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USE OF AMBERLITE XAD-4 FOR EXTRACTION AND RECOVERY OF CHLORINATED INSECTICIDES AND POLYCHLORINATED BIPHENYLS FROM WATER

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SUMMARY

Amberlite XAD macroreticular resinous adsorbents were used for the extraction and recovery of both chlorinated insecticides and polychlorinated biphenyls from water. One litre of tap water was doped at the ppb level* and after passage through the resin the adsorbed insecticides were eluted with a diethyl ether–hexane mixture. When determined by electron capture gas chromatography, aldrin and *p,p'*-DDE were the only insecticides not quantitatively recovered. The recovery of polychlorinated biphenyls was usually around 76%.

INTRODUCTION

Due to the environmental hazards of both chlorinated insecticides and polychlorinated biphenyls (PCBs), much interest has been shown during recent years in their determination.

Rosen and Middleton's method[1] of adsorption on a filter containing activated carbon, and Kahn and Wayman's method[2] of continuous extraction with an organic solvent both present problems. Although adsorption by the carbon is highly efficient, desorption is very difficult, and the recovered material is often different from the original material due to catalytic effects exhibited by the carbon. Extraction with an organic solvent is time consuming, the apparatus is cumbersome and large volumes of solvents are required.

Attempts have recently been made to improve upon these methods. Ahling and Jensen[3] developed a reversed liquid–liquid partition filter which, although it gave recoveries of 93–100% for PCBs, gave recoveries ranging in value from 50–100% for the insecticides used. Uthe *et al.*[4] used porous polyurethane foams as the adsorbent for PCBs and obtained recoveries of 91–98%.

Uthe *et al.*[5] employed similar polyurethane foam coated with chromatographic-

* Throughout this article the American billion (10^9) is meant.

grade greases as the adsorbent for chlorinated insecticides, and obtained recoveries of 92–100% for the insecticides investigated.

Support-bonded silicones in which thick films of silicones are chemically bonded to diatomaceous earth particles, *e.g.* Chromosorb G, were reported by Aue *et al.*[6] as adsorbents suitable for the extraction of chlorinated insecticides from water. Unfortunately no values for recoveries were given.

In this paper a new method is presented in which Amberlite XAD-4, a synthetic polymeric adsorbent, is used for the extraction of organochlorine insecticides and PCBs from water. Burnham *et al.*[7] and Holding[8] have used Amberlite XAD-2 for the extraction of organic contaminants from water. Burnham and his co-workers obtained quantitative recoveries in the ppb range for methyl isobutyl ketone, ethyl butyrate, benzene, naphthalene, benzoic acid, 2,4-dimethylphenol, *p*-nitrophenol, 2-methylphenol, aniline, and *o*-cresol.

The Amberlite XAD macroreticular resinous adsorbents are hard, insoluble beads of porous polymer. Their surface polarities range from non-polar to very highly polar and a variety of surface areas, porosities and pore size distributions are also represented. The surface properties of these four adsorbents are summarised in Table I. These differences in surface properties enable the Amberlite adsorbents to exhibit a wide range of sorption behaviour. The non-polar adsorbents should be particularly effective for adsorbing non-polar solutes from polar solvents.

TABLE I

CLASSIFICATION AND PROPERTIES OF AMBERLITE ADSORBENTS

Amberlite adsorbent	*Functionality*	*Helium porosity*		*Mercury porosity*		*Surface area* (m^2g^{-1})	*Average pore diameter* (Å)	*Skeletal density* ($g\ cm^{-3}$)	*Inherent dipole moment of functional group*
		Volume (%)	cm^3g^{-1}	*Volume* (%)	cm^3g^{-1}				
XAD-2	Styrene-DVB	42.0	0.693	39.3	0.648	300	90	1.081	0.3
XAD-4	Styrene-DVB	51.3	0.998	50.2	0.976	784	50	1.085	0.3
XAD-8	Acrylic ester	52.4	0.822	51.9	0.787	140	235	1.259	1.8
XAD-12	Very polar nitrogen-oxygen group	45.1	0.787	50.4	0.880	22	1300	1.169	4.5

The optimum solvent polarity for eluting the adsorbed insecticides from Amberlite XAD-4 was determined and then a comparison of the abilities of Amberlite XAD-2, XAD-4, XAD-8 and XAD-12 for recovering organochlorine insecticides from water was made.

