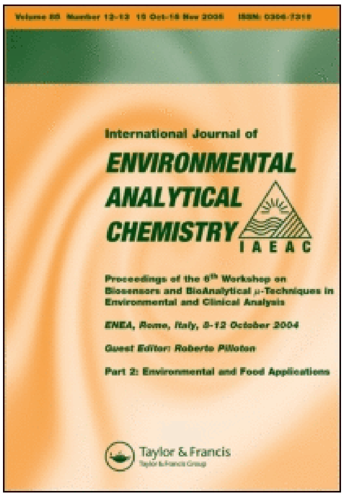

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Determination of pyrethroid, organophosphate and organochlorine pesticides in water by headspace solid-phase microextraction

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Simultaneous determination of pyrethroid, organophosphate (OP) and organochlorine (OC) pesticides in water was achieved with headspace solid-phase microextraction (HS-SPME) followed by gas chromatography-electron-capture detection (GC-ECD). The parameters affecting HS-SPME of pesticides from water were optimized, including extraction temperature, sample and headspace volumes, and sodium chloride amounts. The effects of desorption temperature, desorption time, and position of the fibre in the GC inlet were also investigated. Extraction temperature was the most important factor affecting the recoveries of analytes, and the optimized temperature was 96°C. The addition of salt did not increase extraction efficiencies of the pesticides from the water. The optimized desorption conditions in the GC were as follows: desorption time of 10 min; desorption temperature of 260°C; and a 2 cm position of the fibre in the inlet. The method detection limits were in the low-ng/L level with a linearity range of 50–1000 ng/L for the OCs, 50–5000 ng/L for the OP, and 50–20 000 ng/L for the pyrethroids. These data demonstrated that HS-SPME is a sensitive method for the determination of pyrethroid, OC, and OP pesticides in water.

Keywords: Headspace SPME; Pyrethroid pesticides; Organophosphate pesticides; Organochlorine pesticides; Water

1. Introduction

A relatively new solvent-free non-exhaustive sample preparation technique, solid-phase microextraction (SPME) was introduced by Arthur and Pawliszyn in 1990 [1] and has been used in a number of studies for the analysis of pesticide residues in water [2–5]. In the SPME technique, target analytes are adsorbed or absorbed in the thin layer of extraction phase coated on the fibre which is protected by a needle and then thermally desorbed in the injection port of a gas chromatograph (GC) or solvent-eluted into

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a liquid chromatograph for analysis. SPME extraction can be performed directly, where the coated fibre is immersed into the sample [4], performed with the protection of a membrane, in which the fibre is separated from the sample with a selective membrane [5], or performed in the headspace (HS-SPME), where the fibre is exposed to the gas phase (headspace) above the sample, which is in equilibrium with the sample for the particular target analytes [6].

Considered a selective method for volatile compound analysis [6], HS-SPME has scarcely been used for extraction of less-volatile compounds [7]. In one of the few studies to examine less-volatile compounds, Sakamoto and Tsutsumi [8] tested 174 semi- and less-volatile pesticides in pure water and found that 158 of the 174 tested pesticides could be detected by HS-SPME with elevated temperature at a concentration of 10 μg/L. Though HS-SPME is very useful for extraction of pesticides in environmental matrices, few studies have been conducted using HS-SPMEs to detect pyrethroids from water [9], and no studies were found detailing simultaneous extraction of pyrethroid, organophosphate and organochlorine pesticides by HS-SPMEs. Therefore, the present study used HS-SPME-GC-ECD to simultaneously determine pyrethroid, OP, and OC pesticides in water, and the parameters affecting HS-SPME extraction efficiency were optimized.

2. Experimental

2.1 *Chemicals*

Pyrethroids analysed in this study were bifenthrin, λ-cyhalothrin, permethrin, cyfluthrin, cypermethrin, esfenvalerate and deltamethrin. The organophosphate insecticide, chlorpyrifos also was included along with 20 OC insecticides from four classes including: hexachlorocyclohexanes (BHCs) (α-BHC, β-BHC, λ-BHC and δ-BHC); cyclodiene OCs (aldrin, diedrin, heptachlor, heptachlor epoxide, endrin, endrin aldehyde, endrin ketone, endosulfan I, endosulfan II and endosulfan sulfate); diphenyl aliphatic OCs (p,p'-DDE, p,p'-DDD, p,p'-DDT and methoxychlor); and, chlordanes (α-chlordane and γ-chlordane). Pesticide standards were purchased from Protocol, Middlesex, NJ. The purity of all pesticides used in this study was >96%, as determined by the manufacturers.

