

CHROM. 8924

## EXTRACTANTS FOR ORGANOCHLORINE INSECTICIDES AND POLYCHLORINATED BIPHENYLS FROM WATER

P. R. MUSTY and G. NICKLESS

*Department of Inorganic Chemistry, School of Chemistry, The University, Bristol BS8 1TS (Great Britain)*

(Received December 1st, 1975)

---

### SUMMARY

A reversed liquid-liquid partition system prepared from Chromosorb W, *n*-undecane and Carbowax 4000 monostearate was shown to be suitable for extracting organochlorine insecticides and polychlorinated biphenyls (PCBs) from water (with the exception of Aroclor 1260).

The performances of the partition system, Amberlite XAD-4, porous polyurethane foam and the solvent extraction technique when applied to the analysis of four environmental water samples were comparable (except for Aroclor 1260).

---

### INTRODUCTION

Musty and Nickless demonstrated that Amberlite XAD-4 (ref. 1), a macroreticular styrene-divinylbenzene copolymer, and porous polyurethane foam<sup>2</sup> are suitable materials for extracting organochlorine insecticides and PCBs from water. This paper presents the results of an investigation into the performance of the reversed liquid-liquid partition system composed of Carbowax 4000 monostearate and *n*-undecane coated onto Chromosorb W, first described by Ahling and Jensen<sup>3</sup>, when employed as an extractant for these compounds.

The effects of support inertness, adsorbent composition, water flow-rate, pH and chlorinity on the ability of the system to extract organochlorines from water are presented.

The performances of the Carbowax-undecane system, Amberlite XAD-4, porous polyurethane foam and the solvent extraction technique when applied to the analysis of four environmental water samples were compared and the results are presented.

### EXPERIMENTAL

The Chromosorb-undecane-Carbowax system was prepared by dissolving the required quantities of Carbowax 4000 monostearate and *n*-undecane in a suitable

volume of acetone, adding the specified weight of Chromosorb W (60–80 mesh B.S.S.\*) and agitating the slurry for 1 h before removing the excess solvent and drying the coated support at 110° for 12 h.

*n*-Undecane was purified according to the procedure described by Ahling and Jensen<sup>3</sup> in which 50-ml portions were shaken with concentrated sulphuric acid until the acid remained colourless prior to passage of the hydrocarbon through 10 g of activated alumina (at 250°, for 12 h).

Amberlite XAD-4 (60–85 mesh B.S.S.) and the reversed liquid–liquid partition system were employed in 20 × 1 cm I.D. glass columns while the polyurethane foam (foam A; ref. 2) was utilised in 20 × 2 cm I.D. glass columns. Both the Amberlite XAD-4 and polyurethane foam were treated as previously described<sup>1,2</sup>.

AnalaR quality acetone and diethyl ether were purified by single distillations in all-glass apparatus while *n*-hexane and light petroleum (b.p. 40–60°) were purified by distillation after sulphonation and nitration of the aromatic impurities. A negligible background was obtained after each solvent was reduced from 100 to 1 ml by evaporation and examined under the approximate gas–liquid chromatographic (GLC) operating conditions employed in the actual analysis of organochlorines.

Recovery experiments were conducted by spiking 1-l volumes of tap water with organochlorines followed by passage through the extractant, without the aid of a vacuum or pump, at the specified flow-rate. They were performed in duplicate and the results presented are an average of the two values. A blank run was also included with each set of experiments. Analyses of real water samples were not performed in duplicate.

Florisil, silicic acid, Celite and sodium sulphate were washed free of contaminants by soaking in reagent-grade acetone for 12 h, rinsing three times with pure acetone, soaking in pure hexane for 12 h, rinsing three times with pure hexane, soaking in an diethyl ether–hexane (*ca.* 8:92) mixture for 6 h followed by rinsing twice with pure acetone and drying. Kieselgel G (nach Stahl) was decontaminated in a muffle furnace at 300° for 16 h.

