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Application of solid-phase microextraction to the headspace gas chromatographic analysis of semi-volatile organochlorine contaminants in aqueous matrices

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Abstract

Solid-phase microextraction (SPME) has been applied to the headspace gas chromatographic (HS-GC) analysis of 14 selected halogenated pesticides and contaminants ranging in volatility from hexachlorobenzene (HCB) to decachlorobiphenyl (DCBP). Elevated temperatures were employed to obtain time-efficient HS-SPME of the later-eluting analytes. A larger sample size provided improved method detection limits (MDLs, $S/N=5$, electrolytic conductivity detection) despite slightly reduced extraction efficiencies. With a small 15-ml sample, the HS–SPME efficiencies ranged from ca. 3 to 68%, the repeatabilities (R.S.D.) at 67–670 ng/l ranged from 5.9 to 21.7%, and the MDLs ranged from 3 to ca. 60 ng/l. With a larger 110-ml sample, repeatabilities ranged from 5.6 to 14.6%. MDLs for 10 of 14 analytes ranged from 0.3 to 0.8 ng/l and from 1.5 to 10 ng/l for the others.

Keywords: Extraction methods; Headspace analysis; Water analysis; Pesticides; Organochlorine compounds

1. Introduction

Solid-phase microextraction (SPME) is a simple technique for the solventless extraction and concentration of analytes for gas chromatographic (GC) analysis. Originally developed and studied extensively by Pawliszyn and co-workers [1–4], SPME has now become an important part of an emerging emphasis on reduced solvent use and environmentally-friendly methodology. A number of recent applications of SPME to aqueous environmental samples have been reported [5–9].

The technique of SPME employs a coated fiber, usually polydimethylsiloxane (other coatings are also available), to extract and concentrate non-polar analytes which are then desorbed in the injection port of a gas chromatograph for analysis. The extraction of a sample by SPME can be conducted directly, with the coated fiber immersed in a liquid sample, or in the headspace (HS), where the extracting fiber is suspended above the sample, usually in a closed system. The HS approach is preferred when the sample matrix contains undissolved particles or non-volatile dissolved material which may be transferred to the GC injector, or non-polar non-volatile material which may contaminate the coated fiber. The theory of HS-SPME has been described in detail by Zhang and Pawliszyn [4]. The SPME device is commercial-

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ly available or it can be easily assembled from readily available components [2].

The HS-SPME technique is usually applied in an equilibrated situation with the analytes distributed between the fiber coating, the HS gas, and the aqueous and/or any non-aqueous non-polar phase present in the sealed HS container. The amount of an analyte present in the coating compared to that added or present in the HS vial is a measure of the extraction efficiency, or percent extracted for that analyte under the conditions of that analysis. This equilibrated amount is usually related to that from an appropriately spiked matrix for the HS-SPME quantitation. The addition of salt to the aqueous matrix is often used to increase the extraction efficiency.

Non-polar analytes with low vapor pressure can be analyzed by HS-SPME but the time required to attain an equilibrium for these analytes is greatly increased because of the low analyte vapor pressure. Furthermore, the particular sample matrix, the stirring efficiency in the aqueous phase and that imparted to the gas phase, the amount of sample, the size of the HS container, the ratio of the HS to aqueous phase and the position of the coated fiber in the HS can all affect the time required for the analyte to equilibrate between the HS vial contents and the SPME fiber coating [4]. Increasing the analyte vapour pressure by increasing the temperature will decrease the equilibration time although the equilibrated extraction efficiency will be reduced [4]. Analytes can also be determined in a non-equilibrated state providing adequate repeatabilities for the analytes are demonstrated. This approach is practical with slow equilibrations where the incremental increase in extracted analyte at the time of analysis is small. Alternatively, suitable internal standards, preequilibrated with the target analytes before the SPME step, can be used. If the sample contains lipid material, as in some food samples, the equilibrated analyte extraction efficiencies can be severely reduced [10] as the non-polar food components compete with the SPME coating for analytes.

SPME was initially employed for the direct analysis of non-polar volatiles in water [3], and has been recently applied to the direct or HS extraction of non-polar semi-volatile pesticides, herbicides and other contaminants in water [5–9]. These procedures employ various detection techniques of differing selectivities and sensitivities and report method detection limits (MDLs) of low ng/ml to low ng/l. Apart from the GC detection, however, none of the above studies address in detail the use of a greater sample size and amount of analyte with increased temperature, to improve the practical HS-SPME MDLs while maintaining acceptable extraction times.

