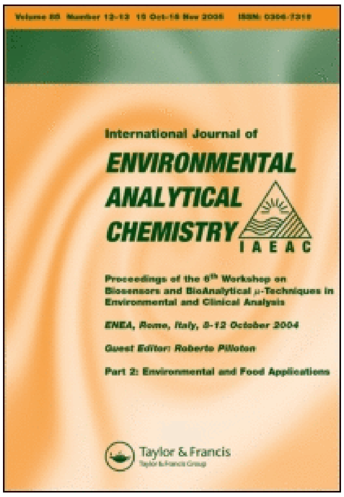

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SOLID-PHASE EXTRACTION OF ORGANOCHLORINE PESTICIDES FROM WATER SAMPLES

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A procedure for the accumulation of organochlorine pesticides by reversed-phase adsorption on octadecylsilica glass microcolumns was used for the isolation and concentration from spiked distilled and natural waters. The pesticides were eluted from the octadecylsilica with light petroleum, and analyzed by gas chromatography using an electron capture detector. The average recovery was over 90% in spiked water samples at 0.1 ng/ml. The performance of the octadecylsilica when applied to the analysis of water samples were compared with the Rodier and the APHA solvent extraction methods.

KEY WORDS: Organochlorine pesticides, octadecylsilica glass microcolumn, gas chromatography, water analysis.

INTRODUCTION

The determination of organochlorine pesticides (OCPs) in waters by using high-resolution gas chromatography with electron capture detection is a widely used procedure. The chromatographic method requires efficient solvent extraction and concentration procedures,[1,2] that makes OCP determination a time-consuming and laborious analytical process with a large consumption of organic solvents. One method extensively applied to reduce these problems involves the use of solid sorbents for extraction of OCPs present in water samples. The adsorbed compounds are then desorbed from the solid phase by an organic solvent.

Macroreticular resins, particularly Amberlite XAD resins, have been used by different workers to obtain good recoveries for organochlorine pollutants in water.[3-9] Adsorbent systems such as activated charcoal,[10,11] graphitized carbon black,[12] porous polyurethane foam,[13] Chromosorb-undecane-Carbowax,[14] Tenax GC,[12,15-17] octylsilica,[18] and octadecylsilica cartridges[9,12,19-21] have also been employed.

The C_{18}-bonded porous silica is the most widely used sorbent for extraction of organic pollutants,[22-26] because of its commercial availability in plastic cartridges. However, when gas chromatography with a highly sensitive electron capture detector is used, some foreign peaks interfere in the analysis.[27] The purpose of this work was to evaluate the use of an octadecylsilica glass microcolumn as solid phase for trace extraction of OCPs, taking advantage of the excellent extractive capacity of C_{18}-bonded porous silica for organic compounds without the interferences caused by commercial cartridges.

EXPERIMENTAL

Reagents

The organochlorine pesticides used were: aldrin, purity 98% (Promochem); endrin, purity 95% (Promochem); HCB, purity 99% (Promochem); heptachlor, purity 99% (Promochem); heptachlor epoxide, purity 99% (Promochem); lindane, purity 99.5% (Guissona, Spain); methoxychlor, purity 95.1% (Guissona, Spain); op'-DDE, purity 99% (Chem. Serv.); pp'-DDE, purity 99% (EGA-Chemie); op'-DDD, purity 99% (EGA-Chemie); pp'-DDD, purity 99% (Aldrich); and pp'-DDT, purity 99.6% (Chem. Serv.). Stock solutions of organochlorine pesticides were prepared in ethyl acetate and diluted further with distilled water.

Preparative octadecylsilica (55–105 μm) was obtained from Waters/Millipore.

Dichloromethane, ethyl acetate, ethyl ether, *n*-hexane, light petroleum (b.p. 40–60 °C), methanol and toluene were glass-distilled and free from interfering residues as tested by gas chromatography (concentration 100:1).

Microcolumn preparation Put 0.5 g of octadecylsilica in a glass column (100 mm × 9 mm i.d.) containing a coarse frit (no. 3) and cover it with a plug of silanized glass-wool. The microcolumn is activated before use with 10 ml of methanol followed by 10 ml of distilled water.

Apparatus

A KoniK 2000-C gas chromatograph with a splitless injector, a nickel-63 high-temperature electron capture detector and a Spectra-Physics SP 4290 integrator were used. A 25 m × 0.25 mm i.d. BP-5 fused silica capillary column from Scientific Glass Engineering was used. The injector and detector temperatures were 260 °C and 300 °C, respectively. Splitless injection at 50 °C was employed, followed by a 0.8 min delay before heating the column to 210 °C, at 30 °C/min. The column temperature was maintained at 210 °C for 2 min, followed by further heating to 260 °C at 2 °C/min; the final temperature was maintained for 2 min.

