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Comparison of different coatings in solid-phase microextraction for the determination of organochlorine pesticides in ground water

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Abstract

A solid-phase microextraction (SPME) procedure using three commercialised fibers (Carbowax–divinylbenzene, Carboxen–polydimethylsiloxane and divinylbenzene–Carboxen–polydimethylsiloxane) is presented for the determination of a selected group of organochlorine compounds in water samples. The extraction performances of these compounds were compared using fibers with two and three coatings. The optimal experimental procedures for the adsorption and desorption of pesticides were determined. The limits of detection with the divinylbenzene–Carboxen–polydimethylsiloxane fiber at levels below ng l^{-1} were similar or lower than values presented in the literature for several of these compounds using polydimethylsiloxane fiber. The advantages of using this fiber, such as no salt addition, are discussed. Finally, the optimised procedures were applied successfully for the determination of these compounds in polluted ground water samples.

Keywords: Solid-phase microextraction; Water analysis; Environmental analysis; Organochlorine compounds; Pesticides

1. Introduction

Pesticides have played an important role in increasing agricultural productivity. Thus, about $5 \cdot 10^8$ kg are currently used world-wide, 50–60% being herbicides, 20–30% insecticides and 10–20% fungicides. They have been widely applied in agriculture, either directly to soil or sprayed over crop fields. Pesticides can enter ground water as contaminants via filtration through the soil, by deposition or by surface run-off [1]. Organochlorine pesticides have very low solubilities in water, are fat soluble, and are resistant to metabolism. Furthermore, because of this, they are considered to be environmental hazards [2] and are a threat to human health. Several compounds, including organochlorine pesticides, are receiving much attention in the European Union and are included in the lists published to maintain water quality [3].

The determination of pesticide residues has increased in the last few decades, as evidenced by the large numbers of papers published. Most determinations of organochlorine pesticides are based on chromatographic methods, with mainly flame ionization detection (FID) [4], gas chromatographic analysis with mass spectrometric (MS) detection [5–10], and electron-capture detection (ECD) [4,8–14]. The qualitative and quantitative determination of pesticides in water samples is usually performed with a previously prepared sample involving liquid–liquid extraction (LLE), preferably with dichloromethane or *n*-hexane [1,15–18], or solid-phase extraction (SPE) with C_{18} cartridges or Empore extraction disks [19,20]. The different extraction procedures for

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sample preparation are well known [4,21,22]. The most widely used technique is LLE [23,24]. However, this procedure, which requires large amounts of toxic and expensive solvents that can be harmful to the operator and to the environment, is time consuming and tedious since it also requires pre-concentration of the extract and it is at this stage that the potential for loss of analytes or contamination of samples is greatest. SPE is an alternative for sample preparation [1,24–32], because it requires smaller amounts of solvent and is less labour intensive. However, disadvantages include background interferences, poor reproducibility between cartridges and high economic cost, since the cartridges are usually disposed of after each extraction [33].

Solid-phase microextraction (SPME) is a sample preparation technique, introduced by Pawliszyn and co-workers [34–36], that has received increasing attention, and is now widely accepted as a reliable technique. Thus, SPME has been applied to the determination of polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs) [37], benzene, toluene, ethylbenzene and xylenes (BTEX) [38], and pesticide residue analysis, such as organophosphorous pesticides [39], nitrogen-containing pesticides [6,10], and organochlorine pesticides [4,39–43]. Most works concerning the determination of organochlorine pesticides are performed using manual SPME, polydimethylsiloxane (PDMS) fiber, direct immersion, and ECD or MS detection. The limit of detection has been reported to range between 0.06 $\mu g\ l^{-1}$ (4,4′-DDD) and 4.7 $\mu g\ l^{-1}$ (endrin aldehyde) [4]; 1 $\mu g\ l^{-1}$ (endosulfan ether) and 20 $\mu g\ l^{-1}$ (δ-hexachlorocyclohexane, δ-HCH) [39]; 0.005 $\mu g\ l^{-1}$ (α-HCH) and 0.032 $\mu g\ l^{-1}$ (β-HCH) [41]; and 0.005 $\mu g\ l^{-1}$ (chlordane) and 0.02 $\mu g\ l^{-1}$ (benzene hexachloride (BHC)) [43]; and the precision was less than 20% in all cases. SPME is used as a prior sample preparation stage, not only in gas chromatography, but in liquid chromatography [44] and capillary electrophoresis [45].

The present study was carried out to evaluate three different fibers, two partially crosslinked with two mixed phase coatings and one highly crosslinked with three mixed phases, in the extraction of 12 organochlorine pesticides in ground water using automatic SPME. The extraction efficiencies were optimised by adjusting the following parameters: stirring, extraction time, salt addition, pH, temperature of desorption and time of desorption. Finally, the optimised SPME procedures were applied by employing GC with ECD to the determination of organochlorine compounds in polluted ground water samples, identifying all compounds in real samples using a mass detector.

2. Experimental

2.1. Reagents

Standards of organochlorine pesticides, lindane (1), heptachlor (2), aldrin (3), triadimefon (4), 2,4′-DDE (5), α-endosulfan (6), dieldrin (7), 4,4′-DDE (8), endrin (9), β-endosulfan (10), 2,4′-DDT (11) and 4,4′-DDT (12), were obtained from Riedel-de Haën (Seelze-Hannover, Germany) with purity >96%. A stock standard solution containing all the analytes (500 $\mu g\ l^{-1}$) was prepared by dissolution in methanol and stored at −4 °C. Diluted solutions were prepared from this solution by diluting with pesticide-free ground water.