A Pye 104 gas–liquid chromatograph equipped with a <sup>63</sup>Ni electron capture detector was employed. It was operated in the pulsed mode and fitted with double coiled glass columns, 1.5 m × 4 mm I.D. The column packings used were 1.5% OV-17 plus 1.95% QF-1 on Gas-Chrom Q (100–120 mesh B.S.S.) and 2% OV-17 on Supasorb (85–100 mesh B.S.S.). The column oven temperature was generally about 200° and the detector temperature maintained at 300°.

## RESULTS AND DISCUSSION

Table I presents the recoveries of ten organochlorine insecticides from spiked tap water using 5 g of the partition material prepared from 100 g of Chromosorb W, 30 g of *n*-undecane and 10 g of Carbowax 4000 monostearate. Both AW HMDS-treated and untreated supports were employed. The average water flow-rate was 5 ml/min and elution was achieved with 50 ml of light petroleum. The necessity for support inertness is immediately evident.

Unfortunately, the recoveries of the BHC compounds remained low, particu-

\* B.S.S. = British Standard Sieves.

TABLE I  
PERFORMANCE OF ADSORBENT PREPARED FROM 100 g OF CHROMOSORB W, 30 g OF UNDECANE AND 10 g OF CARBOWAX

Insecticide	Concentration ( $\mu\text{g/l}$ )	Recovery (%)	
		Untreated support	AW MHDS-treated support
$\alpha$ -BHC	1.0	4	69
Lindane	1.0	4	58
$\beta$ -BHC	1.0	1	12
Aldrin	1.0	75	97
<i>p,p'</i> -DDE	2.0	93	101
Dieldrin	1.0	27	109
Endrin	10.0	23	107
<i>o,p'</i> -DDT	10.0	104	111
<i>p,p'</i> -TDE	2.0	72	105
<i>p,p'</i> -DDT	10.0	108	108

larly  $\beta$ -BHC. In order to determine whether or not these compounds were completely extracted from the water, Carbowax–undecane-extracted spiked water was further analysed by solvent extraction. The unrecovered hexachlorocyclohexanes remained in the water. This particular extractant composition was, therefore, unsuitable for analysing the BHC compounds.

The composition of the adsorbent was, therefore, varied. Chromosorb W, AW-HMDS, was employed as the support, spiked tap water samples were passed through the materials at average flow-rates of 5 ml/min and the insecticides recovered with 50 ml of light petroleum. The results are presented in Table II. The system which yielded the best overall recovery was that prepared from 100 g of support, 50 g of undecane and 5 g of Carbowax.

Table III presents the recoveries of four Aroclor mixtures, heptachlor, endosulfan I and endosulfan II from the 100:50:5 system under the conditions specified above. At least 50% of Aroclor 1260 remained unextracted from the water.

The results shown in Table IV demonstrate the effect of increasing the water flow-rate to 12 ml/min (Chromosorb W, AW-HMDS, was used as support). A decrease in the recovery of  $\beta$ -BHC only was observed.

The results given in Tables V and VI demonstrate the effects of the pH and the chlorinity of the spiked water sample on the performance of the adsorbent. Five grams of the 100:50:5 system were employed (Chromosorb W, AW-HMDS) and the average water flow-rate was 5 ml/min. Elution was achieved with 50 ml of light petroleum.

Amberlite XAD-4, porous polyurethane foam and the Chromosorb–undecane–Carbowax adsorbent were applied to the analysis of "real" environmental water samples and their performances were compared with that of the solvent extraction procedure.

Four samples, two of negligible chlorinity and two containing relatively high chloride ion concentrations, were taken. Table VII presents a brief history of each sample.

Samples were collected in thoroughly washed, silanised Winchester quart glass solvent bottles. The plastic screw caps were lined with aluminium foil. Samples were

TABLE II  
 EVALUATION OF OPTIMUM ADSORBENT (UNDECANE-CARBOWAX) COMPOSITION  
 All systems were prepared with 100 g of support. Adsorbent compositions (undecane-Carbowax) are in grams.

