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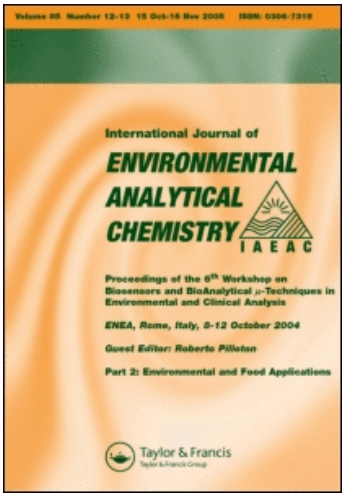

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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Online publication date: 17 September 2010

To cite this Article Zambonin, Carlo G. , Aresta, Antonella and Nilsson, Torben(2002) 'Analysis of Organochlorine Pesticides by Solid-Phase Microextraction followed by Gas Chromatography-Mass Spectrometry', International Journal of Environmental Analytical Chemistry, 82: 10, 651 — 657
To link to this Article: DOI: 10.1080/0306731021000075375
URL: http://dx.doi.org/10.1080/0306731021000075375

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Intern. J. Environ. Anal. Chem., Vol. 82, No. 10, pp. 651–657

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ANALYSIS OF ORGANOCHLORINE PESTICIDES BY SOLID-PHASE MICROEXTRACTION FOLLOWED BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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(Received 30 November 2001; In final form 11 March 2002)

Solid-phase microextraction (SPME) followed by gas chromatography-mass spectrometry (GC-MS) was optimized for the analysis of hexachlorocyclohexanes, DDD, DDE, DDT and other organochlorine pesticides in aqueous samples. Higher extraction efficiency was observed with the SPME fibre coated with 100 μm polydimethylsiloxane than with the fibres coated with 85 μm polyacrylate or 65 μm polydimethylsiloxane/divinylbenzene. Equilibration times were longer than 60 min, except for the hexachlorocyclohexanes, in spite of rapid stirring of the sample. However, precise quantitative analysis could be performed also under non-equilibrium conditions: i.e. repeatability standard deviations below 20%. Salt addition had a positive effect on the response for the hexachlorocyclohexanes, whereas the extraction of the other analytes was affected negatively. The pH of the sample solution did not influence the extraction efficiency. The desorption was performed for 5 min at 275°C directly in the GC injector. At shorter desorption times or lower temperatures a significant carry-over was observed for the heavier analytes. Generally, detection limits in the ng/L range were obtainable.

Keywords: Organochlorine pesticides; Solid-phase microextraction; Water analysis

INTRODUCTION

Organochlorine pesticides have been labelled environmental hazards due to their persistence in the environment, toxicity and ability to bioaccumulate [1]. Thus, many organochlorine pesticides have been withdrawn from registered use. However, they are still widespread in the environment. Usually, these contaminants have been extracted from aqueous samples by liquid–liquid extraction with methylene chloride or solid-phase extraction using catridges or disks [2]. Recently, also the application of solid-phase microextraction (SPME) [3] has been studied [4–8]. The studies had in common SPME fibres coated with either polydimethylsiloxane [4–8] or polyacrylate [7]. The following extraction conditions were examined: Time [4–8], stirring speed

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ISSN 0306-7319 print: ISSN 1029-0397 online © 2002 Taylor & Francis Ltd
DOI: 10.1080/0306731021000075375

[4,7], ionic strength [6–8], pH [5], sampling approach [6], coating thickness [6], coating material [7], temperature [8] and sample size [8].

However, the results reported in these articles are not always in agreement for what concerns the effects related to some typical SPME parameters such as salt addition effect, desorption temperature and fibre choice.

Moreover, although it should be expected [9] that the temperature has a direct influence on an extraction technique based on diffusion and partitioning, this parameter has not been considered by previous solid phase micro-extraction studies on organochlorine pesticides, with the exception of just one article describing on head-space SPME [8]. Thus, a study devoted to clarify all the aspects of SPME extraction of organochlorine is desirable.

In the present article, an SPME/GC-MS method was developed for the simultaneous determination of 13 pesticides, such as hexachlorocyclohexanes, DDD, DDE, DDT and other organochlorine pesticides in aqueous samples. The extraction capabilities of three different fibre coatings (100 μm polydimethylsiloxane, PDMS, 85 μm polyacrylate, PA, and 65 μm polydimethylsiloxane/divinylbenzene, PDMS/DVB) were examined, together with all the SPME extraction parameters including extraction temperature, that have been stated unequivocally. Precise quantitative analysis has been performed with detection limits in the ng/L range. Results obtained on the extraction of different soil samples are also reported.