The methanol used to dissolve standards was HPLC grade from Panreac (Montplet and Esteban, Barcelona, Spain). The nitric acid and sodium hydroxide used for pH adjustment were from Merck. Ultrapure water from a Milli-Q system (Millipore, Bedford, MA, USA) with conductivity 18 MΩ was used in all cases.

2.2. Equipment

A class A volumetric flask, Gilson pipetmans regularly verified for precision and accuracy, a precision balance (Sartorius BP 210-S), and a PHM 64 pH meter from Radiometer (Copenhagen, Denmark) with a previously calibrated glass calomel combination electrode were used to prepare solutions.

2.3. SPME fibers

Three different SPME fibers, Carbowax–divinylbenzene (CW–DVB) with a film thickness of 65 μm, Carboxen (CAR)–PDMS of 75 μm and DVB–CAR–PDMS of 50/30 μm, were purchased

from Supelco (Bellefonte, PA, USA). The temperature programs for conditioning the SPME fibers in the injector were CW–DVB for 30 min at 250 °C, CAR–PDMS for 30 min at 280 °C, and DVB–CAR–PDMS for 240 min at 270 °C.

2.4. Instrumentation

A Varian (Walnut Creek, CA, USA) 3400 gas chromatograph equipped with a ^{63}Ni electron-capture detector, a 1075 split/splitless injector operated in the splitless mode, a Varian 8300 autosampler equipped with automatic SPME, and a fused-silica capillary SPB-5 chromatographic column (30 m× 0.32 mm I.D., 0.25 μm film thickness) from Supelco were employed. Varian Star 4.51 chromatographic workstation software was used for instrument control and data treatment.

Separation conditions were as follows: initial column temperature 80 °C (4 min), increased to 215 °C at 15 °C min^{-1} (hold 0.5 min), increased to 230 °C at 2 °C min^{-1} (hold 3 min) and, finally, increased to 260 °C at 5 °C min^{-1} (hold 2 min). The detector temperature was maintained at 310 °C. The carrier gas was UHP helium (99.5% purity) at a flow-rate of 1 ml min^{-1} and the make-up gas was UHP nitrogen (99.5% purity) at a flow-rate of 50 ml min^{-1}, the injection volume being 1 μl in all cases.

A Varian 3400 with a Saturn 2000 ion trap mass spectrometer detector from Varian Instruments (Sunnyvale, CA, USA) equipped with an 8200 autosampler and a 1077 split/splitless programmed temperature injector operating in the splitless mode was used to confirm the identity of compounds in the quantification of real samples. A fused-silica capillary SPB-5 chromatographic column (30 m×0.32 mm I.D., 0.25 μm film thickness) from Supelco was used with the following temperature program: initial column temperature 70 °C (3 min), increased to 180 °C at 25 °C min^{-1} (hold 1 min) and, finally, increased to 300 °C at 5 °C min^{-1} (hold 10 min). The injector port was set at 250 °C.

The mass spectrometer operating in the electron impact ionization (EI) mode was used for pesticide confirmation with the following conditions: transfer line at 280 °C, trap at 200 °C and manifold at 80 °C. Mass spectra were obtained in the scan range m/z 85–420. The filament emission current was set at 20 μA, and the electron multiplier offset at 100 V. The solvent delay time was 9 min. Helium was the carrier gas at a flow-rate of 1 ml min^{-1}. The injection volume was 1 μl.

2.5. Solid-phase microextraction procedure

All extractions were performed in 2 ml dark glass vials at room temperature, using 1.2 ml of liquid phase, with fibers immersed in the liquid phase. 600 μl of a stock solution of 0.2 ng ml^{-1} made up to a total volume of 1.2 ml with pesticide-free ground water was used in the optimization processes; variable volumes of concentrated stock solutions made up to a total volume of 1.2 ml with pesticide-free ground water were used in calibration and application to real samples. The ionic strength was adjusted using sodium sulphate (0% saturated) or sodium chloride (0% saturated). The pH was adjusted with 0.1 *M* sodium hydroxide or 0.1 *M* nitric acid by measuring in a digital pH meter. After extraction, the analytes were desorbed into the hot injector of the gas chromatograph by thermal desorption. The injection was splitless for 15 min and then the split valve was opened for the remainder of the analytical runs. The SPME fibers were kept in the hot injector for a further 5 min with the split valve open to purge any component not completely desorbed from the fiber during the splitless step. After desorption, fibers were washed by stirring for 5 min in Milli-Q water, and dried at 260 °C for 4 min. A blank solution was run every three samples. All studies were carried out in triplicate and average values calculated.

3. Results and discussion

To develop a SPME procedure for the determination of pesticides using the fibers CW–DVB, CAR–PDMS and DVB–CAR–PDMS, optimisation of several variables related to the extraction and desorption steps is required—stirring, extraction time, ionic strength, pH, as well as the time and temperature of desorption—in order to achieve maximum efficiency of extraction of the compounds studied and to elucidate the selectivity of the different coatings versus other components present in the matrix.

