of the soil were 1.62%, 4.92 and 4.89%, respectively. Soil samples were prepared by spiking appropriate amounts of the diluted working standard solutions to soils to get final concentrations of 0.5–4 ng/g soil. The soils were then shaken in an orbital shaker at 125 rpm to homogenize the OCPs and left for at least 1 h to fully evaporate the solvent. All the samples were fresh spiked and no aged sample was used in this study.

The glassware used in this study was washed with the cleaning solution to remove trace amounts of organics on the surface of vials. To minimize the sorption effect of OCPs on glassware, the SPME vials were further silanized by soaking the glassware overnight in a 10% (v/v) mixture of dichlorodi-

methylsilane (Supelco) in toluene [14,17]. Finally, the vials were rinsed with toluene and methanol and oven-dried at 105°C.

2.2. Chromatographic conditions

A Hewlett-Packard 5890 gas chromatograph equipped with an electron-capture detector was used for the experiments to determine the optimized SPME conditions. The carrier gas was nitrogen with a flow-rate of 1.33 ml/min. The gas chromatograph was operated in a splitless mode and the splitless time was 5 min. The injector was maintained between 240 and 300°C, depending on the fiber used. The temperature of detector was maintained at 280°C. A 30 m×0.32 mm I.D. PTE-5 capillary column (0.25 μm film thickness; Supelco) was used for separating OCPs. The column was held at 100°C for 5 min, increased to 200°C at a rate of 20°C/min for 3 min, and again ramped at 2°C/min to 230°C, held for 1 min, and finally ramped to 250°C at a rate of 4°C/min, and then held for 3 min.

2.3. Solid-phase microextraction procedures

The HS-SPME extractions were performed by placing 0.5–2 g of spiked soil and 5–20 ml of deionized water into 15- or 30-ml amber vials capped with PTFE-coated septa. The concentration of OCPs in soil samples was 2 ng/g soil. Magnetic stirring with a 1-cm long PTFE coated stir bar was used to agitate the slurry at about 1000 rpm. The HS-SPME equilibrium was conducted by immersing the fiber in the headspace of the sample with stirring for an appropriate time period, during which analytes sorb on the stationary phase of the fibers. After extraction, the fiber was thermally desorbed for 5 min into the glass liner of the gas chromatograph injector at 270°C (30- and 100-μm PDMS and 65-μm PDMS–DVB), 300°C (PA and CAR–PDMS) or 320°C (7-μm PDMS). Possible carryover was removed by keeping the fiber in the injector for an additional period of time with the injector in the split mode. Reinserting the SPME fiber after the run showed no obvious carryover.

2.4. Soxhlet extraction

Concentration of OCPs in the spiked soil at concentrations of 25 ng/g soil or the certified reference material (CRM) 804-050 was also determined using Soxhlet extraction procedure. A 10-g amount of soil sample was placed into a thimble filter and the organochlorine pesticides were extracted with 300 ml hexane–acetone (1:1) for 24 h at a rate of 4–6 cycles/h. Pentachloronitrobenzene and decachlorobiphenyl were used as the internal standards to confirm the retention time of the organochlorine pesticides. After the extraction, the extract was preconcentrated to 2 ml on a rotary evaporator. Anhydrous sodium sulfate (ca. 1 cm) was added to all the columns prior to the clean-up procedures. The Florisil solid-phase exctraction (SPE) cartridge was used for clean-up and was conditioned with 10 ml hexane at a rate of 5 ml/min. The extract was then added to the column and the organochlorine pesticides were eluted with 15 ml hexane–diethyl ether (94:6) at a rate of 2 ml/min. Finally, the elute was purged with a gentle stream of nitrogen gas and quantified to 10 ml with hexane.

3. Results and discussion

3.1. Selection of stationary phase of SPME fiber

Six commercially available SPME fibers (100-, 30- or 7-μm PDMS, 85-μm PA, 65-μm PDMS–DVB and 75-μm CAR–PDMS) were compared for efficiently determining 18 OCPs. The extraction time was 60 min. Fig. 1 illustrates the effect of SPME fibers on the adsorption of OCPs. The OCPs with different chemical characteristics showed different extraction behaviors. All SPME fibers provided good extraction efficiencies for cyclodiene pesticides and their metabolites (aldrin, dieldrin, endrin, heptachlor, heptachlor epoxide, endosulfan I and endosulfan II). However, the extraction efficiency of SPME fibers varied for BHC and diphenyl aliphatic pesticides. BHC pesticides could be extracted at levels greater than the detection limits of the method within 60 min using the CAR–PDMS fiber. However, a low adsorption efficiency of the CAR–PDMS fiber was