Analytical-grade sodium chloride and various solvents were purchased from Fisher Scientific (Pittsburgh, PA). Solvents used in this study were pesticide-grade. A stock solution including a mixture of the analytes was prepared at a concentration of 5 μg/mL in acetone. The working solutions were prepared daily using distilled water, and acetone (<2%) was used as a carrier solvent for the pesticides.

2.2 *Instrumentation and chromatographic conditions*

Experiments were conducted using a SPME fibre assembly with 1-cm-long fused-silica fibres coated with 100 μm polydimethylsiloxane (PDMS) (Supelco, Bellefonte, PA). The fibre was conditioned at 260°C for 30 min at the beginning of the experiments and for 10 min every morning prior to test initiation. A Cimarec® SP131015 stirring hot plate (Barnstead International, Dubuque, IA) was used for temperature and stirring rate control, and a screw-cap glass vial equipped with a Teflon®/silicon septa (Quality Environmental Containers, Beaver, WV) was used as a sample container.

Thermal desorption and analysis were performed on an Agilent 6890 series GC equipped with an electron capture detector (Agilent Technologies, Palo Alto, CA), and separation of the analytes was achieved with a DB-608 column (30 m × 0.25 mm × 0.25 µm film thickness) from Agilent Technologies (Palo Alto, CA). Helium was used as the carrier gas at a flow rate of 1.8 mL/min. The initial temperature of the oven was set at 50°C, quickly heated to 100°C at 30°C/min after 2 min of initial time, to 250°C at 10°C/min, then to 280°C at 3°C/min, and held at 280°C for 15 min. The injection port was set at 260°C and placed in pulsed splitless mode with a pulse pressure of 30 psi for 2°min. The detector temperature was 320°C with nitrogen used as the makeup gas (30 mL/min). The peaks were identified by comparison of retention time to standards with a window of 1%.

2.3 *Method optimization for HS-SPME procedures*

Parameters influencing HS-SPME of pesticides from water were optimized including extraction temperature, sample and headspace volumes, and sodium chloride amounts. The effects of desorption temperature, desorption time, and position of the fibre in the GC inlet were also investigated. A list of the optimization parameters in the order they were tested is provided in table 1. After a test parameter was optimized, the next experiment used the optimized values. For example, the optimized extraction temperature (e.g. temperature of the water sample) was 96°C; therefore, all proceeding experiments were conducted at 96°C.

Experiments were initiated by adding 2000 ng/L of the analyte mixture to distilled water. The spiked water was allowed to sit overnight prior to extraction. The general format for the optimization experiments, using the optimized conditions, was as follows. A 30 mL volume of aqueous sample was introduced into a 40 mL screw-cap glass vial. Three replicate samples were used at each concentration. After capping the vial, the solution was stirred at 900 rpm using a PTFE-coated magnetic stir bar to provide a vortex depth of approximately 1 cm, and the solution heated at 96°C for 10 min. The HS-SPME fibre was then exposed to the headspace of the solution for 35 min. Once the extraction was completed, the HS-SPME device was removed from the sampling vial and immediately inserted into the injection port of the GC to allow for thermal desorption of the pesticides. Calibration for the water samples was based on area using five external standards within the linear range of each compound (table 2). Standard solutions were made by dissolving appropriate amounts of each

Table 1. Optimization parameters listed in the order of their use in the study.

Parameter	Values
Extraction temperatures (°C)	45, 50, 65, 75, 80, 85, 90, 96, and 100
Head-space volumes (mL)	10, 20, and 30
Sodium chloride amounts (mg/mL)	0, 50, 100, and 200
Desorption temperatures (°C)	250, 260, and 270
Desorption times (min)	2, 5, 10, and 15
Positions of the fibre in the inlet (cm)	2, 3, and 4

Table 2. Performance characteristics of target pesticides in water samples measured with HS-SPME.