The present study employs HS-SPME–GC with electrolytic conductivity detection (ELCD) to study the effects of salt addition, increased temperature, HS extraction time, increased sample size and resulting reduced HS to aqueous ratios to optimize method detection in aqueous matrices for the 14 non-polar semi-volatile chlorinated pesticides and contaminants in Table 1. The method was then applied to selected bottled water samples.

2. Experimental

2.1. HS-SPME equipment and procedures

The SPME device was constructed as described by Potter and Pawliszyn [2] with minor modifications as described previously [10]. A 1 cm length of 100 μm thick poly(dimethylsiloxane)-coated fused-silica optical fiber was used. A needle spacer, consisting of a 16 or 17 ga luer hub hypodermic needle cut so that the SPME device needle protruded about 0.5 cm when the spacer was attached, was used to standardize needle insertion.

For HS-SPME extraction, 30, 50, 100 and 125 ml (nominal size) crimp-top HS vials (actual capacities about 37, 58, 119 and 153 ml, respectively), 20 mm×2.7 mm laminated silicone–PTFE (0.25 mm) septa, prepierced in place, if required, for facile passage of the SPME needle, and aluminum seals (Supelco, Oakville, Ont., Canada) were used. PTFE-coated, 25×7.5 mm magnetic stirring bars were added to each vial. With the HS vial on the magnetic stirrer or in the headspace extraction oven, the needle was inserted so the spacer pushed firmly on the aluminum cap or septum surface and the fiber assembly extended so the end of the fiber was about 1 cm above the surface of the liquid. The syringe was clamped in this position and the stirring com-

Table 1
Analytes studied in order of elution, reference numbers, relative concentrations and percent extracted by HS-SPME from different volumes in different HS vials at different extraction temperatures and times

Number	Contaminant	Relative concentration	% Extracted				
			15 ml[a] (30 ml)[b] 68°C (0.75 h)	15 ml (30 ml) 87°C (0.75 h)	15 ml (125 ml) 87°C (0.75 h)	110 ml (125 ml) 87°C (1.0 h)	122 ml (125 ml) 87°C (1.0 h)
1	HCB	2	43.9	21.8	6.3	21.3	26.0
2	Lindane (γ-HCH)	5	7.5	2.7	2.8	0.9	0.6
3	Heptachlor	1	46.7	31.8	12.8	29.5	36.3
4	Aldrin	1	58.2	50.1	20.1	43.6	45.0
5	Heptachlor Epox.	1	49.9	44.4	25.3	22.6	17.0
6	γ-Chlordane	1	59.8	52.5	26.8	44.6	37.6
7	*trans*-Nonachlor	1	61.5	59.3	28.8	48.7	53.0
8	*p,p*-DDE	1	66.5	68.0	23.6	51.2	59.5
9	*o,p*-DDT	1	58.2	60.0	27.8	49.9	55.5
10	*p,p*-DDT	1	44.9	52.4	22.0	27.9	42.4
11	Mirex	1	63.3	54.7	32.0	57.3	58.9
12	*cis*-Permethrin	10	3.8	23.0	4.4	14.5	14.1
13	*trans*-Permethrin		2.3	18.7	2.9	10.2	11.2
14	DCBP	1	22.1	47.6	9.7	22.9	21.3

[a] Volumes of water: 15, 110 and 122 ml, with 6, 45 or 50 g added sodium chloride, respectively.
[b] Nominal volume of HS vial; actual volumes about 37 and 153 ml, respectively.

menced at a rate to give a vortex depth of 1 cm. After 45 or 60 min or other predetermined extraction time, the fiber was retracted, the syringe needle withdrawn from the septum, the spacer removed, the needle inserted into the GC injector, the fiber extended, and the oven and injector temperature programs started. The fiber was left in place and desorbed for at least 23 min.

2.2. Headspace extraction oven

A GC oven with an air circulating fan was used to heat the HS sample vials as shown in Fig. 1. The vials were held in the oven at the neck by a metal clip (not shown) and supported by an adjustable aluminum platform so that the septum and seal were about 4 cm below the upper oven inside surface. The SPME needle with spacer was inserted into the oven through a hole in the oven roof. A stand and clamp or other support (not shown) on top of the oven held the SPME device in place. Thus the HS sample vial and contents, the septum and seal, and the lower 4–5 cm of the SPME needle are heated to the oven temperature. Magnetic stirring was achieved using a conventional magnetic stirrer (top removed) under the GC oven (supported on blocks for increased clearance) with a shaft extension through the oven floor to the stirrer magnet.