Helium was used as carrier gas with a flow rate of 25 ml/min (1.5 ml/min on column); argon–methane (95:5) was used as make-up gas at a flow rate of 46 ml/min.

Procedure

A volume of 1 l of water was transferred to a separatory funnel connected by means of glass joints to a chromatographic glass column, containing 0.5 g of octadecylsilica. The water sample was passed through the glass microcolumn at a flow rate of 30–40 ml min^{-1} under a vacuum, allowing it to drain completely. The water was discarded. After the percolation the column was detached from the

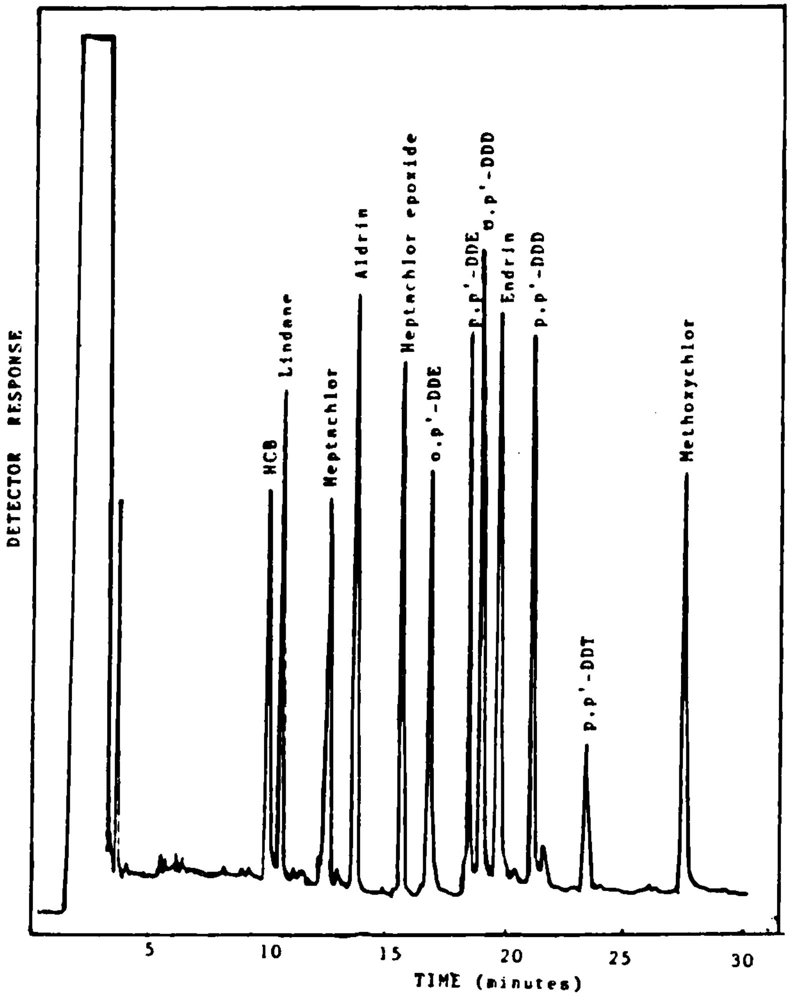

Figure 1 Chromatogram for the separation of OCPs: HCB (60 pg), lindane (70 pg), heptachlor (100 pg), aldrin (100 pg), heptachlor epoxide (100 pg), op'-DDE (65 pg), pp'-DDE (140 pg), op'-DDD (320 pg), endrin (270 pg), pp'-DDD (180 pg), pp'-DDT (65 pg) and methoxychlor (340 pg). For experimental details, see text.

separatory funnel and the adsorbed residues were eluted with 5 ml of light petroleum. The organic layer was concentrated to ca. 150 μl using a gentle stream of nitrogen gas and diluted to 200 μl with light petroleum. Samples of 1 μl were injected with splitless time of 0.8 min. Determinations in unknown or spiked material were done by comparing peak areas with those of standards injected under identical conditions. A blank run was included with each set of experiments.