Compound	Vapour pressure, mmHg (°C)	Linear range (ng/L)	Correlation coefficient (R^2)	RSD (%)[a]	MDL (ng/L)
α-BHC	3.3×10^{-4} (25)[b]	50–15 000	0.9843	25.5	61.0
γ-BHC	3.3×10^{-4} (25)[b]	50–15 000	0.9871	24.1	46.6
β-BHC	3.3×10^{-4} (25)[b]	50–15 000	0.9968	11.5	45.4
δ-BHC	3.3×10^{-4} (25)[b]	50–2500	0.8108	33.5	58.6
Aldrin	2.3×10^{-5} (20)[c]	50–1000	0.9967	6.9	26.5
Dieldrin	1.8×10^{-7} (25)[c]	50–1000	0.9999	15.6	40.4
Heptachlor	3.0×10^{-4} (25)[c]	50–5000	0.9644	51.2	66.0
Heptachlor epoxide	4.7×10^{-7} (25)[b]	50–2500	0.9860	17.4	39.0
Endrin	2.0×10^{-7} (25)[c]	50–2500	0.9966	12.6	25.1
Endrin aldehyde	8.9×10^{-8} (25)[c]	50–20 000	0.9969	13.5	41.6
endrin ketone	1.5×10^{-8} (25)[b]	50–20 000	0.9920	4.2	50.6
Endosulfan I	7.4×10^{-8} (25)[b]	50–10 000	0.9965	52.3	101.7
Endosulfan II	7.4×10^{-8} (25)[b]	50–15 000	0.9973	41.4	67.9
Endosulfan sulfate	6.21×10^{-9} (25)[b]	50–20 000	0.9868	11.8	31.5
p,p′- DDE	9.9×10^{-6} (25)[b]	50–1000	0.9857	7.8	73.6
p,p′- DDD	2.0×10^{-6} (25)[b]	50–1000	0.9979	18.0	50.7
p,p′- DDT	9.4×10^{-7} (25)[b]	50–1000	0.9987	16.2	72.0
Methoxychlor	2.1×10^{-7} (25)[b]	50–20 000	0.9924	16.2	20.2
α-Chlordane	5.0×10^{-7} (25)[b]	50–1000	1.0000	15.8	45.4
γ-Chlordane	5.0×10^{-7} (25)[b]	50–1000	0.9977	10.5	43.0
Chloropyrifos	1.9×10^{-5} (20)[c]	50–5000	0.9773	26.2	44.2
Bifenthrin	1.8×10^{-7} (25)[d]	50–10 000	0.9914	10.9	105.8
λ-Cyhalothrin	1.6×10^{-9} (20)[d]	50–20 000	0.9968	5.8	75.8
Permethrin	1.5×10^{-8} (25)[d]	50–20 000	0.9891	4.2	64.0
Cyfluthrin	2.1×10^{-9} (20)[d]	50–20 000	0.9919	4.3	59.6
Cypermethrin	1.4×10^{-9} (20)[d]	50–20 000	0.9903	2.3	52.6
Esfenvalerate	1.4×10^{-7} (20)[d]	50–20 000	0.9940	4.5	63.4
Deltamethrin	9.3×10^{-11} (25)[d]	50–20 000	0.9959	5.6	12.2

[a]Pesticide concentration: 1 ng/mL, $n = 4$. [b]Verschueren K [17]. [c]Laskowski DA [18]. [d]Scifinder Scholar.

pesticide and surrogate standard in water. These solutions were analysed using the HS-SPME-GC-ECD methods detailed above. A *t*-test was used to compare extraction efficiencies between treatments [10].

The method detection limit (MDL) was defined as the lowest concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and it was computed from seven replicates of extractions of spiked water samples at a concentration of 50 ng/L and were calculated as follows: MDL $= st_{(0.99,\,n-1)}/m$, where s is a standard deviation of the seven replicate measurements, $t_{(0.99,\,n-1)} = 3.14$ is a t-distribution value taken at a confidence level of 0.99 and degrees of freedom of 6, and m corresponds to the slope of the particular calibration curve [11].