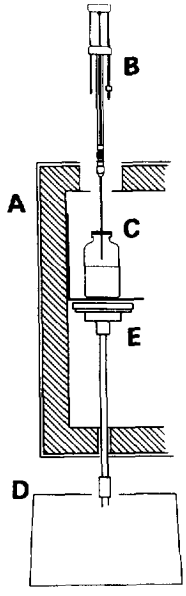

Fig. 1. HS-SPME apparatus for semi-volatiles: A, headspace oven; B, SPME device; C, HS vial; D, stirrer with shaft extension to magnet; and E, magnet.

2.3. Gas chromatograph and detection

A Varian Model Vista 6000 GC with cryogenic oven cooling, a modified on-column injector, and a Hall electrolytic conductivity detector (reductive halogen mode) were used as described previously [10].

A 15 m×0.25 mm DB-5 (0.25 μm film, J&W Scientific, Folsom, CA, USA) fused-silica capillary column was connected to the injector by a 0.5 m×0.53 mm I.D. piece of deactivated fused-silica tubing. The coated SPME fiber was positioned about 2.0–2.5 cm into this tubing for analyte desorption. Helium at 1 ml/min (32 cm/s) was used as a carrier gas. The analytes were desorbed from the fiber in the injector by a temperature program from 60°C to 250°C at 60°C/min with a 23-min hold. The oven was programmed from 60°C (2-min hold) for SPME desorption to 160°C at 30°C/min and then to 270°C at 6°C/min (2-min hold). The ELCD detector base was at 280°C and the reactor at 850°C. A 6-min vent was employed. An electron-capture detector (ECD, Varian 3400 GC, ^{63}Ni, DB-5 capillary column as above) and a mass spectrometric detector (MSD, HP 5890 GC, HP 5970B MS, 30 m×0.25 mm, 0.25 μm film DB-5MS capillary column) were also used to evaluate the potential for lower MDLs. The mass spectrometer was operated in the SIM mode. For each analyte, two prominent ions, selected to minimize interferences, were monitored.

2.4. Standards and reagents

The semi-volatile analytes determined and studied are listed in Table 1. Individual primary stock solutions were prepared at 1 mg/ml in ethanol using chemicals purchased separately except for hexachlorobenzene and mirex which were dissolved in acetone and for DCBP dissolved in toluene–acetone. Stock solutions were diluted as required for spiking in ethanol and in hexane for direct injections. Because of different HS-SPME efficiencies the relative concentrations of the diluted solutions were varied ten-fold as noted in Table 1.

Bottled spring water samples and sodium chloride (analytical reagent) were evaluated for interferences using the same conditions as in the intended study or analysis. Suitable water sources were then selected for studies as described below.

2.5. Studies in aqueous systems

The following HS-SPME studies were carried out by spiking appropriate volumes of water with ≤10-μl samples of ethanolic standard solutions. Typically, 1, 2 or 10 ng of each analyte (see Table 1) in 2 μl were added through the septum into the water and salt in the sealed vial. For estimation of detection limits, one tenth or less of the above amounts again in 2-μl volumes were similarly added.

Extraction efficiencies were determined by comparison of the analyte peak areas from the particular SPME extraction and desorption to those from a direct injection of the same amount that was spiked.

The effects of salt on the extraction efficiencies were determined by comparing the HS-SPME responses from 30-ml sample vials containing 6 g of sodium chloride (to saturate 15 ml water) to those with no added salt at 87°C. Because of the greatly increased peak heights with salt saturation, all further studies were conducted with the aqueous phase saturated with sodium chloride.

To observe the effects of temperature and time, extraction efficiencies were determined at 23, 45, 68 and 87°C for periods of up to 16.5 h. Thirty-ml HS sample vials containing 15 ml of water and 6 g of sodium chloride were spiked as described above.

The extraction efficiencies with increased vial capacity and sample size and constant septum-sample clearance were studied using 30, 50, 100 and 125 ml (nominal size) headspace sample vials containing 6, 14, 34 and 45 g of sodium chloride (for saturation) and 15, 35, 85 and 110 ml of water, respectively. Equilibration times were 45 min (30- and 50-ml vial) or 1 h (100- and 125-ml vial). The actual sample temperatures profiles were determined in separate experiments by inserting a thermometer into the liquid in the headspace vial during heating and stirring in an 87°C oven. The vial capacity and the volume of the saturated sodium chloride solution were measured using graduated cylinders. The headspace volume was determined by difference. The resulting headspace/liquid phase ratios, excluding the stirring bar, were determined for the above 4 sizes of HS vials for comparison to the determined extraction efficiencies. The repeatabilities ($n=6$) of the extraction efficiencies were determined at selected concentrations and HS vial sizes as noted in Table 2.