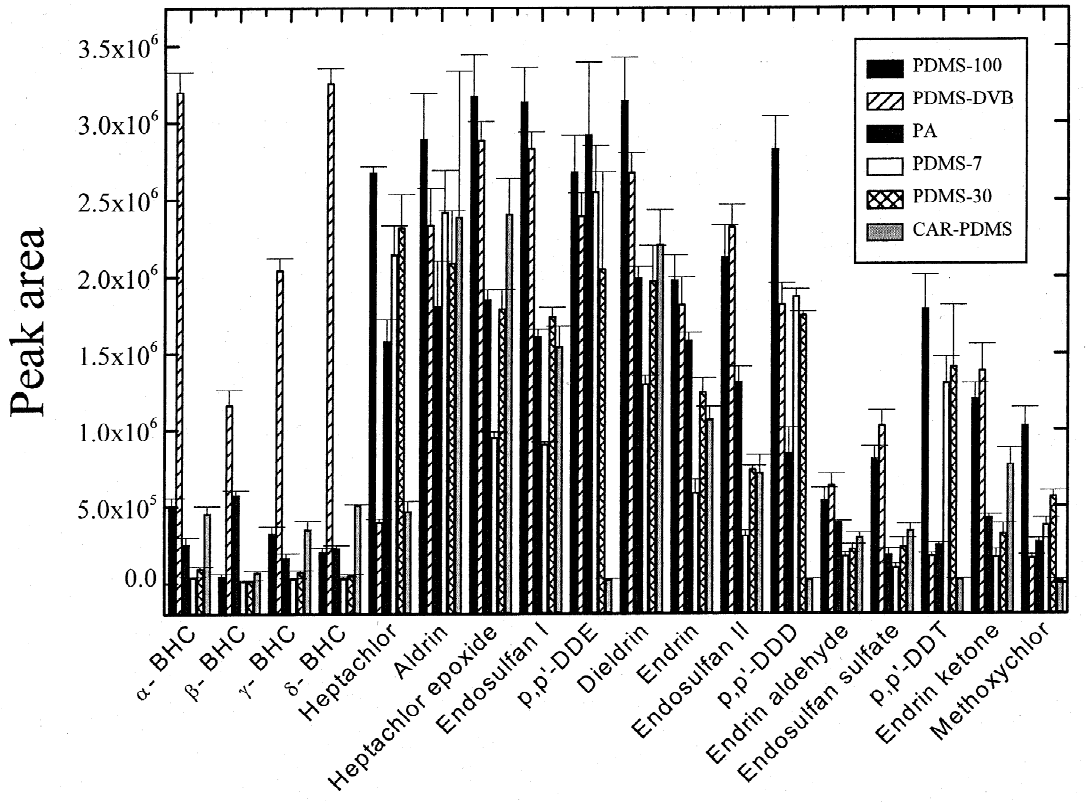

Fig. 1. The comparison of extraction efficiency of organochlorine pesticides with six different SPME fibers. The extraction time of 60 min at room temperature under magnetic stirring was used.

observed for the extraction of *p,p′*-DDT and its metabolites (*p,p′*-DDD and *p,p′*-DDE). When PDMS fibers were used, diphenyl aliphatic pesticides could be extracted effectively with the sorption time of 60 min. The extraction efficiencies decreased with the decreasing coating thickness and 100-μm PDMS fiber extracted the highest amounts of organochlorine pesticides and their metabolites. However, low extraction efficiency of BHC compounds was observed for PDMS fibers.

Application of the 65-μm PDMS–DVB fiber showed a significant increase in signal response of BHC pesticides relative to the PDMS fiber. The PDMS–DVB fiber is designed for the extraction of aromatic hydrocarbons and some small volatile analytes. These results clearly show that the PDMS–DVB fiber are also suitable for the extraction of BHC compounds. However, a low extraction efficiency for *p,p′*-DDT and heptachlor was also demonstrated. Moreover, less effective extraction of OCPs by using the PA fiber was observed because the PA fiber has a more polar coating and also has a low affinity to OCPs.

The OCPs are typically considered as hydrophobic organic compounds. The log values of octanol–water partition coefficients (K_{ow}) range from 3.7 to 7.4 and the water solubilities were from 5 μg/l (*p,p′*-DDT) to 7.3 mg/l (γ-BHC). Therefore, these analytes would be expected to partition readily into a more non-polar fiber coating rather than a polar one. The PDMS polymeric coating with higher film thickness and PDMS–DVB showed good sorption for organochlorine pesticides. However, due to the high capacity of the PDMS–DVB coating to extract volatile

compounds, some additional peaks appeared on the chromatogram of OCPs when applied to soil extraction. Therefore, the 100-μm PDMS fiber was selected for further optimization experiments.

3.2. Effect of extraction temperature

Sample temperature has a double influence. Higher temperatures can decrease the diffusion coefficient of analytes in water and shorten the extraction time. Also, elevated temperatures decrease the distribution coefficient of SPME fibers (K_{spme}) between stationary phase and analytes, subsequently shifting the sorption equilibra. Moreover, elevated temperatures can decrease the partition coefficient of OCPs in soil particles. Although several researchers did not recommend the extraction of analytes in aqueous solution, the effect of temperature should be optimized on the extraction of analytes in soil.