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EXPERIMENTAL

Materials

Hexachlorocyclohexanes (α-HCH, β-HCH, lindane), diphenyl aliphatics (o,p′-DDD, p,p′-DDD, o,p′-DDE, p,p′-DDE, o,p′-DDT, p,p′-DDT, methoxychlor) and cyclodienes (aldrin, dieldrin, heptachlor) where purchased from Dr. Ehrenstorfer (Augsburg, Germany). Methanol stock solutions of each pesticide were prepared and stored in the dark at 4°C. All working solutions were prepared with triply distilled water and analytical grade reagents.

Apparatus

GC-MS analysis were performed with a Varian 3400 gas chromatograph equipped with a septum programmable injector and interfaced, by a jet-separator and a transfer line, to a Finnigan ITS-40 ion trap mass spectrometer. Data were acquired with the Saturn I software (Varian). The carrier gas was helium. The GC chromatographic column consisted of a Supelco fused silica SPB-5 capillary column (30 m length, 0.20 mm i.d. with 0.25 μm film thickness).

Gas Chromatography-Mass Spectrometry Conditions

Initial experiments to optimise the gas-chromatographic and MS detection conditions were performed by direct injection of 1 μL of the standard compounds in hexane. The oven temperature programme was 50 (5 min)–180°C at 12°C/min, 180–230°C at 5°C/min, 230–245°C at 2°C/min. A carrier gas flow at 25 mL/min and an injector

TABLE I Quantitation ions and retention times obtained for the different analytes.

Retention order	*Compound*	*Formula*	*Molecular weight*	*Retention time* (min)	*Quantitation ions*
1	α-HCH	$C_6H_6Cl_6$	290.8	17.20	181 + 183
2	β-HCH	$C_6H_6Cl_6$	290.8	17.55	181 + 183
3	Lindane	$C_6H_6Cl_6$	290.8	18.08	181 + 183
4	Heptachlor	$C_{10}H_5Cl_7$	373.3	20.05	272
5	Aldrin	$C_{12}H_8Cl_6$	364.9	21.07	263
6	o,p′-DDE	$C_{14}H_8Cl_4$	318.1	23.12	246
7	p,p′-DDE	$C_{14}H_8Cl_4$	318.1	24.17	246
8	Dieldrin	$C_{12}H_8Cl_6O$	380.9	24.24	263
9	o,p′-DDD	$C_{14}H_{10}Cl_4$	320.1	24.30	235
10	p,p′-DDD	$C_{14}H_{10}Cl_4$	320.1	25.43	235
11	o,p′-DDT	$C_{14}H_9Cl_5$	354.5	25.47	235
12	p,p′-DDT	$C_{14}H_9Cl_5$	354.5	27.06	235
13	Methoxychlor	$C_{16}H_{15}Cl_3O_2$	345.7	29.34	227

temperature of 275°C were used. The GC transfer line was maintained at 250°C. The mass spectrometer was operated in the electron impact positive ion (EI^+) mode with a source temperature of 200°C. The electron energy was 70 eV and the filament current 200 μA.

Mass spectra were acquired scanning from m/z 50 to 450 in 1.5 s. Detection of analytes was also accomplished in selected ion monitoring (SIM) mode, using the fragment ions reported, together with the retention time obtained for the different analytes, in Table I.

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Solid-phase Microextraction

Three different silica fibres coated with a 100 μm thick polydimethylsiloxane (PDMS) film, a 85 μm thick polyacrylate (PA) and a 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) film, respectively, were employed for comparative studies. A manual SPME device (Supelco) was used to hold the fibres. The SPME device and procedure have been extensively described elsewhere [3]. Standard solutions were prepared by spiking 5 mL of triply distilled water into 7 mL clear vials (Supelco) at the required concentration level (typically in the range 10 ng/L–1 μg/L). Subsequently, the vials were sealed with hole caps and Teflon-faced silicone septa (Supelco). The extraction was performed by direct immersion of the fibre in the solution at 20°C for 60 min under magnetic stirring in order to improve mass transfer from the aqueous sample into the fibre coating. Thermal desorption (5 min desorption time) was performed directly into the GC injection port maintained at 275°C.

Soil Samples

Six euro soils samples were used for the preparation of soil samples with different organic matter content and texture. The characteristics of these standard soil have been reported previously [13]. The soils were air-dried at 35°C and sieved through a 1 mm sieve.