The MDLs for HS-SPME, defined as that concentration of analyte in a clean water matrix that gives a peak with S/N ratio of 5, were estimated for the 30-ml sample vial containing 15 ml of water and for the 125-ml vial containing 110 ml of water spiked as noted above.

3. Results and discussion

3.1. Equipment and apparatus

The described headspace oven permitted heating of the entire HS vial including the aluminum seal, septum and neck of the sealed vial. Heating the vial by immersion in a waterbath fails to heat these areas and sample water will condense on the exposed neck of the vial and the septum, possibly dripping onto the fiber. This condensate will become a second liquid phase in the vial, as it will not be saturated with sodium chloride and may be at a different temperature. The effect on the HS-SPME efficiency is not known. The heating of the HS vial contents in the oven, however, is slower than in a waterbath. The recorded temperature profiles with magnetic stirring indicated that a 15-ml water sample in a 30-ml HS vial takes 18 min to reach within 1°C of the 87°C oven air temperature whereas only 5 min were required in a 150-ml water bath at 87°C. The times required for the 35, 85 and 110 ml contents to reach within 1°C of 87°C for the 50-, 100-, and 125-ml HS vials used in our study were 24, 32, and 41 min, respectively. The actual (measured) volumes of the 30-, 50-, 100- and 125-ml HS vials were 37, 58, 119, and 153 ml, respectively. With salt-saturated water the gas to liquid ratios were 1.1, 0.49, 0.27, and 0.25, respectively. The analytes were desorbed from the SPME fiber coating in the injector for 23 min. This ensured complete desorption as no carryover was observed on redesorption.

Table 2
HS-SPME repeatability and estimated method detection limits (MDLS) at several concentrations, HS vial sizes and temperatures using ELCD

Analyte	Repeatability, R.S.D. (%), 87°C, spike			MDL (S/N=5, ng/l)[a]			
	15 ml	110 ml	110 ml	SPME (68°C)	SPME (87°C)	EPA (Method number)[b]	
	67 ng/l	67 ng/l	10 ng/l	15 ml	110 ml		
HCB	6.8	14.6	12.4	7	0.8	2	(505)
Lindane (γ-HCH)	21.7	10.6	–[c]	13	11	3	(505)
Heptachlor	7.2	6.9	9.5	5	0.8	3	(505)
Aldrin	8.8	5.6	5.3	4	0.4	80	(508)
Heptachlor epox.	5.9	12.3	9.0	3	0.5	4	(505)
γ-Chlordane	7.3	9.6	5.5	3	0.3	2	(508)
trans-Nonachlor	6.3	10.4	8.1	3	0.4	10	(505)
p,p-DDE	13.8	8.0	11.7	6	0.6	10	(508)
o,p-DDT	11.4	12.4	14.2	8	0.7	–	
p,p-DDT	9.1	6.6	21.5	6	0.7	60	(508)
Mirex	8.0	5.7	25.7	3	0.5	–	
cis-Permethrin	16.1	10.0	25.8	30	6	500	(508)
trans-Permethrin	11.7	13.9	30.7	60	8	500	(508)
DCBP	14.7	14.4	14.7	9	2	–	

[a] MDL=estimated method detection limit for SPME defined as that concentration of analyte in a clean water matrix that gives a peak with S/N ratio of 5.
[b] E.P.A. method (indicated) with lowest MDL.
[c] – Not determined, peak too small.

3.2. Studies in aqueous systems

We have previously demonstrated [10] that salt increases the equilibrated SPME efficiency for relatively volatile analytes. With the semi-volatile analytes currently under study, saturation of the aqueous sample with sodium chloride also increased the extraction efficiency for each analyte. The % increase ranged from about 20% to 600%. These extraction efficiencies were determined in a 30-ml HS vial with 15 ml of water at 87°C and a 45-min extraction. Under these conditions, however, some analytes are not equilibrated as noted below. Because of these significant increases in extraction efficiency, sodium chloride was added in all other studies and determinations.