Fig. 2 illustrates the amounts of OCPs absorbed by a 100-μm PDMS fiber with an extraction time of 60 min at temperatures ranging from 35 to 95°C. An increase in extraction efficiency of organochlorine pesticides and the metabolites was observed when temperature increased. This may be attributed to that the increase of extraction temperature decreases the partition coefficient between OCPs and soil particle, thereby increasing the desorption rates of OCPs and the metabolites from the surface of soil particle to solution. Also, the elevated temperature significantly enhances the diffusion of the analytes from the solution to gaseous phase. However, a decrease in sensitivity was also observed for BHCs, heptachlor, heptachlor epoxide, and endosulfan I when the extraction temperature exceeded 60°C. These compounds have relatively high vapor pressures ($3\cdot10^{-4}$–$6.3\cdot10^{-6}$ mmHg; 1 mmHg=133.3 Pa). Since the absorption of analytes by the fiber is an exothermic process, the SPME distribution coefficients (K_{spme}) between coating materials and analytes also decreased at the elevated temperature [22,23]. Santos et al. [23] also showed that increasing the extraction temperature did not improve the response for chlorobenzenes, as explained by the reduction in the partition coefficients between the fiber and the headspace. Therefore, the extracted amounts of OCPs having high vapor pressures decreased at elevated temperatures, and a working temperature of 70°C was selected for further experiments.

3.3. Extraction time profiles

The time required to reach equilibrium between the fiber stationary phase and the soil sample was determined. The soil was spiked with 2 ng/g OCPs and was exposed for times which ranged from 20 to 660 min. The sample was continuously stirred to decrease the time required for the analytes to reach the equilibrium. Fig. 3 illustrates the extraction time profiles of nine of the 18 OCPs using the 100-μm PDMS fiber at the extraction temperature of 70°C. The equilibrium time was 20 min for BHC compounds (α-, β-, γ-, δ-BHCs), 40 min for aldrin, heptachlor, and heptachlor epoxide, 120 min for other cyclodiene compounds (dieldrin, endrin, endosulfan I, endosulfan II and the metabolites) and *p,p′*-DDE, and 220 min for diphenyl aliphatic compounds (*p,p′*-DDD, *p,p′*-DDT and methoxychlor). Magdic and Pawliszyn [14] used a 100-μm PDMS fiber for the determination of OCPs in water samples at room temperature and found that equilibration times ranged from 15 to 180 min, which is consistent with our results in the soil system. It is noted that the responses of most organochlorine pesticides, except for diphenyl aliphatic compounds, decreased when the extraction time exceeded 120 min. The elevated extraction temperature can decrease the distribution coefficient of the analyte, especially for the compounds with small SPME distribution constants [8,14].

Since the extraction of analytes with SPME is based on an equilibrium distribution process, the equilibrium time must be reached for extracting the maximum amount of analyte by the fibers. Different responses were found for the OCPs, dependent on volatilities, distribution constants and the structures of OCPs. BHC compounds have relatively low K_{ow} values and exhibited the shortest equilibrium time, which is also consistent with the reported data [14]. The short equilibration time for aldrin and heptachlor may be due to the high vapor pressures at 70°C. Moreover, the low water solubilities and high K_{ow} values are possible reasons for the long equilibrium time for diphenyl aliphatic compounds. However, the equilibrium time of 220 min for all the OCPs to