3.1. Optimisation of the SPME conditions

Since SPME is a process dependent on the equilibrium process involving partitioning of the analytes from the liquid sample into the stationary phase, the amount of analyte extracted depends on the mass transfer of the analyte through the aqueous phase and consequently depends on the stirring and extraction time. Therefore, a study of the extraction efficiencies of the analytes (all at 0.1 μg l^{-1}) under static conditions and with stirring at different extraction times (1–50 min) was performed under the following conditions: no salt addition and no pH adjustment, desorption temperature 250 °C, and desorption time

Table 1
Chromatographic responses, expressed as area counts, for the different analytes at 0.1 μg l^{-1} as a function of extraction time for the fibers CW–DVB, CAR–PDMS and DVB–CAR–PDMS. Desorption temperature 250 °C, desorption time 10 min

Compound	Area count ($\times 10^5$)						
	1 min	5 min	10 min	15 min	20 min	30 min	50 min
CW–DVB							
Lindane	5.49	7.59	9.88	9.53	8.70	8.49	8.01
Heptachlor	6.37	7.38	7.60	7.99	8.10	8.69	8.89
Aldrin	9.32	13.33	19.75	19.60	18.84	17.14	17.48
Triadimefon	7.98	12.51	19.49	18.94	18.34	18.66	18.79
2,4′-DDE	10.20	12.75	18.79	18.59	18.01	17.89	18.76
α-Endosulfan	1.44	12.66	15.91	14.26	14.53	13.12	13.30
4,4′-DDE	8.30	14.35	18.43	25.42	24.89	25.84	25.98
Dieldrin	9.34	16.24	21.82	27.18	27.68	28.55	28.25
Endrin	12.86	18.23	21.92	24.94	25.26	25.52	25.60
β-Endosulfan	12.33	14.71	15.75	16.90	16.08	16.32	16.94
2,4′-DDT	8.73	14.57	17.55	19.70	19.35	19.55	19.71
4,4′-DDT	9.47	9.84	11.38	17.71	17.12	19.95	19.48
CAR–PDMS							
Lindane	1.50	5.44	9.79	14.48	17.06	27.31	27.22
Heptachlor	1.02	1.62	8.20	11.93	18.60	23.01	21.07
Aldrin	4.27	29.02	37.57	47.14	49.48	56.58	52.01
Triadimefon	23.94	34.62	47.12	44.04	46.22	45.79	44.25
2,4′-DDE	3.57	4.75	12.98	20.96	22.06	49.95	48.43
α-Endosulfan	2.83	11.32	20.87	33.42	35.72	41.45	41.24
4,4′-DDE	4.49	6.02	7.69	12.87	23.89	26.71	26.92
Dieldrin	5.93	15.18	26.50	40.26	42.30	52.91	52.62
Endrin	2.40	8.19	14.97	24.78	28.44	41.85	41.03
β-Endosulfan	2.29	8.10	14.86	23.55	25.61	35.91	36.02
2,4′-DDT	3.52	9.89	17.09	27.67	27.74	55.00	55.51
4,4′-DDT	2.30	5.82	10.16	16.38	16.32	36.74	36.30
DVB–CAR–PDMS							
Lindane	6.21	9.09	16.62	21.72	26.63	32.63	32.32
Heptachlor	5.35	7.34	9.37	9.98	11.53	14.56	14.85
Aldrin	3.52	20.91	23.50	25.24	30.76	39.36	37.05
Triadimefon	1.45	2.47	5.16	6.59	9.06	11.08	11.39
2,4′-DDE	3.79	5.86	8.54	10.48	14.18	15.80	15.49
α-Endosulfan	4.61	12.12	28.25	37.18	39.81	45.90	45.03
4,4′-DDE	7.06	13.62	33.74	39.54	43.84	45.52	45.62
Dieldrin	2.74	4.80	5.80	7.16	9.91	14.11	14.69
Endrin	2.64	6.04	14.26	18.74	20.20	26.50	21.85
β-Endosulfan	3.39	7.46	19.71	26.73	31.03	35.34	34.58
2,4′-DDT	2.30	2.72	9.44	10.76	14.15	13.39	12.24
4,4′-DDT	1.77	1.99	8.15	10.49	11.25	11.25	11.23

10 min. It was observed that the peak areas for each analyte were higher after stirring than when static, so stirring was selected for the remainder of the experiments. Table 1 shows the chromatographic response of the organochlorine compounds for each fiber under stirring at different extraction times. As can be seen, the extraction time depends on the type of stationary phase used. Thus, the chromatographic response of these compounds using the CW–DVB fiber increased as the extraction time increased to 15 min, the signal diminishing for several of the compounds when longer times were employed. In the case of CAR–PDMS and DVB–CAR–PDMS the optimum extraction time was 30 min and no significant improvement in the extraction was obtained at longer times. In subsequent studies, 15 min for CW–DVB, 30 min for CAR–PDMS, and 30 min for DVB–CAR–PDMS were selected as the extraction time. It can also be seen from Table 1 that the chromatographic response varies depending on the fiber, the best results being obtained for most of the compounds with the CAR–PDMS fiber, which can be explained not only by the nature of the fiber, but by the slightly larger volume of this fiber with respect to the others and hence the slightly larger capacity for the analytes.