The optimum conditions for maximum recoveries were determined by varying the amount of resin, the resin mesh size and the flow-rate of doped water; this was also applied to the analysis of the PCBs.

The adsorption by the glass and glass-wool was then determined, and, finally, the amount of lindane which can be passed through Amberlite XAD-4 before leakage occurs was determined.

EXPERIMENTAL

Amberlite XAD resin, as purchased from Rohm & Haas (Philadelphia, Pa., U.S.A.) was ground and sieved to the required mesh size and then washed with hexane and acetone. AnalaR acetone and diethyl ether were used, the diethyl ether being distilled in an all-glass apparatus. The hexane was purified by distillation after sulphonation and nitration of the aromatic impurities. A negligible background was obtained with a 50-fold concentration.

The required amount of resin was weighed into a 20 × 1 cm I.D. glass column between a sintered glass disc, which acted as a base for the resin, and a glass-wool plug.

One litre of tap water, doped with the chlorinated insecticides of interest, was passed through the resin at a flow-rate of 8 ml min^{-1} without vacuum and 32 ml min^{-1} with vacuum. After sampling, the resin was dried by drawing air through and the insecticides eluted with a volume of the required ratio of hexane–diethyl ether. Each experiment was performed in duplicate, and the results quoted are an average of the two experiments.

The extracts were concentrated down to 5 ml and injected into a Pye 104 gas–liquid chromatograph fitted with a ^{63}Ni electron capture detector (ECD) operating in the pulse mode and fitted with a 5 ft. 6 in. glass column of 4 mm I.D. The column was packed with Gas-Chrom Q (100–120 mesh) coated with 1.5% OV-17 + 1.95% QF-1. Argon was the carrier gas at a flow-rate of 10 ml min^{-1}. The column temperature was 200° and the detector temperature 300°.

RESULTS AND DISCUSSION

The results given in Table II show the effect of varying the polarity of the eluting solvent on the recoveries of five chlorinated insecticides. Elution was with 50 ml of solvent, the polarity being altered by varying the percentage of diethyl ether in hexane. No single polarity gave the best recoveries for all five insecticides, but 10% diethyl ether in hexane gave the best overall recovery. It was, therefore, decided to use this solvent for all future work.

The results given in Table III give a comparison of the abilities of Amberlite

TABLE II

EFFECT OF VARYING POLARITY OF ELUTING SOLVENT

2 g of Amberlite XAD-4 (60–85 mesh). Each insecticide was doped in 1 litre of tap water at 1 ppb. Water flow-rate, 8 ml min^{-1}. Eluting solvent, 50 ml.

Insecticide	*Recovery (%)*						
	100% hexane	*1% diethyl ether in hexane*	*5% diethyl ether in hexane*	*10% diethyl ether in hexane*	*15% diethyl ether in hexane*	*20% diethyl ether in hexane*	*30% diethyl ether in hexane*
α-BHC	72	93	76	90	80	80	74
Lindane	80	97	87	107	101	91	85
β-BHC	0	7	21	81	95	71	76
Aldrin	43	77	68	50	65	69	61
Dieldrin	76	91	76	107	66	66	66

TABLE III

COMPARISON OF AMBERLITE XAD-2, XAD-4, XAD-8, AND XAD-12

2 g of each resin (60–85 mesh, except XAD-12, which was 36–60 mesh). Each insecticide was doped in 1 litre of tap water at 1 ppb. Water flow-rate, 8 ml min^{-1}, except for XAD-12, where the water flow-rate was approximately 20 ml h^{-1}. Eluting solvent, 50 ml of 10% diethyl ether in hexane.

Insecticide	*Recovery (%)*			
	XAD-2	*XAD-4*	*XAD-8*	*XAD-12*
α-BHC	53	90	28	9
Lindane	45	107	17	10
β-BHC	71	81	0	32
Aldrin	51	50	63	25
Dieldrin	61	107	82	25

TABLE IV

DEPENDENCE OF RECOVERY ON AMOUNT OF RESIN

Insecticides doped in 1 litre of tap water at the concentrations shown. Flow-rate, 8 ml min^{-1}. Eluting solvent, 100 ml of 10% diethyl ether in hexane.