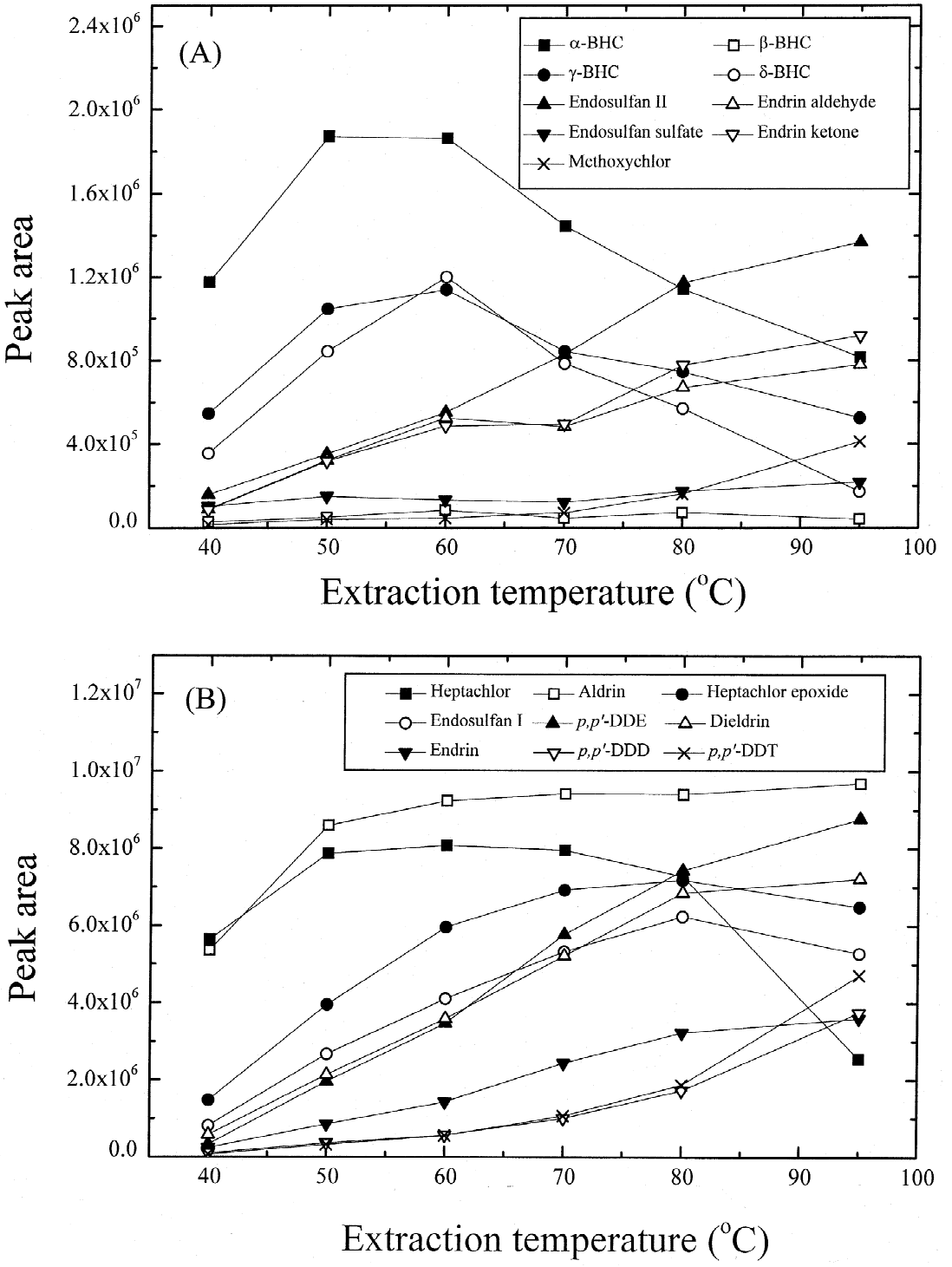

Fig. 2. The amounts of organochlorine pesticides absorbed by a 100-μm PDMS fiber with the different extraction temperatures ranging from 35 to 95°C. The extraction time was 60 min.