The following step in the optimisation process was to select the optimum desorption conditions, which were determined by testing different temperatures and different times, considering the optimum values to be those obtained when all analytes were desorbed from the fiber coating with minimal carryover to the following analysis. This study was carried out under the following conditions: no salt and no pH adjustment. For the DVB–CAR–PDMS fiber, desorption temperatures ranged between 230 and 270 °C, the optimum temperature being 260 °C; for CAR–PDMS from 240 to 300 °C, the optimum being 280 °C; and for CW–DVB between 200 and 260 °C, the optimum being 250 °C. The time of desorption was also optimised, varying between 1 and 30 min for each fiber, 15 min being the most appropriate value. These values of temperature and desorption time for each fiber were selected for subsequent studies.

The effect of ionic strength, of great importance in SPME procedures, was tested using two electrolytes (NaCl and Na_2SO_4). The optimization was performed with no pH adjustment. The NaCl and Na_2SO_4 contents ranged from 0% to saturated. Table 2 shows the effect of sodium chloride (NaCl) on the extraction efficiency of the three fibers. It can be seen that the optimum percentage of salt depends on the type of fiber and the solute analysed. For the CAR–PDMS fiber the optimum values ranged between 0 and 30% depending on the compound, and no addition of salt was selected to achieve a faster preparation of the samples. For the CW–DVB and DVB–CAR–PDMS fibers, no addition of NaCl gave

Table 2
Chromatographic responses, expressed as area counts, for the different analytes at 0.1 μg l^{-1} as a function of NaCl content for the fibers CW–DVB, CAR–PDMS and DVB–CAR–PDMS. Chromatographic conditions are given in the Experimental section

Compound	Area count ($\times 10^5$)											
	CW–DVB				CAR–PDMS				DVB–CAR–PDMS			
	0	20%	30%	Saturated	0	20%	30%	Saturated	0	20%	30%	Saturated
Lindane	5.44	4.99	5.08	5.14	22.97	24.74	20.42	18.79	17.29	19.16	15.94	16.65
Heptachlor	5.25	6.35	4.98	5.28	10.14	10.37	9.31	6.37	11.19	4.67	6.31	5.13
Aldrin	12.91	10.61	11.74	11.60	8.91	8.51	8.58	5.41	21.66	18.99	20.93	16.35
Triadimefon	6.74	7.71	6.28	7.83	12.33	18.69	13.21	10.95	9.35	12.59	11.50	8.59
2,4′-DDE	6.98	6.03	6.35	6.50	8.67	9.49	11.77	8.50	5.96	2.26	2.30	1.89
α-Endosulfan	5.46	5.42	5.72	5.11	11.19	10.02	11.86	8.43	22.45	20.39	17.03	11.24
4,4′-DDE	9.59	7.85	8.53	8.58	5.44	6.10	6.22	5.42	22.38	18.35	17.22	13.21
Dieldrin	12.28	10.34	11.65	11.34	10.78	8.00	9.31	4.96	7.92	3.72	3.29	2.32
Endrin	14.05	13.84	15.00	14.00	10.17	7.55	7.63	7.33	16.69	11.45	8.83	6.37
β-Endosulfan	8.25	9.16	8.41	8.37	13.63	14.41	12.17	5.32	14.03	15.04	12.85	9.76
2,4′-DDT	8.36	7.65	8.30	8.28	5.78	4.93	5.94	5.03	4.31	1.53	2.57	1.22
4,4′-DDT	9.75	8.89	9.16	9.54	5.88	3.77	5.11	3.67	7.72	2.75	5.00	2.31

a higher extraction for the majority of solutes analysed. The effect of sodium sulphate (Na_2SO_4) on the extraction efficiency was also studied by varying the salt percentage between 0% and saturated solution, but no improvement in the extraction efficiency was obtained. The response of some solutes in the triple coated fiber diminished drastically as the salt content of the solution increased. This behaviour has been described previously [11], and can be explained by the triple coating on this fiber and the lower polarity of the coating, which makes a high salt content unnecessary to increase the mass transfer of the solutes. No salt addition was used in subsequent studies. Although the influence of pH was studied by varying it with nitric acid or sodium hydroxide, it was not necessary to make adjustments in subsequent analyses because its influence on the extraction efficiency was minimal.

Fig. 1 shows chromatograms of a mixture of the selected pesticides spiked at 0.1 μg l^{-1} in ground water samples obtained using the optimum conditions previously established. As can be seen, the relative response depends on the type of fiber and compound. In relative terms, the best results were obtained using the CAR–PDMS fiber for most of the compounds with the exception of α-endosulfan (6), dieldrin (7) and β-endosulfan (10), which had a higher response with the DVB–CAR–PDMS fiber. We can also see from Fig. 1 the selectivity of the separation change as a function of the nature of the fiber. Drastic changes were observed in the retention times of the different compounds, even though the reversal migration time of several of them depended of the fiber type, which can be very useful for identification purposes when no sophisticated detection systems (i.e. mass detector) or columns of different polarity are available in the laboratory.