The extraction efficiencies obtained at 23 and 87°C at extraction times from 0.25 to 16.5 h are shown in Fig. 2. The room temperature (23°C) data for the permethrins and DCBP are not plotted as their peaks were not observed in the chromatogram. The data at the intermediate temperatures were found to lie between these two plots. Only HCB, the most volatile analyte (evidenced by earliest GC elution) reached an equilibrium at 23°C. For our purposes, an equilibrium between the silicone fiber coating and the other HS sample vial contents is defined as an apparent plateau, a levelling off or a maximum in the plot of extraction efficiency vs. time. All other analytes continued to increase, whereas the permethrins and DCBP, as noted above, were not detected at all. At 87°C, however, the earlier eluting HCB, lindane and heptachlor are moderately decreasing after about 1 h, aldrin and heptachlor epoxide have slightly decreased and the other analytes have levelled off or are still slightly increasing. The reasons for decreasing extraction efficiencies with time are not known, but analyte leakage from the HS vial, the headspace being under pressure due to thermal expansion, adsorption by exposed silicone at the HS septum puncture site, or analyte decomposition or interactions are possible explanations.

Practical considerations for our routine analysis require an extraction time not more than 1 h with good repeatability and method sensitivity. With such an extraction time an elevated temperature is required to give good sensitivity for most of the target analytes. Good repeatability should be achieved with

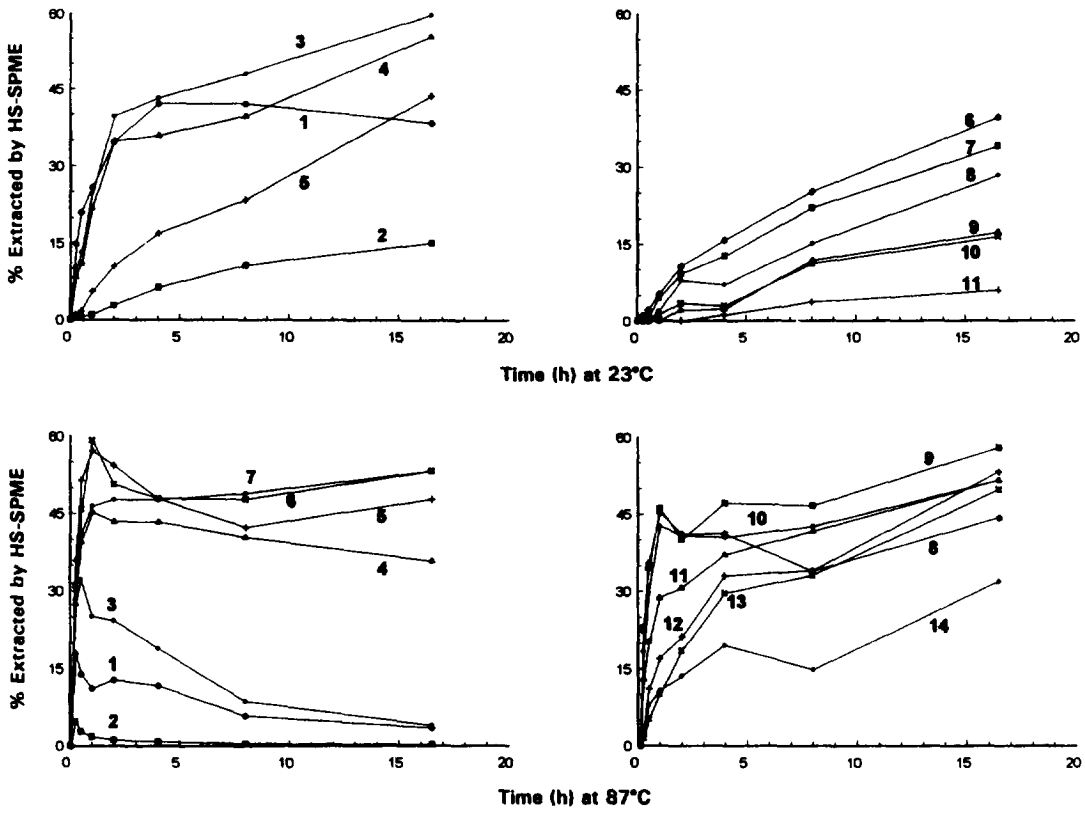

Fig. 2. Extraction efficiency–time profiles of the 14 target analytes listed in Table 1 at 23 and 87°C.

extraction periods extending to an apparent levelling off in the % extraction or even a continuing gradual increase, as a small change in extraction time should give only very small changes in peak area of the extracted analyte. Consistent stirring is also required for a repeatable analysis. For the 14 target analytes a 45-min extraction at 87° was chosen, emphasizing the extraction of the less volatile analytes. As expected [4], the earlier eluting HCB or lindane, required a lower extraction temperature for an optimum extraction. With the range of volatility in our target analytes, it is not possible to optimize the extraction conditions for all analytes. A chromatogram of the target analytes by direct injection is shown in Fig. 3A. Fig. 3B shows the HS-SPME chromatogram of the same amounts spiked into 15 ml of water under the chosen SPME conditions.