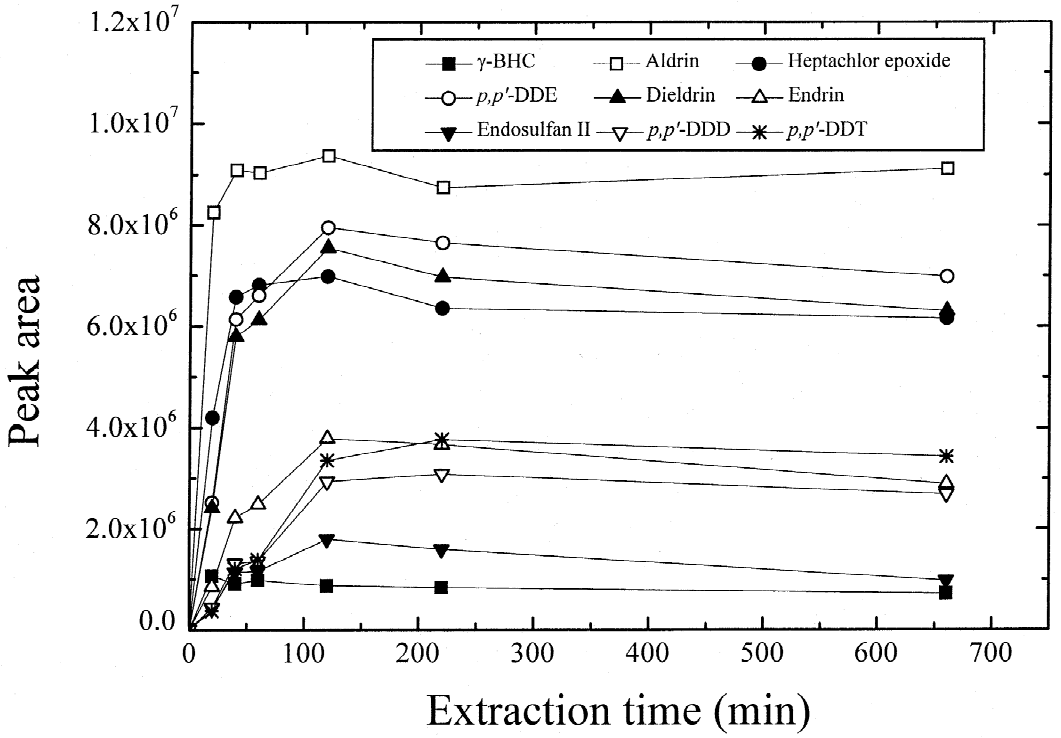

Fig. 3. The SPME sorption time profiles for nine of 18 organochlorine pesticides with a 100-μm PDMS fiber at the extraction temperature of 70°C.

reach equilibrium is too long and will significantly reduce the sensitivities of BHC and cyclodiene compounds. Therefore, an extraction time of 60 min was selected to perform the sample analysis.

3.4. Effect of water and organic solvent

The degree of partitioning of semivolatile organic compounds between the soil and the headspace is generally low, and the addition of water can enhance the release of volatile organic compounds (VOCs) from the soil matrix [24–26]. To enhance the release of organochlorine pesticides from soil, different amounts of water ranging from 5 to 20 ml were added into the 0.5 g soil-amended system. Fig. 4 illustrates the effect of water/soil ratio on the extraction of organochlorine pesticides using the HS-SPME procedure at 70°C. The responses of OCPs decreased with the increasing water/soil ratio. A maximum response was obtained when 5 ml of water was added to the system. Llompart et al. [26] also showed that the addition of water is necessary to release the volatile organic compounds into the gaseous phase and that the response decreased when the amount of water added exceeded 5 ml, which is similar to our results. Since the analytes were analyzed by HS-SPME, the addition of higher amounts of water would dilute the concentration of the analytes and increase the diffusion barrier of OCPs from aqueous phase to gaseous phase. Moreover, the decrease in signal response was compound- and structure-dependent. The responses of aldrin and heptachlor were not significantly different when the amounts of water added increased from 5 to 20 ml. However, the signal responses of OCPs decreased 49–67% for BHC compounds, 27–41% for cyclodiene compounds, and 7–15% for DDT compounds. This discrepancy may probably be attributed to the different water solubilities and vapor pressures of the organochlorine pesticides. Aldrin and hepta-