3. Results and discussion

Extraction temperature was the most important factor affecting the recoveries of the analytes, and the optimized temperature for pyrethroids was much higher than that for OCs and the OP. Figure 1 demonstrates the influence of extraction temperature on the HS-SPME extraction of pyrethroids, chlorpyrifos, BHCs, cyclodiene OCs,

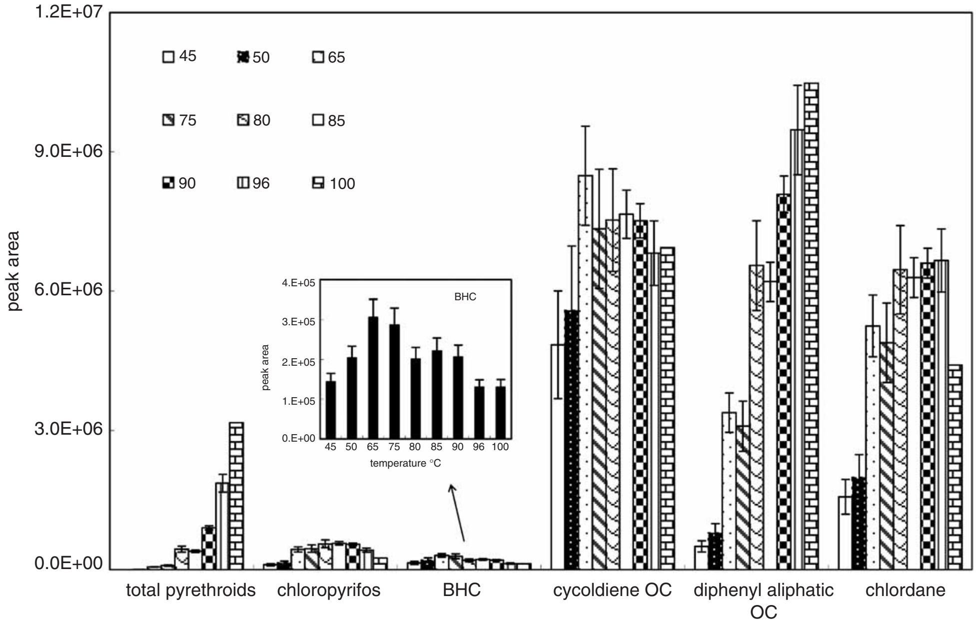

Figure 1. Influence of extraction temperature on HS-SPME extraction efficiency (total peak areas, $n = 3$; $n = 1$ for 100°C; error bars: ±SD) of total pyrethroids, chlorpyrifos, total BHCs, total cyclodiene OCs, diphenyl aliphatic OCs, and chlordanes from water.

diphenyl aliphatic OCs and chlordanes at the temperature range of 45–100°C. As shown in the figure, pyrethroids were not detected when employing HS-SPME when the temperature was lower than 50°C. Increases in detection response of the target pesticides, especially pyrethroids, were observed with an increase in extraction temperature. The most effective extraction was at 80–85°C for chlorpyrifos, the only OP tested. The four classes of OCs presented different temperature-peak area profiles. With relatively higher vapour pressures, the BHCs reached maximum extraction efficiency at the lower temperatures of 65–75°C. The temperature-extraction profiles of the chlordanes produced a plateau in the range of 80–96°C. The optimized temperatures for the cyclodiene OCs ranged from 65°C for heptachlor to 100°C for endosulfan II, endosulfan sulfate, endrin ketone and endrin aldehyde. A higher temperature (>96°C) was needed for the extraction of the diphenyl aliphatic OCs (e.g. DDT serial compounds) and pyrethroids which have lower vapour pressures than the other tested pesticides.

The differences in the extraction-temperature profiles among the target pesticides can be explained by two separate converse absorption phenomenon. The influence of temperature on the SPME absorption can have two effects. From a kinetic view, higher temperatures increase the transfer rate of the analytes from the matrix (e.g. water) to the headspace, while thermodynamically higher temperatures decrease the analytes' partition coefficients between the headspace and fibre [6, 8]. For the less-volatile, lower-vapour-pressure compounds analysed in this experiment, mass transfer of analytes from the aqueous phase to the gas phase was the dominant process controlling extraction efficiencies, and it was enhanced significantly by heating the sample, so an elevated temperature was preferred. However, the partition coefficients