Insecticide	*Concentration of insecticide (ppb)*	*Recovery (%)*	
		2 g of XAD-4, 60–85 mesh	*1 g of XAD-4, 60–85 mesh*
α-BHC	1	114	97
Lindane	1	106	106
β-BHC	1	112	99
Aldrin	1	61	82
p,p'-DDE	2	97	77
Dieldrin	1	106	88
Endrin	10	115	85
o,p'-DDT	10	111	81
p,p'-DDD	10	102	85
p,p'-DDT	10	114	84

XAD-2, XAD-4, XAD-8, and XAD-12 for recovering chlorinated insecticides from water. Elution was with 50 ml of 10% diethyl ether in hexane in each case. Amberlite XAD-4 gave the best recoveries for four of the five insecticides used, XAD-8 giving a slightly better recovery for aldrin (63% compared with 50%). It was therefore decided to use XAD-4 for all future work.

The results given in Table IV show how the recoveries are dependent on the amount of resin used. Elution was with 100 ml of 10% diethyl ether in hexane. The recoveries obtained using 2 g of XAD-4 were 100% or above for all insecticides except aldrin, 61%, and *p,p'*-DDE, 97%. The recoveries obtained using 1 g of XAD-4 were all lower, except for lindane, which was the same, and aldrin, which was higher (82% compared with 61%). This suggests that the lower recovery of aldrin when 2 g of resin were used was due to difficulty in desorbing it from the resin.

An attempt was made to improve the recoveries when using 1 g of resin by varying the resin mesh size and the flow-rate of the doped water. The results obtained are shown in Table V. On decreasing the particle size, the recoveries of some insecti-

TABLE V

EFFECT OF VARYING RESIN MESH SIZE AND WATER FLOW-RATE

Insecticides doped in 1 litre of tap water at the concentrations and flow-rates shown. Eluting solvent, 100 ml of 10% diethyl ether in hexane.

Insecticide	*Concentration of insecticide (ppb)*	*Recovery (%)*	
		1 g of XAD-4, 85–120 mesh; water flow-rate 8 ml min^{-1}	*1 g of XAD-4, 60–85 mesh; water flow-rate 32 ml min^{-1}*
α-BHC	1	78	55
Lindane	1	98	66
β-BHC	1	108	98
Aldrin	1	72	41
p,p'-DDE	2	105	47
Dieldrin	1	77	55
Endrin	10	85	98
o,p'-DDT	10	99	83
p,p'-DDD	10	113	81
p,p'-DDT	10	109	81

cides increased. However, the recoveries of α-BHC, aldrin, and dieldrin decreased. On increasing the flow-rate of the doped water through the resin, the recoveries of most insecticides decreased.

Therefore, the optimum conditions for maximum recoveries of insecticides are: (1) 2 g of Amberlite XAD-4 (60–85 mesh B.S.S.), (2) a flow-rate of water through the resin of 8 ml min^{-1}, and (3) 100 ml of 10% diethyl ether in hexane as eluting solvent. This was then applied to PCBs (10 ppb in 1 litre of tap water), recoveries of only 76% being obtained under the above conditions.

The results given in Table VI show the adsorption by the glass and glass-wool.

TABLE VI

ADSORPTION OF INSECTICIDES BY GLASS AND GLASS-WOOL

Insecticides doped at 1 litre of tap water in the concentrations shown. Flow-rate, 8 ml min^{-1}. Eluting solvent, 100 ml of 10% diethyl ether in hexane.

Insecticide	*Concentration of insecticide (ppb)*	*Adsorption by glass and glass-wool (%)*
α-BHC	1	1
Lindane	1	2
β-BHC	1	0
Aldrin	1	21
p,p'-DDE	2	32
Dieldrin	1	7
Endrin	10	0
o,p'-DDT	10	29
p,p'-DDD	10	12
p,p'-DDT	10	16

The doped water sample was passed through columns containing no resin and elution was again with 100 ml of 10% diethyl ether in hexane.

The results given in Table VII show that up to 30 mg of lindane can be passed through 2 g of XAD-4 before leakage or breakthrough occurs.

TABLE VII

AMOUNT OF LINDANE WHICH CAN BE PASSED THROUGH 2 g OF XAD-4 (60-85 MESH) BEFORE LEAKAGE

Flow-rate of doped tap water 8 ml min^{-1}. 100 ml of 10% diethyl ether in hexane as eluting solvent.

Amount of lindane (mg)	*Recovery (%)*
1	107
6	103
30	103
40	94
50	59

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