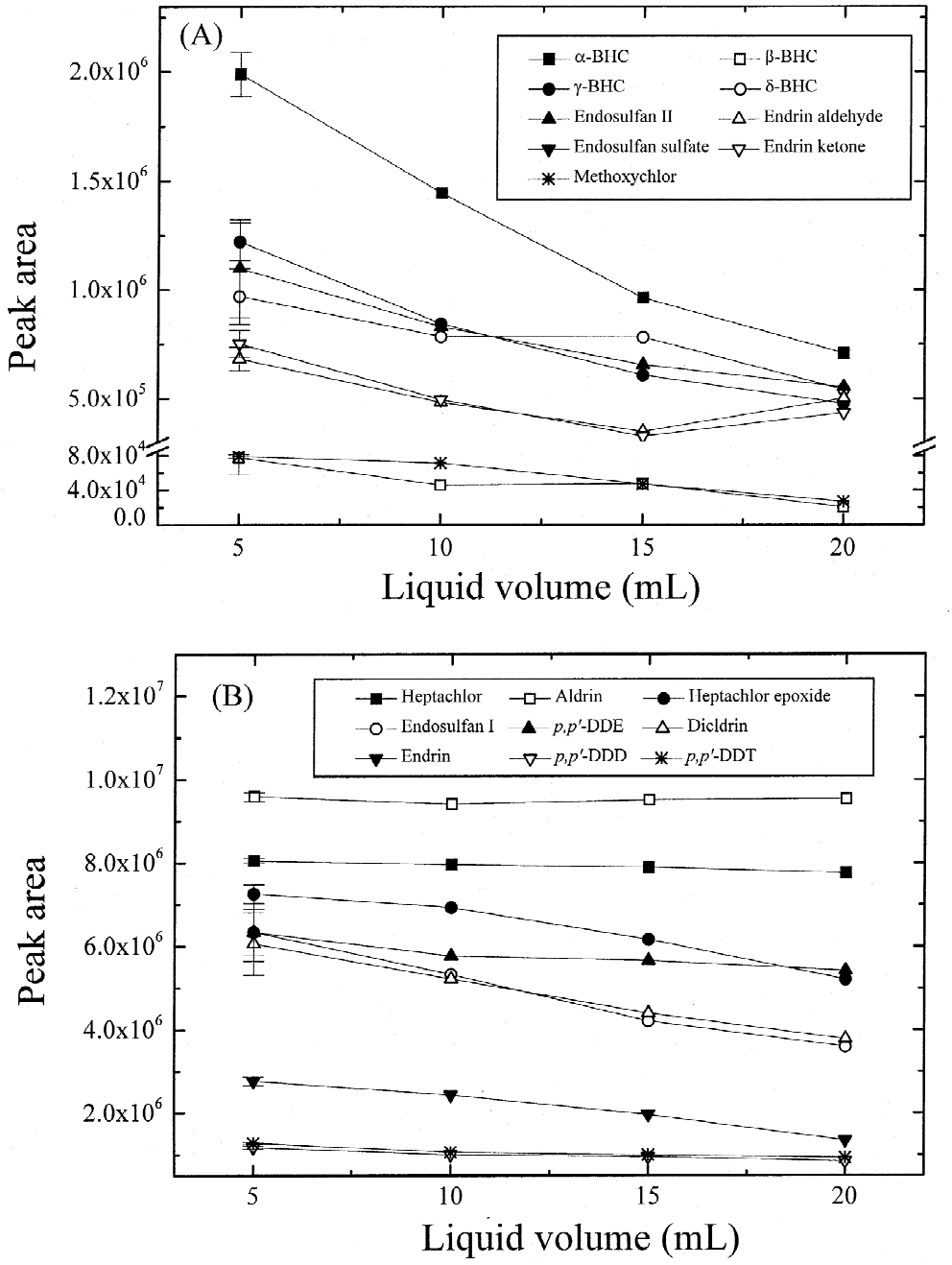

Fig. 4. Effect of liquid volume on the extraction of organochlorine pesticides with a 100-μm PDMS fiber. The extraction time and temperature were 60 min and 70°C, respectively.

chlor have low water solubilities (0.027–0.056 mg/l) and high vapor pressure ($7.5\cdot10^{-5}$–$3\cdot10^{-4}$ mmHg). The desorbed OCPs will be easily released from aqueous solution to gaseous phase. However, BHC compounds have relatively high water solubilities (0.1–7.3 mg/l) and low vapor pressures. The BHC compounds released from the soil matrix will be retained in aqueous solution, subsequently decreasing the signal response significantly as the total amounts of water added increased. Also, a positive relationship between water solubility and the decreasing ratio of peak area between 5 and 20 ml was also established ($r=0.74$, $n=11$), showing that water solubility of the analytes is an important factor influencing the signal response of analytes as the amounts of water changed.

The addition of hydrophilic solvents can also promote the release of organic compounds from soils. Several researches have demonstrated that the presence of a high concentration of organic solvent led to a significant decrease in extraction efficiency of analytes [19,22,25]. Therefore, only a small amount of solvent was recommended for use as amendment. Fig. 5 shows the responses obtained after the addition of 100 μl of different solvents to the system containing 5 ml water and 0.5 g of soil. The ratio of solvent/water was at 2%. Acetone, acetonitrile and light petroleum were selected in this study. The addition of 100 μl of acetone decreased the responses of OCPs. Changing the solvent to acetonitrile or light petroleum can slightly enhance the sensitivities of the metabolic compounds of OCPs, such as endrin aldehyde, endrin ketone and *p,p′*-DDE. The increase in sensitivity of polar metabolites with the addition of hydrophilic solvent may be due to the displacement of the analytes from the active sites in the soil [26]. The active sites are usually polar functional groups that have more affinity for polar compounds. The addition of acetonitrile or light petroleum will partly substitute for