3.2. Analytical parameters

The calibration graphs for all fibers were produced from results obtained by injecting extracted standard solutions in the range 1.0–1000 ng l^{-1} in pesticide-free water samples. Blank samples were analysed to test the correct desorption of the analytes from the fiber. Each point of the calibration graph corresponded to the mean value obtained from three independent area measurements, and no statistically

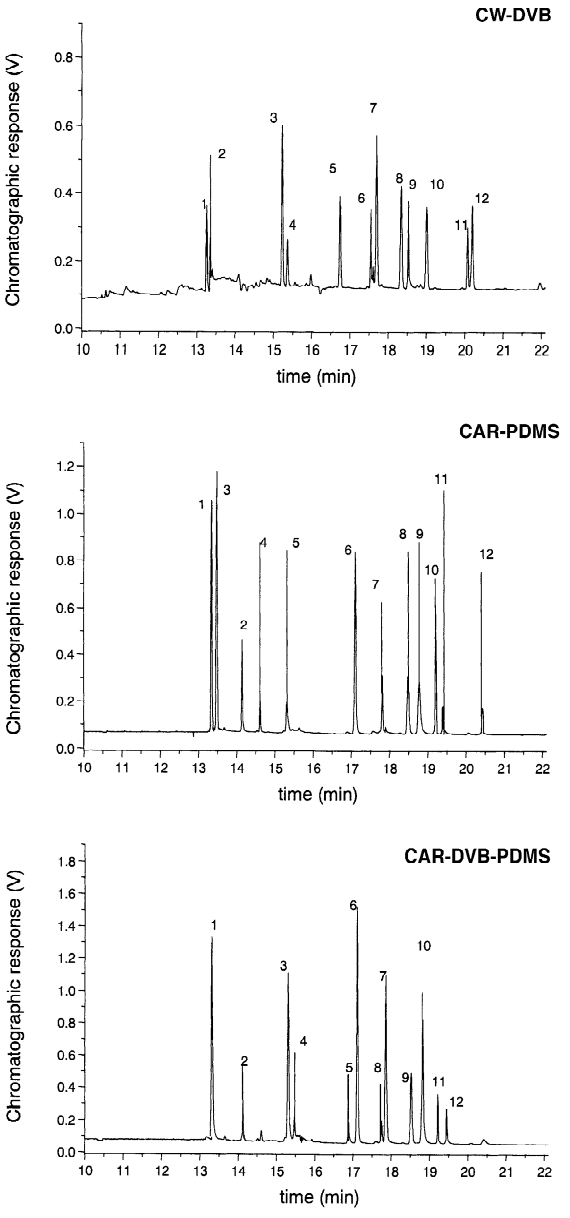

Fig. 1. Comparison between the different fibers in the extraction of a spiked sample with organochlorine compounds at the 0.1 μg l^{-1} level. Peaks: lindane (1), heptachlor (2), aldrin (3), triadimefon (4), 2,4′-DDE (5), α-endosulfan (6), dieldrin (7), 4,4′-DDE (8), endrin (9), β-endosulfan (10), 2,4′-DDT (11) and 4,4′-DDT (12). Chromatographics conditions are described in the Experimental section.

significant lack of fit was found. The corresponding linear dynamic range, linear correlation coefficient, repeatability, reproducibility and limit of detection for the three fibers are shown in Table 3. The limits of detection (LODs) were calculated from the signal-to-noise ratio of the individual peaks, assuming a minimum detectable signal-to-noise level of 3. These LODs varied between 0.6 ng l^{-1} (2,4′-DDE) and 10.2 ng l^{-1} (2,4′-DDT) for the CW–DVB fiber, between 0.5 ng l^{-1} (aldrin) and 11.6 ng l^{-1} (2,4′-DDT) for the CAR–PDMS fiber and between 0.4 ng l^{-1} (aldrin) and 7.4 ng l^{-1} (triadimefon) for the DVB–CAR–PDMS fiber, the lowest LOD values being obtained in general terms with the triple coating fiber DVB–CAR–PDMS. However, depending on the type of solute, each of the fibers tested provided LODs similar to, or lower than, typical fibers with PDMS coating [4,39,41,43].

In order to evaluate the repeatability and reproducibility, the optimised SPME methods were applied to solutions of 0.1 μg l^{-1} of each pesticide spiked in a ground water matrix five times each day over five different days, and the results are shown in Table 3. These results are acceptable and vary depending on the type of fiber and compound. It can be seen that the intra-day relative standard deviation (RSD) varied between 0.7% (lindane) and 4.7% (α-endosulfan) for the CW–DVB fiber, between 0.8% (α-endosulfan) and 5.4% (2,4′-DDT) for the CAR–PDMS fiber and between 2.0% (aldrin) and 6.4% (2,4′-DDE) for the DVB–CAR–PDMS fiber. The inter-day results show that, for most of the compounds, the lowest RSDs were obtained using the CW–DVB fiber, with the exception of endrin, α-endosulfan and β-endosulfan, which show lower RSDs with the CAR–PDMS fiber. The precision obtained (<10%) was better than those obtained using manual SPME with PDMS fibers (<20%) [46].

3.3. Application to real samples

The optimised SPME methods for each fiber were applied successfully to the analysis of polluted ground water samples. The levels of pesticides in the samples were low. However, they could be quantified with all fibers of different sensitivity depending on the type of compound. Confirmation of the peaks was realised using a MS detector, comparing the spectra of each compound with the standard and confirming the retention time for each fiber. Fig. 2 shows the chromatogram and spectra of a polluted sample extracted with the DVB–CAR–PDMS fiber. However, as stated above, the selectivity of sepa-