RESULTS AND DISCUSSIONS

Figure 1 shows the chromatogram for the separation of the OCPs after octadecyl-

Table 1 Recovery of pesticides from water (spiked at 0.1 ng/ml) using C-18-bonded porous silica and different eluents

Pesticide	*Ethyl acetate*	*n-Hexane*	*Light petroleum*	*Toluene*
HCB	70	72	82	41
Lindane	100	109	105	54
Heptachlor	68	66	84	32
Aldrin	63	58	80	31
Hept. epoxide	92	96	101	55
op'-DDE	71	81	85	60
pp'-DDE	68	75	85	51
op'-DDD	79	87	94	55
Endrin	95	92	100	70
pp'-DDD	92	95	95	57
pp'-DDT	80	81	88	68
Methoxychlor	95	96	98	74

Table 2 Recovery of pesticides from water (spiked at 0.1 ng/ml) using different amounts of C-18-bonded porous silica

Pesticide	*0.2 g*	*0.3 g*	*0.4 g*	*0.5 g*	*0.8 g*
HCB	56	64	77	82	83
Lindane	81	83	102	105	102
Heptachlor	58	72	76	84	88
Aldrin	43	68	69	80	79
Hept. epoxide	77	84	96	101	95
op'-DDE	50	58	71	85	86
pp'-DDE	43	57	70	85	87
op'-DDD	58	69	80	94	94
Endrin	80	86	102	100	101
pp'-DDD	60	70	77	90	89
pp'-DDT	63	75	80	88	90
Methoxychlor	76	82	101	98	100

Table 3 Recovery of pesticides from water (spiked at 0.1 ng/ml) using APHA and Rodier methods for solvent extraction and C-18-bonded porous silica for solid phase extraction

Pesticide	*% recovery with*		
	APHA	*Rodier*	*C-18*
HCB	73±11	86±9	82±8
Lindane	108±12	81±10	105±7
Heptachlor	83±10	73±9	84±9
Aldrin	75±6	70±11	80±8
Hept. epoxide	103±8	90±7	101±9
op'-DDE	90±9	91±9	85±7
pp'-DDE	84±9	80±10	85±8
op'-DDD	93±10	87±7	94±9
Endrin	106±8	107±9	100±7
pp'-DDD	97±10	90±9	95±7
pp'-DDT	92±9	103±8	88±6
Methoxychlor	90±8	97±10	98±7

Table 4 Retention times (t_R) and limit of detection (LOD)

Pesticide	t_R *(min)*	*LOD (ng/l)*
HCB	10.33	0.021
Lindane	10.95	0.018
Heptachlor	13.31	0.037
Aldrin	14.74	0.039
Hept. epoxide	16.71	0.026
op'-DDE	18.25	0.065
pp'-DDE	19.55	0.047
op'-DDD	20.07	0.093
Endrin	21.09	0.071
pp'-DDD	22.09	0.047
pp'-DDT	24.46	0.069
Methoxychlor	94.70	0.092

Table 5 Results from surface waters using C-18-bonded porous silica for solid-phase extraction and the APHA method for solvent extraction of pesticides

Sample	*Concentration in ng/l*		
	Pesticide	*C-18*	*APHA*
1	Lindane	15	13
	op'-DDD	10	11
2	Aldrin	42	38
	op'-DDD	25	28
3	Lindane	537	520
	op'-DDE	10	8
	op'-DDD	15	20
4	Lindane	606	635

bonded porous silica glass microcolumn extraction from water. This chromatogram, obtained using an electron capture detector did not contain extraneous peaks. The recoveries reported are means of five analyses. The pesticide concentrations in water was 0.1 ng/ml in all tests.

Table 1 gives the recoveries obtained using 0.5 g of octadecylsilica and ethyl acetate, *n*-hexane, light petroleum and toluene as eluents for OCPs spiked into water at 0.1 ng/ml. The 200 μl of eluate from 1 l of water correspond to a concentration factor of 5000:1. The best results were obtained with light petroleum. A study of the effect of different octadecylsilica amounts on OCP recovery showed (Table 2) that 0.5 g of adsorbent gives satisfactory recoveries. Table 3 shows that the present method gives results with spiked tap water similar to those obtained employing classic solvent extraction methods, such as those proposed by Rodier[1] and APHA[2].

A summary of the GC retention data and absolute limits of detection is presented in Table 4.

Application

Table 5 gives the results obtained when surface water samples were analyzed using octadecyl-bonded porous silica glass microcolumn and conventional solvent extraction. The data are seen to show good mutual agreement.

The extraction of OCPs from water with octadecylsilica requires less solvent than conventional solvent extraction methods; moreover, the method is faster and easier to perform. The procedure is readily adapted to larger sample volumes and produces very low method blanks. The use of glass microcolumn has the advantage of leading to no contamination of the sample with plasticizers, which give extraneous peaks when an electron capture detector is used.[25]

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