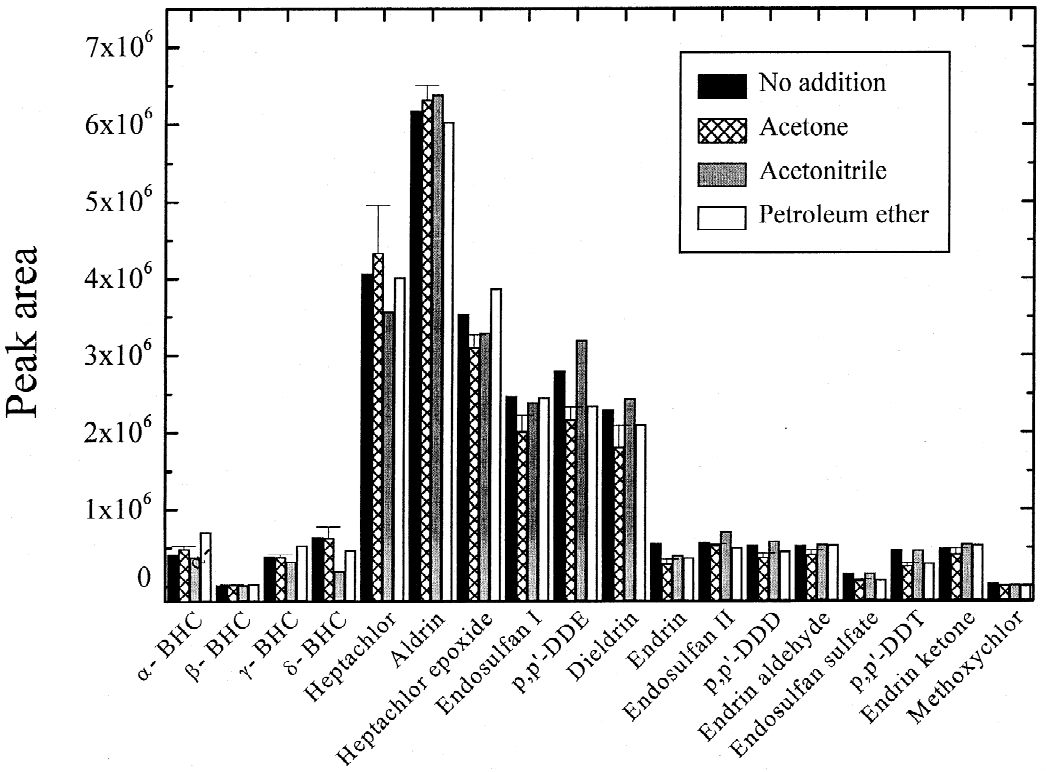

Fig. 5. Influence of the organic solvents on the response after the addition of 100 μl polar solvent to the system containing 5 ml water and 0.5 g soil. The extraction time and temperature were 60 min and 70°C, respectively.

the polar OCPs on the active sites. However, these added solvents would also decrease the responses of certain OCPs, like δ-BHC, endrin, *p,p′*-DDT and methoxychlor. Therefore, 5 ml of water was selected for further optimization.

3.5. Linearity, precision and detection limits

The linearity of the method was tested by extracting the OCPs in the gaseous phases. The concentrations applied were over the range 0.2 to 4 ng/g soil. Also, to fully validate the SPME procedure, its performance was compared to that of the conventional procedure based on Soxhlet extraction of 10 g of soil sample with acetone–hexane (1:1) and subsequent clean-up by Florisil SPE. The procedure was applied to spike 25 ng/g pesticides into soil samples. Table 1 shows the comparison of the linear range, linearity, precision and limit of detection (LOD) of OCPs using the HS-SPME procedure and Soxhlet extraction. The SPME procedure showed a good linear behavior in the tested range, with correlation coefficients ranging between 0.972 to 0.999. Low correlation of BHCs and endosulfan sulfate may be due to the low sensitivities of these compounds to PDMS fiber.

The precision of SPME and Soxhlet extraction was determined by performing six and five consecutive extractions with concentrations of 2 ng/g and 25 ng/g, respectively. The relative standard deviations (RSDs) were in the range from 3.2% (heptachlor) to 26.3% (endrin aldehyde), which is similar to those obtained from Soxhlet extraction (2.6–19.6%). Also, high RSDs may be due to the use of a PTFE-coated stirrer. Paschke et al. [27] showed that the PTFE-coated stirrer could not be recommend for the analysis of hydrophobic organic compounds because of its poor reproducible and the likely considerable adsorption of analytes. Moreover, the LODs of the OCPs obtained from SPME procedures ranged from 0.06 to 0.65 ng/g. The detection limits achieved in this study are comparable to those obtained from Soxhlet extraction (1.03–5.91 ng/g) and the detection limits reported by US Environmental Protection Agency (EPA) Method 8081 (1.1–5.7 ng/g).

3.6. Analysis of CRM soil

To validate the HS-SPME procedure, its performance was compared to that of Soxhlet extraction based on the extraction of OCPs in CRM 804-050 soil. The CRM soil contained γ-BHC, aldrin, diel-

Table 1
Comparison of the linear range, linearity, precision and LOD of OCPs using SPME procedure and Soxhlet extraction