Insecticide	Concentration ( $\mu\text{g/l}$ )	Recovery (%)									
		30:1	40:1	50:1	30:5	40:5	50:5	60:5	30:10	30:15	30:20
$\alpha$ -BHC	1.0	95	98	106	106	100	103	103	69	89	105
Lindane	1.0	88	101	110	109	103	101	105	58	76	104
$\beta$ -BHC	1.0	74	61	65	61	66	86	51	12	23	31
Aldrin	1.0	74	61	63	76	67	73	73	97	92	69
<i>p,p'</i> -DDE	2.0	96	86	80	89	79	92	98	101	81	96
Dieldrin	1.0	106	108	110	103	101	107	109	109	103	103
Endrin	10.0	99	105	109	103	104	103	104	107	108	108
<i>o,p'</i> -DDT	10.0	106	110	111	104	111	107	113	111	106	108
<i>p,p'</i> -TDE	2.0	83	100	109	105	93	102	100	105	107	86
<i>p,p'</i> -DDT	10.0	106	107	106	101	110	107	104	108	101	110

TABLE III  
RECOVERIES OF PCBs, HEPTACHLOR, ENDOSULFAN I AND II

<i>Organochlorine</i>	<i>Concentration (<math>\mu\text{g/l}</math>)</i>	<i>Recovery (%)</i>
Aroclor 1242	10.0	97
Aroclor 1248	10.0	90
Aroclor 1254	20.0	72
Aroclor 1260	20.0	48
Heptachlor	1.0	106
Endosulfan I	2.0	100
Endosulfan II	2.0	104

TABLE IV  
PERFORMANCE OF ADSORBENT AT A WATER FLOW-RATE OF 12 ml/min

<i>Insecticide</i>	<i>Concentration (<math>\mu\text{g/l}</math>)</i>	<i>Recovery (%)</i>
$\alpha$ -BHC	1.0	106
Lindane	1.0	101
$\beta$ -BHC	1.0	57
Aldrin	1.0	76
<i>p,p'</i> -DDE	2.0	90
Dieldrin	1.0	98
Endrin	10.0	102
<i>o,p'</i> -DDT	10.0	107
<i>p,p'</i> -TDE	2.0	100
<i>p,p'</i> -DDT	10.0	106

TABLE V  
EFFECT OF pH ON ADSORBENT PERFORMANCE

<i>Insecticide</i>	<i>Concentration (<math>\mu\text{g/l}</math>)</i>	<i>Recovery (%)</i>				
		<i>pH 5</i>	<i>pH 6</i>	<i>pH 7</i>	<i>pH 8</i>	<i>pH 9</i>
$\alpha$ -BHC	1.0	105	106	105	103	109
Lindane	1.0	106	110	100	101	110
$\beta$ -BHC	1.0	77	74	69	86	76
Aldrin	1.0	54	73	66	73	70
<i>p,p'</i> -DDE	2.0	71	75	74	92	70
Dieldrin	1.0	92	96	95	107	100
Endrin	10.0	98	103	102	103	102
<i>o,p'</i> -DDT	10.0	98	103	109	107	108
<i>p,p'</i> -TDE	2.0	74	85	83	102	90
<i>p,p'</i> -DDT	10.0	106	101	102	107	106

filtered within 24 h of their return to the laboratory and were analysed as soon as filtering was complete. The samples were filtered through (i) Whatman No. 541 filter paper, (ii) a 0.45- $\mu\text{m}$  Millipore filter.

Filtering was necessary because of the high suspended sediment content of two of the samples. A substantial proportion of the organochlorines in water samples

TABLE VI  
EFFECT OF CHLORINITY ON RECOVERY

Insecticide	Concentration ( $\mu\text{g/l}$ )	Recovery (%)				
		Chloride ion concentration (mg/l)				
		10	100	1,000	10,000	25,000
$\alpha$ -BHC	1.0	96	101	106	104	109
Lindane	1.0	106	106	106	109	107
$\beta$ -BHC	1.0	58	61	69	58	72
Aldrin	1.0	59	71	67	84	72
<i>p,p'</i> -DDE	2.0	87	87	67	65	76
Dieldrin	1.0	96	101	105	108	98
Endrin	10.0	106	108	110	109	—*
<i>o,p'</i> -DDT	10.0	84	99	74	83	86
<i>p,p'</i> -TDE	2.0	93	100	79	78	82
<i>p,p'</i> -DDT	10.0	83	98	64	63	76

\* No recovery values were obtained for endrin at a chloride ion concentration of 25,000 mg/l because of a very large impurity peak in that region of the chromatogram.

is adsorbed onto these particles and extraction with cold solvents for short periods of time leads to incomplete recoveries and erroneous results.