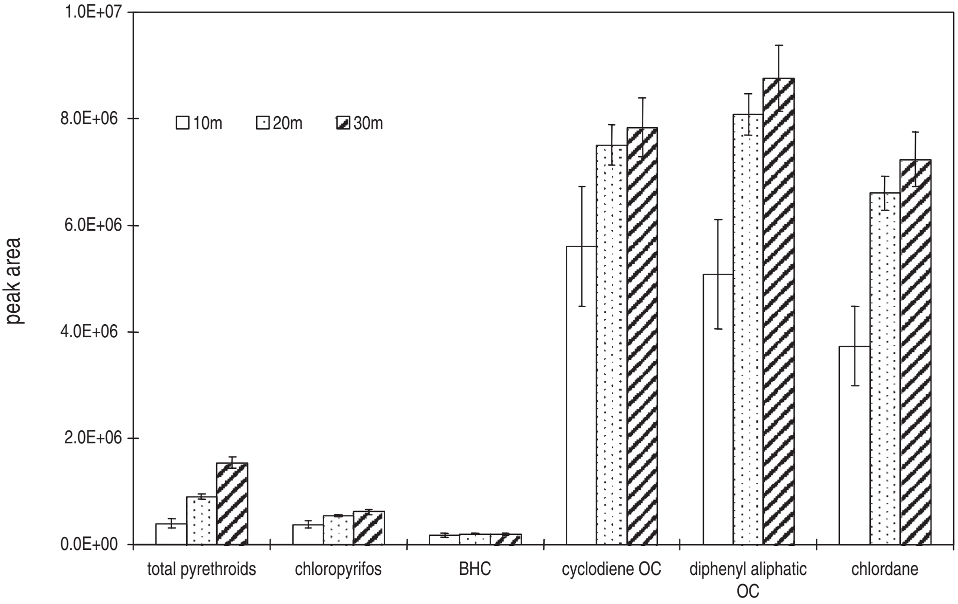

Figure 2. Influence of sample volume on HS-SPME extraction efficiency (total peak areas, $n = 3$; error bars: ±SD) of total pyrethroids, chlorpyrifos, total BHCs, total cyclodiene OCs, diphenyl aliphatic OCs, and chlordanes from water.

between the headspace and the fibre dominated the extraction efficiency for the high-vapour-pressure, more volatile pesticides, so a further increase in temperature resulted in a decrease in their extraction efficiencies. To maximize the extraction of pyrethroids, whose sensitivities on GC-ECD were lower than the OCs and the OP, a higher temperature was needed. To avoid the possible explosion of the SPME vial due to the high pressure of boiling samples, 96°C was chosen for this study.

Headspace volume affected not only the concentration of pesticides in the headspace, but also equilibration times [12]. Different sample and headspace volumes were compared for the extraction of pesticides, and the results are shown in figure 2. Significant differences in peak areas were observed when the water volume increased from 10 to 20 mL, with the exception of total BHCs that were not affected by the sample volumes tested. The best results for pyrethroids were achieved with 30 mL of water placed into a 40 mL vial. With an increase in water sample volume, the gas–liquid ratio decreased, which resulted in higher concentrations of the pesticides in the headspace, which favoured the extraction process [9]. As shown in figure 2, the extraction efficiency of the lower-vapour-pressure compounds (e.g. pyrethroids) was more strongly influenced by headspace volume.

Previous studies [2] have shown that the addition of sodium chloride to the water sample can increase the extraction efficiency for many compounds, so the influence of this parameter was also investigated (figure 3). No significant difference in extraction efficiency was found for diphenyl alphatic OCs and the chlordanes, while the extraction efficiency of BHCs, chlorpyrifos, and the cyclodiene OCs was slightly enhanced with the addition of 50–200 mg/mL of sodium chloride. However, a decrease in extraction efficiency was found for the pyrethroids with the addition of sodium chloride.