Table 3
Figures of merit for the SPME procedure

Compound	CW–DVB				CAR–PDMS				DVB–CAR–PDMS			
	Linear range[a] (ng l^{-1})	r^2[b]	R^c/r^d	LOD[e]	Linear range (ng l^{-1})	r	R/r	LOD	Linear range (ng l^{-1})	r	R/r	LOD
Lindane	1.0–1000	0.9960	0.7/2.0	1.0	1.1–500	0.9923	2.9/3.0	1.1	0.5–200	0.9995	2.5/4.5	0.5
Heptachlor	4.1–500	0.9839	2.6/2.9	4.1	4.4–700	0.9997	1.3/4.5	4.4	1.2–900	0.9940	4.6/5.0	1.2
Aldrin	0.8–200	0.9903	2.2/3.8	0.8	0.5–500	0.9794	4.9/6.7	0.5	0.4–700	0.9999	2.0/7.1	0.4
Triadimefon	7.6–1000	0.9884	1.2/3.6	7.6	7.6–1000	0.9772	1.4/11.6	7.6	7.4–1000	0.9743	4.3/8.9	7.4
2,4′-DDE	0.6–1000	0.9989	3.7/4.8	0.6	1.0–1000	0.9951	3.9/5.6	1.0	1.4–1000	0.9972	6.4/7.5	1.4
α-Endosulfan	1.3–300	0.9999	4.7/5.7	1.3	0.8–1000	0.9994	0.8/2.1	0.8	1.5–800	0.9894	3.0/5.1	1.5
Dieldrin	4.7–300	0.9941	3.6/4.8	4.7	0.9–300	0.9997	3.7/8.9	0.9	1.5–400	0.9946	3.3/6.6	1.5
4,4′-DDE	1.6–700	0.9828	1.9/2.0	1.6	1.4–400	0.9784	1.3/2.6	1.4	1.2–600	0.9946	3.1/4.3	1.2
Endrin	6.2–500	0.9839	1.9/3.5	6.2	1.1–400	0.9919	3.0/3.1	1.1	0.6–800	0.9999	2.6/7.8	0.6
β-Endosulfan	8.9–600	0.9880	4.0/5.9	8.9	1.6–800	0.9995	1.8/2.0	1.6	0.8–1000	0.9999	3.1/3.2	0.8
2,4′-DDT	10.2–800	0.9937	3.7/7.3	10.2	11.6–600	0.9979	5.4/10.1	11.6	2.8–900	0.9979	5.7/8.2	2.8
4,4′-DDT	4.3–400	0.9988	2.0/2.8	4.3	1.4–700	0.9943	2.1/6.6	1.4	1.4–800	0.9881	4.3/7.6	1.4

[a] Linear dynamic range.
[b] Linear correlation coefficient.
[c] Repeatability (RSD, %).
[d] Reproducibility (RSD, %).
[e] Limit of detection (ng l^{-1}).