Four-litre volumes of the River Leadon and River Severn samples were extracted with:

- (i) 2 g of Amberlite XAD-4, average water flow-rate 8 ml/min;
- (ii) 5 g of the 100:50:5 Chromosorb-undecane-Carbowax system (Chromosorb W, AW-HMDS), average water flow-rate 5 ml/min;
- (iii) two porous polyurethane ( $8 \times 2.2$  cm) plugs of foam A, average water flow-rate 100 ml/min.

The adsorbed compounds were eluted with 100 ml of diethyl ether-hexane (1:9) followed by 100 ml of hexane, 50 ml of light petroleum and 50 ml of acetone followed by 100 ml of hexane, respectively. One-litre volumes were also extracted twice with 60 ml of diethyl ether-hexane (15:85) followed by 60 ml of hexane.

In the case of the Long Ashton sample, 1-l portions were extracted by each procedure.

The two River Severn samples were sufficiently high in suspended materials for the sediments to be analysed separately. These were dried at  $60^\circ$  for 72 h and Soxhlet-extracted with an azeotropic hexane-acetone mixture (41:59) for 12 h. Unfortunately, the samples taken from the River Leadon and Long Ashton Research Station did not contain sufficient suspended materials to permit such a determination.

Extracts were dried by passage through approximately 15 g of anhydrous sodium sulphate. Interfering coextractives were removed by Florisil cleanup<sup>4</sup> and a modification of the Armour and Burke silicic acid separation technique<sup>5</sup>.

Kieselgel G (nach Stahl) was employed as the adsorbent for thin-layer chromatography (TLC) and carbon tetrachloride as the developer.

Lindane and  $\alpha$ -BHC were detected in the River Leadon sample. The concentrations, as determined by each extraction system, are presented in Table VIII. The presence of these two compounds was confirmed by TLC. Silicic acid separations were not necessary.

TABLE VII  
SAMPLE HISTORIES

<i>Location of sampling point</i>	<i>Grid reference</i>	<i>Description of waterway</i>	<i>Weather conditions</i>	<i>Date of sampling</i>	<i>Chloride ion concentration (mg/l)</i>
Highleadon Bridge on the River Leadon	235776	Slow-flowing, non-tidal river; very low in suspended sediment	Dry	31/10/74	110
Broadoak on the River Severn	698129	Fast-flowing, tidal river; very high in suspended sediment	Dry	31/10/74	3,800
Sharpness on the River Severn	667022	Fast-flowing, tidal river; high in suspended sediment	Dry	22/11/74	2,900
Long Ashton Research Station (Bristol University)	695540	Rainwater run-off from land sprayed with organochlorine insecticides	Sampling preceded by approx. 12 h of heavy rain	10/12/74	Not determined

TABLE VIII  
CONCENTRATION OF ORGANOCHLORINES IN RIVER LEADON SAMPLE

<i>Procedure</i>	<i>Organochlorine</i>	<i>Concentration (ng/l)</i>
Amberlite XAD-4	Lindane	21
	$\alpha$ -BHC	5
Porous polyurethane foam	Lindane	16
	$\alpha$ -BHC	4
Chromosorb-undecane-Carbowax	Lindane	15
	$\alpha$ -BHC	5
Solvent extraction	Lindane	15
	$\alpha$ -BHC	3

Lindane,  $\alpha$ -BHC and Aroclor 1260 were detected in the Broadoak sample. The levels, as determined by each procedure and also the quantity extracted from the sediment, are presented in Table IX. The residues were confirmed by TLC.

The concentration of Aroclor 1260 in the water, as determined by the three adsorbents, was much lower than that determined by the solvent extraction technique. Since the adsorbents all recover this mixture with 40–50% efficiency while solvent extraction recovers it with 90–100% efficiency, the adsorbent determined level of Aroclor 1260 should be approximately one half the solvent extraction determined level. However, it is considerably less than one half. This cannot be explained but a further River Severn sample was analysed to determine whether or not this is a consistent phenomenon.