The effect on the extraction efficiencies of increasing sample size in increasingly larger HS vials was studied using the 1 cm length of coated fiber while maintaining the distance between the septum and the aqueous surface at a practical, yet arbitrary 35 mm, the same as that in the 30-ml vial used in the above studies. Thus, as the vial capacities and amounts of sample and analytes increase, the gas to liquid ratio decreases as noted above, even though the gas phase volume also increased because of the larger diameter HS vials.

Table 1 lists the extraction efficiencies obtained at selected times and temperatures for the target analytes in 30- and 125-ml HS vials. The effects of temperature on the extraction efficiency are shown in the first two data columns. At 68°C the earlier-eluting analytes are extracted with a greater efficiency than at 87°C, the three last-eluting analytes with less efficiency, and the mid-range eluting analytes are extracted with a similar efficiency. The equilibrated extraction efficiency of HCB, the most volatile (earliest eluting) analyte, decreases from 43.9% at 68°C to 21.8% at 87°C. This reduction in

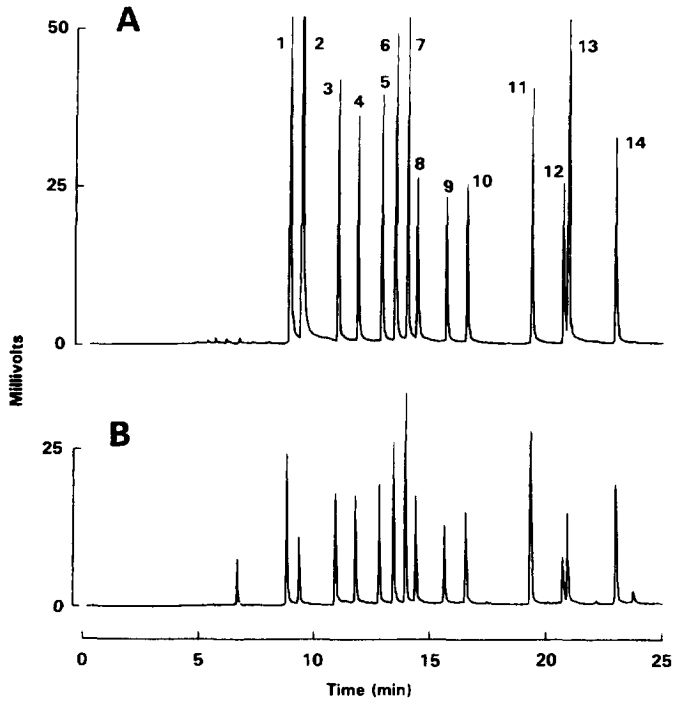

Fig. 3. Chromatograms of: (A) target analytes (about 1, 2, 5 or 10 ng each analyte, peak identities as in Table 1) by direct injection; (B) as in (A) but by HS-SPME over 15 ml salt-saturated water at 87°C.

the equilibrated extraction efficiency with increasing temperature is predicted by theory [4]. A similar trend is noted for lindane and to a lesser extent for the other earlier-eluting analytes. For the permethrins and DCBP, the extraction efficiencies after 0.75 h are found to increase with temperature. With these analytes, however, an equilibrium extraction is not attained. The higher extraction efficiencies at 87°C result from a greater vapor pressure and faster extraction even though the equilibrated extraction efficiency would be lower at 87°C than at lower temperatures.

A comparison of the second and third data columns of Table 1; 15 ml of water in a 30-ml or a 125-ml HS vial, respectively, demonstrates the decrease in extraction efficiency with an increase in the gas to liquid ratio. Additionally, in the larger 125-ml vial the fiber is also farther from the aqueous surface and the headspace volume is much larger and less effectively mixed. These factors which reduce the rate of analyte transfer to the fiber, increase the time required to attain or approach analyte equilibrium. On the other hand, the sample surface area in the larger vial is greater, a factor which should increase the rate of transfer to the gas phase, but is probably of less importance.