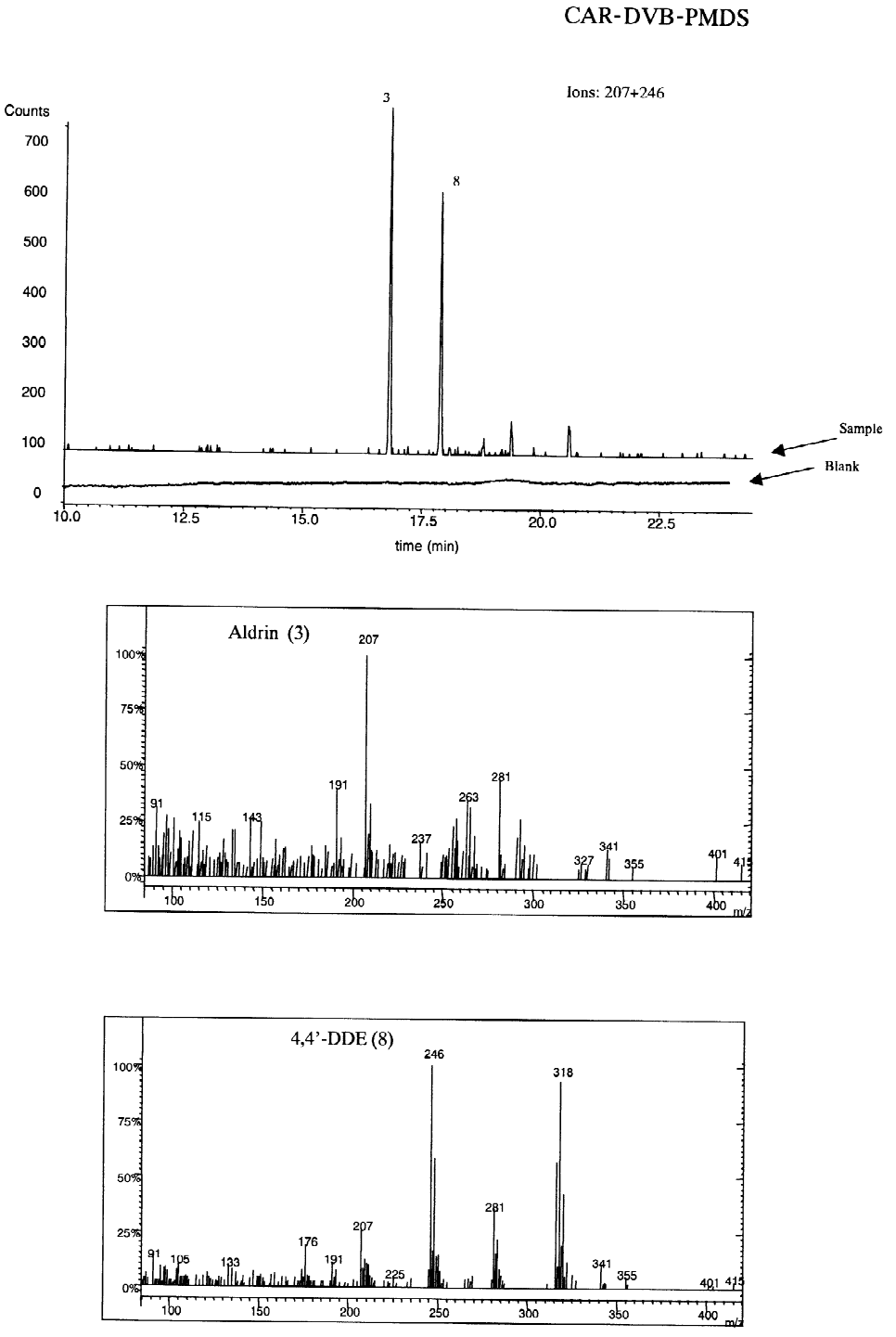

Fig. 2. Chromatogram of a polluted ground water sample and spectra of aldrin and 4,4′-DDE extracted with the DVB–CAR–PDMS fiber.

Table 4
Determination of organochlorine compounds in polluted ground water samples

Compound	S1[a]			S2			S3			S4			S5			S6			S7		
	CW–DVB	CAR–PDMS	DVB–CAR–PDMS	CW–DVB	CAR–PDMS	DVB–CAR–PDMS	CW–DVB	CAR–PDMS	DVB–CAR–PDMS	CW–DVB	CAR–PDMS	DVB–CAR–PDMS	CW–DVB	CAR–PDMS	DVB–CAR–PDMS	CW–DVB	CAR–PDMS	DVB–CAR–PDMS	CW–DVB	CAR–PDMS	DVB–CAR–PDMS
Lindane	2.4	2.7	2.5	<LOD	<LOD	1.3	2.9	2.3	2.9	<LOD	<LOD	<LOD	51.1	53.3	54.2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heptachlor	<LOD[b]	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Aldrin	18.3	18.6	18.2	<LOD	<LOD	<LOD	5.7	5.8	5.8	6.8	6.2	6.8	<LOD	<LOD	<LOD	1.5	1.1	1.1	3.1	3.4	3.5
Triadimefon	<LOD	<LOD	<LOD	13.2	15.7	14.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	61.4	61.6	60.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
2,4′-DDE	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10.2	9.7	10.8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
α-Endosulfan	<LOD	<LOD	<LOD	18.7	18.3	19.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	22.4	20.1	19.6	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Dieldrin	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4,4′-DDE	3.3	3.1	3.4	3.5	3.5	3.8	3.3	3.6	3.5	2.3	2.9	2.8	4.1	4.2	4.5	1.9	2.0	1.8	<LOD	<LOD	1.8
Endrin	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
β-Endosulfan	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
2,4′-DDT	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	12.1	12.5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4,4′-DDT	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2.5	2.6	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

[a] Number of samples (average of three analyses).

[b] Minor limit of detection.

ration depends on the fiber type. The levels of pesticides in the water samples analysed (Table 4) showed that pesticides such as aldrin and 4,4′-DDE were present in five or six samples, and other pesticides such as lindane, 2,4′-DDE, 2,4′-DDT, α-endosulfan, 4,4′-DDT and triadimefon were present in some samples, and the rest of the compounds are not present. The presence of these compounds is related to their application as commercial formulas used by farmers. As can be seen from Table 4, when the concentrations obtained for the different fibers were compared, only slight differences were observed and it could be deduced that it is necessary to use a preconcentration technique to quantify these low levels in the samples analysed. The changes in selectivity using the new double or triple coating fibers opens up new opportunities for the identification of such compounds without the necessity of using expensive detection systems.

4. Conclusions

This comparative study of SPME procedures using different fibers with two and three coatings showed that the use of these coatings is very useful for the determination of organochlorine compounds in ground water samples. The differences in selectivity provided by the different coatings can be used not only for quantification purposes, but also for identification of these compounds in complex samples. The SPME procedures presented are precise, reproducible and linear over a wide range. The detection limits obtained were lower than those in US Environmental Protection Agency method 508. The optimal extraction conditions for the three fibers were: desorption temperature (250 °C for CW–DVB, 280 °C for CAR–PDMS and 260 °C for DVB–CAR–PDMS), desorption time (15 min for the three fibers), extraction time (15 min for CW–DVB and 30 min for CAR–PDMS and DVB–CAR–PDMS), and without salt addition or pH adjustment. The optimised SPME procedures with the three fibers were successfully applied to the analysis of organochlorine compounds in polluted ground water samples and could be applicable to the analysis of other non-polar compounds of environmental concern.