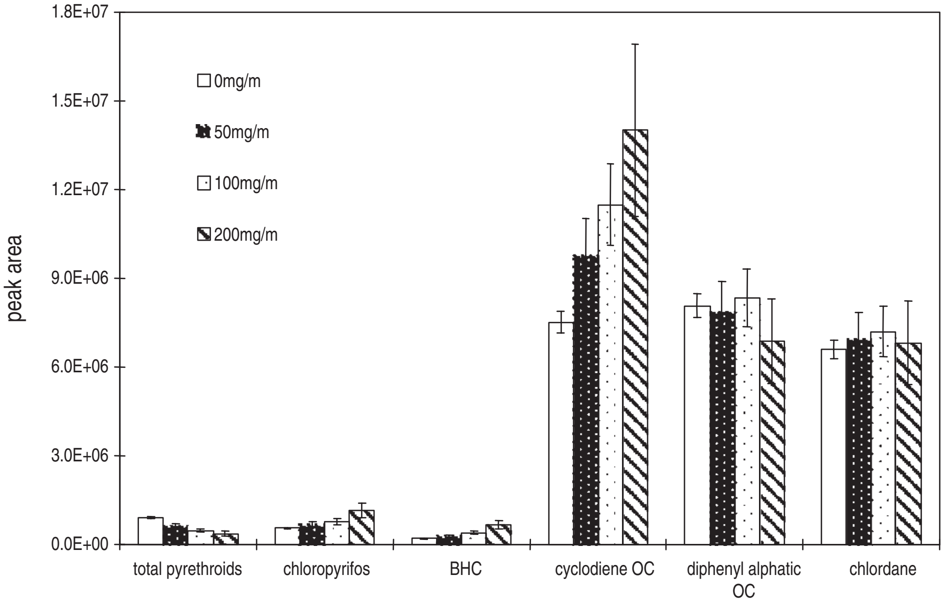

Figure 3. Influence of sodium chloride on HS-SPME extraction efficiency (total peak areas, $n = 3$; error bars: ±SD) of total pyrethroids, chlorpyrifos, total BHCs, total cyclodiene OCs, diphenyl aliphatic OCs, and chlordanes from water.

Two factors can help explain the influence of salinity of a sample on the extraction of pesticides from water. First, by adding sodium chloride, the solubility of the target compounds in water was reduced, permitting a higher distribution of the compounds in the headspace and onto the SPME fibres. This 'salting-out' effect has previously been shown to be effective in enhancing the extraction efficiencies for some polar compounds, such as phenol [13]. In our study, the positive attributes of sodium chloride on extraction efficiencies were only noted for BHCs, chlorpyrifos, and the cyclodiene OCs. On the other hand, the presence of higher concentrations of sodium chloride within the matrix may reduce the molecular movement of the target analytes, resulting in a decrease in extraction efficiency [14]. The influence of molecular movement on the extraction process was examined in the present study by comparing the extraction efficiency of target pesticides using different stirring rates. The ratios of the extraction efficiency at stirring rates of 700 and 900 rpm were 136.2, 103.8, 110.9, 98.1, 85.9, and 53.1% for BHCs, chlorpyrifos, cyclodiene OCs, chlordanes, diphenyl alphatic OCs, and pyrethroids, respectively. These results showed a correlation between molecular movement and extraction efficiency and that stirring rate affected pyrethroid insecticide extraction efficiencies to the greatest extent. These results supported the observation of a negative effect of salt addition for the extraction of pyrethroids. Therefore, the use of sodium chloride was not considered helpful in increasing extraction efficiencies in this study.

Three thermal desorption parameters, including desorption temperature, desorption time and position of the fibre in the GC inlet were also investigated. First, desorption temperatures were tested in the range of 250–270°C, and no significant change in peak area of the test pesticides was observed. Second, without enough desorption time, carryover may occur for higher-boiling-point compounds [3, 15], so desorption times in the range of 2–15 min were tested to minimize carryover. Carryover for all the test pesticides was lower than 1% when the desorption time was equal to or longer than 10 min. The position of the fibre in the GC inlet had a significant impact on the peak area of the test pesticides. The total peak area of the test compounds at the 2 cm position of the SPME fibre assembly (1.3×10^7) was five times higher than that at the 3 cm position (2.8×10^6) and seven times higher than at the 4 cm position (1.8×10^6). Therefore, 10 min, 260°C, and the position of fibre in the GC inlet of 2 cm were chosen as the optimum thermal desorption conditions.

SPME sensitivity reached a maximum when the analytes achieved equilibrium between the sample and the fibre. Equilibrium time between the headspace and fibre was determined after the parameters affecting SPME efficiency were optimized. The equilibrium time was approximately 60 min for the pyrethroids, and is similar to the results of Barrionuevo *et al.* [15]. A relatively shorter equilibration time was needed for the OCs and OP. The equilibrium time was 10 min for the BHC pesticides; 20 min for chloropyrifos, heptachlor, aldrin, heptachlor epoxide, endosulfan I, and endosulfan II; 30 min for the chlordanes, dieldrin, and endrin; 45 min for diphenyl aliphatic OCs, endosulfan sulfate, and endrin ketone; and 60 min for endrin aldehyde. A decrease in signal was observed for the pesticides with shorter equilibrium times as the extraction times increased. A decrease in signal (and corresponding higher relative standard deviations, RSDs) for these particular pesticides when using the longer extraction times may be caused by compound replacement on the fibre coating. Moreover, higher RSDs can also be caused when using shorter extraction times than needed to reach equilibrium conditions, because samples may be in the steep portion of the extraction profile, and a small change in conditions can cause a large change in RSDs. Therefore, strict control of extraction time is essential to obtain reproducible results.