Samples (3.0 g) were pre-mixed with water (5 mL) in order to hydrate the active sites, thus allowing the analytes to evenly distribute over the soil and to interact with active sites. Then, 50 μL of a pesticides standard mix in methanol were added and the resulting

mixture stirred for 0.5 h and left at room temperature overnight. The samples were then centrifuged (6000 rpm, 5 min) and the supernatant subjected to SPME.

RESULTS AND DISCUSSION

Fibre Coating Material

Preliminary experiments were performed in order to compare the extraction efficiency of PDMS, PA and PDMS/DVB coated fibres. In effect the choice of the best stationary phase is extremely important, since it directly affects the magnitude of the partition coefficient between the sample and the fibre. The selected fibres were found to extract the analytes to different extents. Between the three selected coatings, PDMS was clearly capable of the most efficient extraction for all the target analytes and was then chosen for further experiments.

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Extraction Time and Temperature

The extraction time profiles were established by plotting the area counts versus the extraction time. The equilibrium was considered reached when a further increase in the extraction time did not produce a significant increase in the response values. Table II reports the equilibration times for all the studied analytes, at three different extraction temperatures. Regardless of the rapid magnetic stirring of the sample, equilibration times higher than 2 h were obtained for the heaviest analytes at room temperature. Similar equilibration times were obtained by sonicating the sample during the extraction. Then, some further experiments were performed by heating the extraction vial in a water bath at 50 and 90°C, respectively. At higher temperatures (see Table II) shorter equilibration times were obtained, since the mass transfer increases with the temperature [10]. Furthermore, as clearly shown in Fig. 1, that reports the area counts obtained for some representative pesticides at different temperatures, the absolute responses were higher at 50°C while a drastic decrease was observed at 90°C.

TABLE II Equilibration times obtained for the different analytes at 20, 50 and 90°C

Compound	*Equilibration time* (min)		
	20°C	*50°C*	*90°C*
α-HCH	40	30	15
β-HCH	30	20	< 15
Lindane	40	30	< 15
Heptachlor	210	150	60
Aldrin	180	140	60
o,p′-DDE	210	150	90
p,p′-DDE	210	150	90
Dieldrin	150	90	45
o,p′-DDD	> 210	150	90
p,p′-DDD/ o,p′-DDT	210	150	60
p,p′-DDT	180	120	60
Methoxychlor	180	120	60

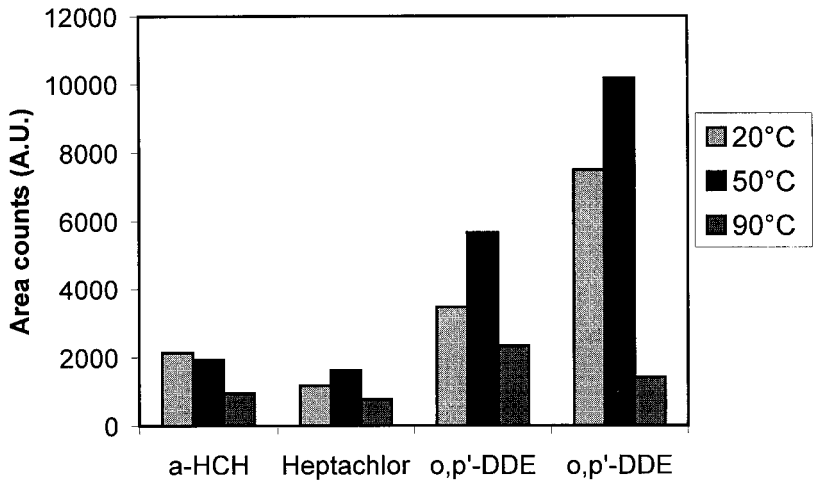

FIGURE 1 Area counts obtained for some representative pesticides at different temperatures in equilibrium conditions.

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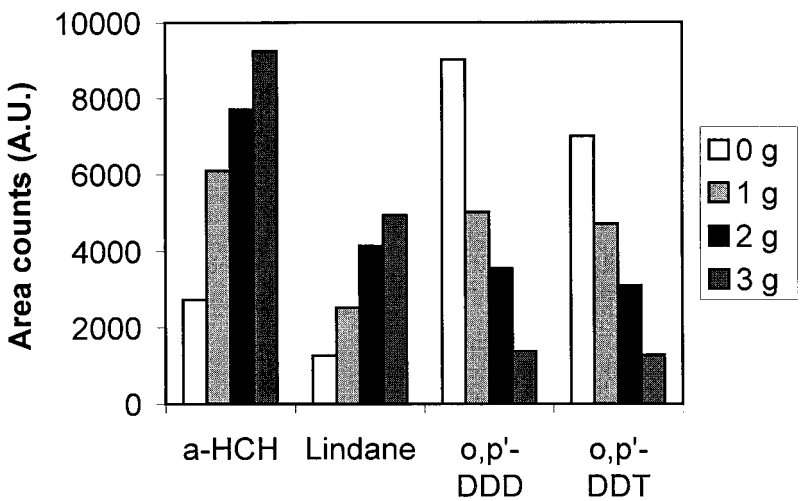