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References

[1] D. Barceló, J. Chromatogr. 643 (1993) 117.
[2] M. Fielding, D. Barceló, A. Helweg, S. Galassi, L. Torstensson, P. Van Zoonen, R. Wolter, G. Angeletti, in: Pesticides in Ground and Drinking Water, Water Pollution Research Report, Vol. 27, Commission of the European Communities, Brussels, 1992, p. 1.
[3] N.F. Gray, Drinking Water Quality Problems and Solutions, Wiley, London, 1994.
[4] S. Magdic, J.B. Pawliszyn, J. Chromatogr. A 723 (1996) 111.
[5] C. Aguilar, S. Peñalver, E. Pocorull, F. Borrull, R.M. Marcé, J. Chromatogr. A 795 (1998) 105.
[6] W.H. Ho, S.J. Hsieh, Anal. Chim. Acta 428 (2001) 111.
[7] A.A. Boyd-Boland, S. Magdic, J. Pawliszyn, Analyst 121 (1996) 929.
[8] I. Brás, L. Santo, A. Alves, J. Chromatogr. A 891 (2000) 305.
[9] R.A. Doong, P.L. Liao, J. Chromatogr. A 918 (2001) 177.
[10] C. Aguilar, S. Peñalver, E. Pocurull, F. Borrul, R.M. Marce, J. Chromatogr. A 795 (1998) 105.
[11] G.P. Jackson, A.R.J. Andrews, Analyst 123 (1998) 1085.
[12] R.E. Shirey, J. High Resolut. Chromatogr. 18 (1995) 495.
[13] M.T. Almeida, P.M.A.R. Conceicao, M.F. Alpendurada, Analusis 25 (1997) 51.
[14] R. Young, V. Lopez Avila, W.F. Beckert, J. High Resolut. Chromatogr. 19 (1996) 247.
[15] Z.G. Tang, R.Q. Zhou, Z.T. Duan, J. Chem. Technol. Biotechnol. 76 (2001) 757.
[16] E.A. Nonato, F. Carazza, F.C. Silva, C.R. Carvalho, Z.D. Cardeal, J. Agric. Food Chem. 49 (2001) 3533.
[17] S.K. Golfinopoulo, T.D. Lekkas, A.D. Nikolaou, Chemosphere 45 (2001) 275.
[18] M.D. Garcia Vidal, J.L. Galera, C.R. Torreblanca, C. Gonzalez, J. Assoc. Off. Anal. Chem. Int. 80 (1997) 633.
[19] M. Gerard, J.P. Barthelemy, A. Copin, Int. J. Environ. Anal. Chem. 80 (2001) 281.
[20] L.V. Podhorniak, J.F. Negron, F.D. Griffith, J. Assoc. Off. Anal. Chem. Int. 84 (2001) 873.
[21] P.F. Pace, S.A. Senseman, M.L. Ketchersidm, H.T. Cralle, Arch. Environ. Contam. Toxicol. 37 (1999) 440.
[22] J. Engebretson, G. Hall, M. Hengel, T. Shibamoto, J. Agric. Food Chem. 49 (2001) 2198.
[23] V. Laabs, W. Amelung, W. Zech, J. Environ. Qual. 28 (1999) 1778.
[24] O.J. de Blas, J.L. de Paz, J. Assoc. Off. Anal. Chem. Int. 82 (1999) 1436.

[25] K.A. Caldwell, V.M.S. Ramanujan, Z. Cai, M.L. Gross, Anal. Chem. 65 (1993) 2372.
[26] J. Quintana, I. Martí, F. Ventura, J. Chromatogr. A 938 (2001) 3.
[27] A. Di Corcia, R. Samperi, A. Marcomini, S. Stelluto, Anal. Chem. 65 (1993) 907.
[28] J.C. Moltó, Y. Picó, G. Font, J. Mañes, J. Chromatogr. 555 (1991) 137.
[29] B. Buszewski, T. Ligor, Water Air Soil Pollut. 129 (2001) 155.
[30] J.M. Huen, R. Gillard, A.G. Mayer, B. Baltensperger, H. Kern, Fresenius J. Anal. Chem. 348 (1994) 606.
[31] C. De la Colina, P.A. Heras, G.D. Cancela, F.S. Rasero, J. Chromatogr. A 655 (1993) 127.
[32] I.J. Branabas, J.R. Dean, S.M. Hitchen, S.P. Owen, Anal. Chim. Acta 291 (1994) 261.
[33] G. Font, J. Mañes, J.C. Moltó, Y. Picó, J. Chromatogr. 642 (1993) 135.
[34] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[35] Z. Zhang, J. Pawliszyn, Anal. Chem. 65 (1993) 1843.
[36] J. Pawliszyn, Trends Anal. Chem. 14 (1995) 113.
[37] D.W. Potter, J. Pawliszyn, Environ. Sci. Technol. 28 (1994) 298.
[38] D.W. Potter, J. Pawliszyn, J. Chromatogr. 625 (1992) 247.
[39] F.J. López, E. Pitarch, S. Egea, J. Beltrán, F. Hernández, Anal. Chim. Acta 433 (2001) 217.
[40] C. Arthur, D.W. Potter, K.D. Buchholz, S. Motlagh, J. Pawliszyn, LC–GC 10 (1992) 656.
[41] P. Popp, K. Kalbitz, G. Oppermann, J. Chromatogr. A 687 (1994) 133.
[42] B.D. Page, G. Lacroix, J. Chromatogr. A 757 (1997) 173.
[43] G.P. Jackson, A.R.J. Andrews, Analyst 123 (1998) 1085.
[44] S.H. Salleh, Y. Saito, Y. Kiso, K. Jinno, Anal. Chim. Acta 433 (2001) 207.
[45] K. Jinno, Y. Han, H. Sawada, M. Taniguchi, Chromatographia 46 (1997) 309.
[46] J. Beltrán, F.J. López, F. Hernández, J. Chromatogr. A 885 (2000) 389.