3.1 *Performance characteristics*

Table 2 illustrates the linearity, precision, and MDL of the target pesticides by the proposed HS-SPME method for spiked water samples. The linear range for the pyrethroids (50–20 000 ng/L) was wider than that for the OCs (50–1000 ng/L) and OP (50–5000 ng/L), while the correlation coefficients for most of the tested analytes showed a good linearity with a range of correlation coefficients from 0.96–1.00. The low correlation coefficient found for *delta*-BHC (0.81) may be caused by its low affinity for the PDMS fibre, since it has the lowest octanol–water partition coefficient ($\log K_{\mathrm{ow}} = 2.80$ [16]) of the tested compounds. Precision was determined using a quad study (e.g. four water samples were spiked with all of the analytes at a concentration of 1 ng/mL). The precision of the HS-SPME method for most of the pesticides was good with the RSDs being lower than 20%, with the exception of α-BHC, γ-BHC, delta-BHC, heptachlor, endosulfan I, endosulfan II, and chlorpyrifos, which had higher RSDs. The higher RSDs for these pesticides may have been due to their lower affinity for the PDMS fibre, low GC instrumental sensitivity [3], or shorter equilibrium time of these compounds on the PDMS fibre (as described earlier). The MDLs were quite low and ranged from 12.2 to 105.8 ng/L for pyrethroids, 20.2–101.7 ng/L for OCs, and 44.2 ng/L for chlorpyrifos, respectively (table 2). Overall, these data showed that HS-SPME is a sensitive method for the determination of pyrethroid, OC, and OP pesticides in water.

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References

[1] C.L. Arthur, J. Pawliszyn. *Anal. Chem.*, **62**, 2145 (1990).
[2] A.A. Boyo-Bcland, S. Magdic, J.B. Pawlizyn. *Agro-Food-Industry Hi Tech*, November/December, 26 (1996).
[3] K.K. Chee, M.K. Wong, H.K. Lee. In *Application of Solid Phase Microextraction*, Pawliszyn, J. (Ed.), pp. 212–226, The Royal Society of Chemistry, Cambridge (1999).
[4] D.A. Lambropoulou, V.A. Skkas, T.A. Albanis. *Anal. Bioanal. Chem.*, **374**, 932 (2002).
[5] L. Hou, H.K. Lee. *J. Chromatogr. A*, **1038**, 37 (2004).
[6] Z. Zhang, J. Pawliszyn. *Anal. Chem.*, **65**, 1843 (1993).
[7] H.P. Li, G.C. Li, J.F. Jen. *J. Chromatogr. A*, **1012**, 129 (2003).
[8] M. Sakamoto, T. Tsutsumi. *J. Chromatogr. A*, **1028**, 63 (2004).
[9] B.D. Page, G. Lacroix. *J. Chromatogr. A*, **757**, 173 (1997).
[10] J.C. Miller, J.N. Miller. *Statistics for Analytical Chemistry*, 3rd edn, Ellis Horwood, Chichester, UK (1993).
[11] D.C. Harris. *Quantitative Chemical Analysis*, 6th edn, W.H. Freeman & Co., New York (2003).
[12] T. Górecki, J. Pawliszyn. *Analyst*, **122**, 1079 (1997).
[13] K.D. Buchholz, J. Pawliszyn. *Environ. Sci. Technol.*, **27,** 2844 (1993).
[14] C. Goncalves, M.F. Alpendurada. *J. Chromatogr. A*, **963**, 19 (2002).
[15] W.R. Barrionuevo, F.M. Lancas, *J. High Resol. Chromatogr.*, **23**, 485 (2000).
[16] J.H. Montgomery. *Agrochemical Desk Reference: Environmental Data*. Lewis, Boca Raton, FL (1993).
[17] K. Verschueren. *Handbook of Environmental Data on Organic Chemicals*, 2nd edn, Van Nostrand Reinhold, New York (1983).
[18] D.A. Laskowski. *Rev. Environ. Contam. Toxicol.*, **174**, 49 (2002).