FIGURE 2 Effect of the addition of sodium chloride to the aqueous sample in the extraction of some representative analytes.

In any case, it is possible to obtain good extraction yields and reliable analysis also in non-equilibrium conditions. In fact, the amount of the analyte absorbed into the fibre is proportional to the initial concentration in the sample matrix [11], once the agitation conditions and the sampling time are held constant, and hence, SPME quantitation is feasible even before adsorption equilibrium is reached.

Ionic Strength and pH

Salt addition often improves the recovery, especially in the case of polar (hydrophilic) compounds, which are difficult to extract due to their low hydrophobicity. As reported in Fig. 2, also in the case of SPME, the addition of sodium chloride (ranging

from 0 to 3.5 g in 10 mL) to the aqueous sample showed a positive effect in the extraction of hexachlorocyclohexanes, whereas the other compounds behaved differently. In fact, their response decreased with salt addition.

On the contrary, no significant effects on the response were observed for any of the analytes by varying the pH (from 4 to 10) of the extraction solutions.

Desorption Conditions and "Carry-over"

It has already been reported [12] that the desorption temperature should be just slightly higher than the boiling point of a given compound to ensure its complete desorption from the fibre coating. However, in the present work desorption was carried out for 5 min at 275°C. In fact, significant "carry-over" was observed for the heaviest analytes when desorbing at lower temperatures or shorter desorption times.

Linear Range, Detection Limits and Precision

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The linear dynamic range of the developed SPME/GC-MS procedure (SIM mode) resulted linear for all the analytes from the lowest concentration at which they were detected over at least two concentration decades, with correlation coefficients better than 0.996 and intercepts not significantly different from zero at 95% confidence level.

Table III reports the repeatability standard deviations and the estimated detection limits (at a signal-to-noise ratio of 3) obtained in this study for all the investigated compounds compared to those reported in EPA methods 508 and 505.

Soil Analysis

Analyses of soil samples by combined water extraction-SPME showed very low recoveries. This could be explained by the non-polarity of the analytes, since more polar pesticides were previously well extracted by the same approach [13,14]. However, this represents the limit of any SPME method applied to the determination of organic

TABLE III Repeatability standard deviations and estimated detection limits (at a signal-to-noise ratio of 3) obtained in this study for all the investigated compounds compared to those reported in EPA methods 508 and 505

Compound	*Repeatability standard deviation* (%)	*Detection limit* (ng/L)	
		This study	*EPA 508*[2]
α-HCH	4.8	15[a]	30
β-HCH	6.0	100[a]	10
Lindane	7.5	20[a]	3[b]
Heptachlor	11.5	15	3[b]
Aldrin	10.4	2°	80
o,p′-DDE	17.9	3	–
p,p′-DDE	16.2	3	10
Dieldrin	15.4	30	10[b]
o,p′-DDD	14.7	3	–
p,p′-DDD/ o,p′-DDT	14.5	3	3/-
p,p′-DDT	17.8	5	60
Methoxychlor	12.5	5	50

[a]salt, 30 min. 20°C; [b]EPA 505

compounds in soil samples, as the critical step that determines the recovery is not the SPME procedure itself but the equilibration of the analytes between soil and water. This equilibration mainly depends on the content of organic matter in the soil [13,15].

CONCLUSIONS

SPME/GC-MS was successfully applied to the simultaneous determination of 13 organochlorine pesticides in aqueous samples.

All the SPME extraction parameters, including the extraction capabilities of three different fibre coatings (100 μm polydimethylsiloxane, 85 μm polyacrylate and 65 μm polydimethylsiloxane/divinylbenzene) and the extraction temperature, have been carefully examined.

In most cases, the detection limits, which were obtained (in the ng/L range) with the presented SPME/GC-MS method, were lower than those reported for EPA methods 508 and 505. The low recoveries obtained in the analysis of different soil samples have to be ascribed to the low polarity of the considered analytes.

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