The extraction efficiencies in the last two columns in Table 1 represent the lowest gas to liquid ratios, 0.25 and 0.1 for 125-ml HS vials containing 110 and 122 ml of water, respectively, with salt to saturate. The vial containing 122 ml of water has a headspace clearance of 25 mm, which represents practical minimum. With these larger sample volumes the extraction times were increased by 15 min to compensate for the slower heating and transfer in the liquid phase. With a 1-h extraction there is a slight increase in the extraction of the earliest eluting analytes, except for lindane.

A comparison of the second and fourth data columns in Table 1 show that a 7.7-fold increase in sample volume has only a slight effect on the extraction efficiency, except for the last three eluting analytes. Thus, the increased amount (mass) of analyte available for HS-SPME resulting from this

increased sample volume results in the lower MDLs as noted below in Section 3.4.

3.3. Repeatability

Acceptable repeatabilities ranging from about 7 to 21%, 6 to 15% and 5 to 31% were determined at 67 ng/l (15 ml), 67 ng/l (110 ml) and 10 ng/l (110 ml) respectively, all at 87°C as shown in Table 2.

3.4. Method detection limits (MDLS)

The MDLs for the HS-SPME procedure using ELCD are given in Table 2. A recent review of drinking water analysis [11] list the MDLs for a number of US Environmental Protection Agency (EPA) methods. EPA methods often provide a benchmark for evaluation and comparison of newer procedures. MDLs for two EPA procedures are also given in Table 2. These EPA procedures both involve a liquid–liquid extraction with or without concentration and GC with electron-capture detection (ECD). For a 15-ml water sample at 68°C the HS-SPME MDLs are comparable to those of the most sensitive EPA procedures except for lindane. Lindane is unique in that its octanol–water partition coefficient is 2–3 orders of magnitude lower than those of the other target analytes [12], and its relatively poor SPME is not unexpected. The SPME of lindane is more efficient at 68°C than at 87°C. At 87°C and with a larger 110-ml water sample the MDL for lindane is not improved, whereas those for the other analytes are. The increase of the sample volume from 15 to 115 ml, increases the amount (mass) of the analytes extracted and transferred to the GC for analysis and lowers the MDLs. These increases more than compensate for any decrease in extraction efficiency noted in Table 1. Except for lindane, the overall HS-SPME sensitivity with a 110-ml sample surpasses that of the EPA procedures by a factor of at least 10. A HS-SPME chromatogram with ELCD of a 125-ml HS sample vial containing 110 ml of a blank water spiked to give about 1, 2, 5 or 10 ng/l of the target analytes is shown in Fig. 4A. Fig. 4B shows the unspiked water.

A number of other analytical procedures for the determination of organochlorine contaminants, however, report detection at levels much lower than those in Table 2. These lower detection limits, however, are attained by the liquid–liquid extraction of large volumes of water, concentration of extracts to low ml, and sensitive GC detection. Compared to the simplicity of HS-SPME, these procedures, as well as the cited EPA methods, use solvents, are more time-consuming and in some instances require specialized extraction equipment.

The excellent sensitivity of the HS-SPME procedure depends on the efficient extraction of the non-polar analyte by the non-polar fiber coating from the polar aqueous matrix, and the complete transfer of the isolated analyte to the GC. The ELCD used in our study is less sensitive than ECD or MS detection. In a limited additional application, these latter detectors were found to give about 10 times better sensitivity for the 15-ml water sample in the 30 ml HS vial. General interferences by phthalate esters (EDC) and silicone material from the HS septum (MSD) reduced the MDL with several analytes. The ELCD chromatograms, however, were interference free.

The described HS-SPME procedure should be readily applicable to the analysis of other non-polar semi-volatile analytes of environmental and regulatory interest in water and possibly other aqueous systems. For example, Fig. 4C shows the HS-SPME chromatogram of Arochlor 1254 spiked at 45 ng/l into 110 ml of water. Fig. 4D shows the unspiked water. The Arochlor peak profile by HS-SPME is similar to that of the direct injection (not shown).