TABLE IX  
CONCENTRATION OF ORGANOCHLORINES IN BROADOAK SAMPLE

<i>Procedure</i>	<i>Organochlorine</i>	<i>Concentration (ng/l)</i>
Amberlite XAD-4	Aroclor 1260	81
	Lindane	30
	$\alpha$ -BHC	3
Porous polyurethane foam	Aroclor 1260	88
	Lindane	40
	$\alpha$ -BHC	3
Chromosorb-undecane-Carbowax	Aroclor 1260	13
	Lindane	20
	$\alpha$ -BHC	5
Solvent extraction	Aroclor 1260	675
	Lindane	55
	$\alpha$ -BHC	8
Sediment	Aroclor 1260	174.6*
	Lindane	5.0*
	$\alpha$ -BHC	1.0*

\* Concentrations in sediment are in  $\mu\text{g}/\text{kg}$ .



TABLE X  
CONCENTRATION OF AROCLOR 1260 IN SHARPNESS SAMPLE

<i>Procedure</i>	<i>Concentration</i>
Amberlite XAD-4	51 ng/l
Porous polyurethane foam	62 ng/l
Chromosorb-undecane-Carbowax	64 ng/l
Solvent extraction	135 ng/l
Sediment	522.7 $\mu\text{g}/\text{kg}$

The Chromosorb-undecane-Carbowax determined level of Aroclor 1260 was substantially lower than the Amberlite XAD-4 or polyurethane foam determined level due to the incomplete recovery of Aroclor 1260 from the silicic acid.

Aroclor 1260 only was detected in the Sharpness sample. The concentrations are presented in Table X. The values are as expected, the adsorbent determined levels being consistent and about one half the solvent extraction determined level. The presence of Aroclor 1260 was confirmed by TLC.

Lindane and  $\alpha$ -BHC were detected in the Long Ashton sample. The concentrations are presented in Table XI. The residues were confirmed by TLC.

TABLE XI  
CONCENTRATION OF ORGANOCHLORINES IN LONG ASHTON RESEARCH STATION SAMPLE

<i>Procedure</i>	<i>Organochlorine</i>	<i>Concentration (ng/l)</i>
Amberlite XAD-4	Lindane	91
	$\alpha$ -BHC	53
Porous polyurethane foam	Lindane	79
	$\alpha$ -BHC	38
Chromosorb-undecane-Carbowax	Lindane	91
	$\alpha$ -BHC	46
Solvent extraction	Lindane	66
	$\alpha$ -BHC	38

## CONCLUSIONS

(i) A highly inert support is essential to produce a partition system which efficiently recovers organochlorines from water.

(ii) The superior adsorbent was that prepared from 100 g of Chromosorb W, 50 g of *n*-undecane and 5 g of Carbowax 4000 monostearate.

(iii) Aroclor 1260 was only about 50% extracted from water by the 100:50:5 system.

(iv) At a water flow-rate of 12 ml/min the recovery of  $\beta$ -BHC decreased.

(v) The effect of the pH of the spiked water between 5 and 9 and the chloride ion concentration up to 25,000 mg/l on the adsorbent performance was relatively insignificant.

(vi) There was reasonably good agreement between the results obtained from analysis of the four "real" water samples by the four extraction systems except for Aroclor 1260. It may, therefore, be expedient to perform a solvent extraction when determining Aroclor 1260.

#### REFERENCES

- 1 P. R. Musty and G. Nickless, *J. Chromatogr.*, 89 (1974) 185.
- 2 P. R. Musty and G. Nickless, *J. Chromatogr.*, 100 (1974) 83.
- 3 B. Ahling and S. Jensen, *Anal. Chem.*, 42 (1970) 1483.
- 4 A. Bevenue and J. N. Ogata, *J. Chromatogr.*, 50 (1970) 142.
- 5 J. A. Armour and J. A. Burke, *J. Ass. Off. Anal. Chem.*, 53 (1970) 761.