Pesticide	Linear range		Linearity		Precision		LOD (ng/g)	
	SPME (ng/g)	Soxhlet (ng/g)	SPME	Soxhlet	SPME (n=6)	Soxhlet (n=5)	SPME	Soxhlet
α-BHC	0.2–4.0	5–50	0.998	0.988	6.9	5.2	0.14	2.55
β-BHC	0.6–4.0	5–50	0.985	0.997	5.2	8.2	0.65	1.18
γ-BHC	0.3–4.0	5–50	0.997	0.997	7.8	6.6	0.09	1.89
δ-BHC	1.0–4.0	5–50	0.972	0.998	22.2	5.4	0.35	1.03
Heptachlor	0.3–3.0	5–50	0.993	0.997	3.2	17.2	0.22	2.29
Aldrin	0.3–3.0	5–50	0.998	0.997	3.3	7.7	0.06	2.67
Heptachlor epoxide	0.3–4.0	5–50	0.998	0.998	4.3	5.2	0.08	1.53
Endosulfan I	0.3–4.0	5–50	0.997	0.998	7.2	6.5	0.07	1.31
p,p′-DDE	0.2–4.0	5–50	0.999	0.998	4.6	3.2	0.10	1.40
Dieldrin	0.2–4.0	5–50	0.997	0.998	6.6	2.6	0.07	1.76
Endrin	0.3–4.0	5–50	0.995	0.998	4.8	7.6	0.09	1.86
Endosulfan II	0.2–4.0	5–50	0.998	0.998	8.4	6.8	0.16	1.61
p,p′-DDD	0.2–4.0	5–50	0.998	0.997	9.2	4.6	0.15	1.68
Endrin aldehyde	0.2–4.0	5–50	0.996	0.999	26.3	19.6	0.06	5.91
Endosulfan sulfate	0.4–4.0	5–50	0.985	0.997	25.1	18.1	0.36	1.32
p,p′-DDT	0.2–4.0	5–50	0.997	0.997	8.9	9.3	0.15	1.35
Endrin ketone	0.2–4.0	5–50	0.996	0.998	16.7	19.1	0.15	4.29
Methoxychlor	0.4–4.0	5–50	0.996	0.998	14.5	6.5	0.32	2.76

drin, endrin, endosulfan I, *p,p′*-DDE, endosulfan II, *p,p′*-DDD and *p,p′*-DDT. Due to the high concentrations of OCPs in CRM soil, 0.02 g of CRM was used and mixed with other uncontaminated soil to get the total mass of 0.5 g. For HS-SPME and Soxhlet extraction, three replicates of CRM soil were performed. The results obtained with HS-SPME and Soxhlet extraction procedures are shown in Table 2. The mean values obtained by Soxhlet extraction and certified values and ranges of OCPs in CRM soil are also given. The analytical significance of the mean value was statistically studied using the *t*- and *F*-tests. In general, the results obtained with HS-SPME agreed with the mean values obtained using Soxhlet extraction. No significant difference between SPME and Soxhlet extraction with CRM mean values were observed, except for *p,p′*-DDE and dieldrin. Moreover, the results obtained using the *F*-test (95% confidence interval) showed that there was no difference between SPME and Soxhlet extraction. Comparable standard deviations were obtained for the two methods, which ranged from 4.8 to 15.3% and 1.0 to 22.6% for Soxhlet extraction and HS-SPME procedures, respectively. Also, the mean values obtained with HS-SPME agreed with the certified values of CRM soil. The certified values ranged from 18.04 to 1530.6 mg/kg and the average analyzed concentrations of those compounds using HS-SPME were between 16.5 to 1459.6 mg/kg. This corresponds to the recoveries of 68 to 127%. These results indicate that HS-SPME can be considered as an alternative for the determination of OCPs in soil environments.

4. Conclusion

The application of HS-SPME has shown to be a suitable methodology for the determination of 18 OCPs in soil samples. The extraction time of 60 min at the working temperature of 70°C was optimized. The addition of 5 ml of water produced higher sensitivity in extracting OCPs from soil. The developed method provides good performance in terms of precision (RSD between 3 and 26%), linearity and LOD values (0.06 to 0.65 ng/g). The optimized HS-SPME procedure was applied to the analysis of OCPs in CRM 804-050 soil and was compared with Soxhlet extraction procedure. The results obtained were in good agreement with those obtained using Soxhlet extraction and the mean value obtained using HS-SPME technique agreed closely with those certified values, with recoveries of 68 to 127%.

Acknowledgements

The authors would like to thank National Science Council, Taiwan for financial support of this investigation under contract No. NSC 89-2113-M-007-070.

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Table 2
Analysis of OCPs in CRM 804-050 soil using HS-SPME and Soxhlet extraction procedures

OCP	Certified value (μg/kg)	Prediction interval (μg/kg)	Headspace SPME		Soxhlet extraction	
			Mean (μg/kg)	RSD (%)	Mean (μg/kg)	RSD (%)
γ-BHC	491.6	212.04–771.24	623.8	22.6	493.2	7.8
Aldrin	18.04	0–38.37	16.5	13.4	17.78	15.3
Endosulfan I	1464.3	533.57–2395.06	1023.4	4.0	940.9	8.6
p,p′-DDE	1519.6	632.58–2406.73	1028.1	2.0	1553.1	8.1
Dieldrin	1862.5	437.00–3287.99	1316.9	1.0	1784.3	8.9
Endrin	62.2	42.12–82.19	75.9	13.5	74.5	12.6
Endosulfan II	1128.2	246.73–2009.72	1078.0	6.0	923.6	6.9
p,p′-DDD	1530.6	498.99–2562.26	1459.6	14.8	1324.9	4.8
p,p′-DDT	1060.1	464.95–1655.28	1175.7	16.9	1221.2	7.5

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