4. Conclusions

SPME is demonstrated to be applicable to HS sampling for capillary GC of a wide range of non-polar halogenated pesticides and contaminants in water. The procedure was optimized for the later-eluting analytes and required a 45-min extraction at 87°C for a 15-ml sample in a 30-ml HS sample vial and a 1-h extraction for a 110-ml sample in a 125-ml HS vial at the same temperature. The samples were saturated with salt. The optimized procedures gave acceptable repeatabilities, ranging from about 7 to 21%, 6 to 15% and 5 to 31% which were determined at 67 ng/l (15 ml sample), 67 ng/l (110 ml) and 10 ng/l (110 ml), respectively. With the exception of

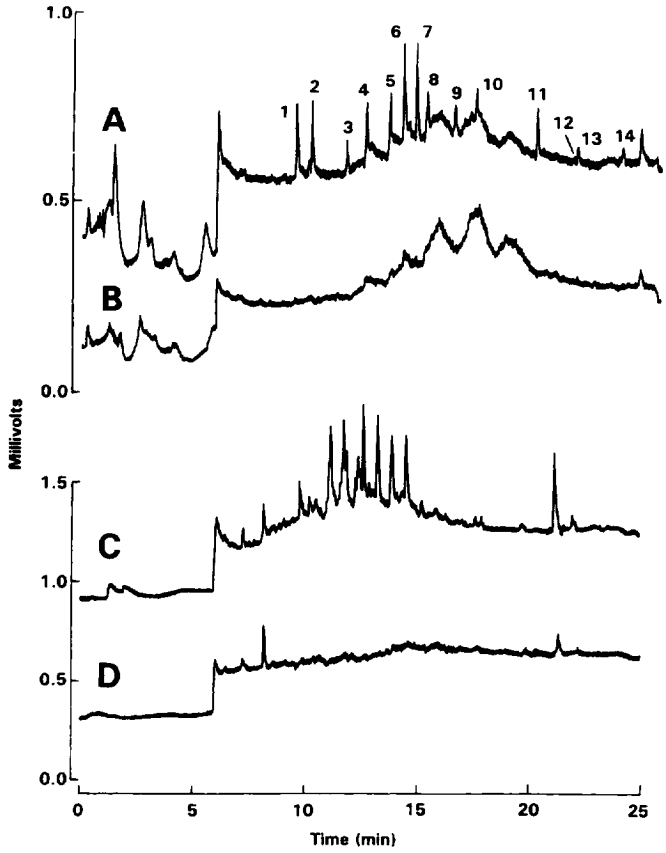

Fig. 4. Chromatograms of: (A) target analytes (about 1, 2, 5 or 10 ng/l of each analyte, peak identities as in Table 1) by HS-SPME over 110 ml of salt-saturated water at 87°C; (B) as in A but 110 ml of unspiked salt-saturated water; (C) about 45 ng of Arochlor 1254 by HS-SPME over 110 ml of salt-saturated water at 87°C; and (D) as in C, but 110 ml unspiked salt-saturated water.

lindane, the MDLs for the HS-SPME procedure using ELCD for a 15-ml water sample are comparable to those of the most sensitive EPA procedures. With a 110-ml water sample, again with the exception of lindane, the HS-SPME sensitivity surpasses the EPA procedures by a factor of at least 10. The described HS-SPME procedure should be readily applicable to the analysis of other non-polar semivolatile analytes of environmental and regulatory interest in water and possibly other aqueous systems.

References

[1] R.P. Belardi and J.B. Pawliszyn, Water Pollut. Res. J. Canada, 23 (1989) 179.
[2] D.W. Potter and J. Pawliszyn, J. Chromatogr., 625 (1992) 247.
[3] C.L. Arthur, K. Pratt, S. Motlagh and J. Pawliszyn, J. High. Resolut. Chromatogr., 15 (1992) 741.
[4] Z. Zhang and J. Pawliszyn, Anal. Chem., 65 (1993) 1843.
[5] J.J. Langenfeld, S.B. Hawthorne and D.J. Miller, Anal. Chem., 68 (1996) 144.
[6] R. Eisert, K. Levsen and G. Wünsch, J. Chromatogr. A, 683 (1994) 175.
[7] P. Popp, K. Kalbitz and G. Oppermann, J. Chromatogr. A, 687 (1994) 133.
[8] R. Eisert and K. Levsen, J. Am. Soc. Mass Spectrom., 6 (1995) 1119.
[9] S. Magdic and J.B. Pawliszyn, J. Chromatogr. A, 723 (1996) 111.
[10] B.D. Page and G.M. Lacroix, J. Chromatogr., 648 (1993) 199.
[11] C.J. Koester and R.E. Clement, Crit. Rev. Anal. Chem., 24 (1993) 263.
[12] A. Noble, J. Chromatogr., 642 (1993) 3.