Journal of Chromatography, 642 (1993) 135–161
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 2749

Review

Solid-phase extraction in multi-residue pesticide analysis of water

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ABSTRACT

The determination of pesticides in water is fundamental to the solution of environmental problems as natural waters are usually contaminated with a large number of pesticides. The selection of an isolation and/or concentration technique depends largely on the class of pesticides to be determined. It is often necessary to determine simultaneously a wide variety of compounds in a water sample. Application of solid-phase extraction techniques offers a solution. The mechanisms of solid-phase extraction, types of sorbents and their application to multi-residue pesticide analysis are reviewed.

CONTENTS

1. INTRODUCTION

The determination of pesticide residues in water samples is necessary for solving various environmental and biological problems [1]. The accuracy and precision of analysis are dependent on both sample preparation and instrumental performance. The analysis is carried out using gas chromatography (GC) [2] or liquid chromatography (LC) [3]. These chromatographic techniques require efficient isolation and concentration procedures, such as liquid–liquid, supercritical fluid and solid-phase extraction [4,5].

Liquid–liquid extraction (LLE) is frequently used but it produces emulsions and different extraction efficiencies for various compounds; it also requires

0021-9673/93/$24.00

large amounts of solvent and is slow, laborious and difficult to automate [6,7].

Solid-phase extraction (SPE) is attracting increasing attention and constitutes an alternative to LLE. Desorption of retained organic compounds can be carried out by elution with a suitable solvent. SPE is widely used for the trace enrichment of very dilute solutions such as natural waters, where large sample volumes may have to be processed, to yield concentrations of analyte sufficient for detection. The technique has been reviewed in a variety of areas such as extraction of organic compounds [8–12], on-line precolumn techniques [13,14] and sample preparation in drug analysis [15]. Svoboda [16] reviewed the use of sorbents for the preconcentration of one or a few pesticides.

Supercritical fluid extraction (SPE) is in the early stages of development and so far has been used mainly with solid samples. However, it can readily be used with liquids if the sample is immobilized on a solid support. This means that the technique can be used to extract pesticides from water samples [8].

Although a single residue method is often used in analyses required by legislation or to confirm results, for the analysis of real environmental water samples, when nothing is known about the nature of possible contaminants, multi-residue methods are needed. Pesticides form a large group of compounds with widely differing structures and biological activities. Ideally, multi-residue methods should provide rapid identification and quantification of as many different pesticides as possible at the required sensitivity limit. This diversity poses problems for the analyst who is trying to develop methods that cover as many pesticides as possible [17–22].

Considering the above problems associated with this kind of analyte and matrix, we present here a detailed review of several multi-residue SPE procedures that have been proposed in the last 10 years for the determination of organochlorine, organophosphorus and organonitrogen pesticides in water.

2. MECHANIMS OF SOLID-PHASE EXTRACTION

The two major mechanisms of analyte retention on solid support are adsorption and partitioning. Extraction of trace amounts of organic compounds from water with solid sorbent is a method in which adsorption on a solid substance is used in order to isolate compounds dissolved in water. Sorbent extraction can also be based on the distribution of the dissolved compound between the solid sorbent and water. In these instances, provided that the sorbent has been selected correctly, the partition coefficient is shifted even more towards the sorbent than in water.

2.1. Adsorption

Pesticides have some affinity for binding on solid surfaces. Common adsorbents are charcoal and porous polymers. The adsorptive capacity of a given adsorbent depends in part on the treatment or manufacturing conditions and on the composition of the adsorbent (references are given in Table 1).

Charcoal was the first sorbent to be used for the extraction of organic compounds from water [10]. The advantage of this material was the high retention of low-molecular-mass polar pesticides and their metabolites [23–30].

Polymers have been used as alternative sorbents to carbon for trace enrichment since the late 1960s. Their homogeneous structure results in greater reproducibility of trace enrichment experiments. The most often used types of polymers are styrene–divinylbenzene copolymers (Polysorb S [31], Amberlite XAD-2 [32,35,36,39] and XAD-4 [33,34,37,38], PRP-1 [40–42]), acrylate polymers (Amberlite XAD-7 [39] and XAD-8 [36], Separon SE [43–45]), 2,6-diphenyl-*p*-phenylene oxide (Tenax GC [46–48]), ethylvinylbenzene–divinylbenzene (Porapak Q [40]), amide esters (polyurethane foam [49]) and organic polymeric sorbents without functional groups (Wolfatit Y77 [50]) (Table 2).

TABLE 1

ADSORPTION TECHNIQUES

Adsorbent	Ref.
Charcoal	23, 24, 25, 26, 27, 28, 29, 30
Porous polymers:	
Amberlites	32, 33, 34, 35, 36, 37, 38, 39
PRP-1	40, 41, 42
Separon SE	43, 44, 45
Tenax CG (polymide)	23, 46, 47, 48
Polyurethane foams	34, 49
Wolfatit	50

TABLE 2

DETERMINATION OF TRACES OF PESTICIDES IN WATER BY ADSORPTION ON CHARCOAL OR POROUS POLYMER SORBENTS

Extraction	Pesticides[a]	Recovery (%)	Concentration ratio	Determination method	Detection limit	Ref.
200 or 100 mg graphitized carbon black in glass column (GCB) 50 ml hexane–diethyl ether (50:50) Samples: river water, sea water and drinking water	PCBs	30–40	10–50	GC with ECD and FID	–	23
	Di-syston	95				
	Malathion	97				
	Parathion	100				
	Ronel	90				
	α-Endosulfan	98				
	p,p'-DDD	92				
	α-BHC	101				
	Heptachlor	93				
	Aldrin	102				
	γ-BHC	102				
	β-Endsulfan	100				
	Heptachlor epoxide	99				
	Dieldrin	103				
	Endrin	104				
	p,p'-DDE	93				
	o,p'-DDD	95				
	o,p'-DDE	–				
GCB in glass column 6 ml light petroleum–toluene (2:1)	Diclobenil	95.9	*ca.* 100	GC—ECD GC–MS	2–50 μg l^{-1}	24
	Trifluoralin	98.1				
	2,4-D ME	90.0				
	Propazine	76.1				
	Simazine	72.1				
	Atrazine	74.0				
	2,4,5-T ME	95.0				
	DCPA	98.4				
	Silvex ME	91.0				
50 mg GCB in catridges 1 ml light petroleum–toluene (1:1) 1 l drinking water	α-BHC	94	1000	GC–FID GC–MS	10 ng l^{-1}	28
	β-BHC	96				
	Heptachlor	87				
	δ-BHC	94				
	Aldrin	90				
	Heptachlor epoxide	97				
	p,p'-DDE	92				
	Dieldrin	97				
	Endrin	99				

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TABLE 2 (*continued*)

Extraction	Pesticides[a]	Recovery (%)	Concentration ratio	Determination method	Detection limit	Ref.
Compares with Tenax, Porapak P and C_{18}	*p,p'*-DDD	94				
	p,p'-DDT	95				
	2,4-DME	92				
	Trifluoralin	92				
	Simazine	97				
	Atrazine	93				
	Propazine	97				
	2,4,5-TME	92				
	DCPA	98				
50 mg GCB in cartridges 3 ml methanol–7 ml dichloromethane 50 ml pond water (pH 8)	$(DEDTP)^-$	82	1–50	GC–NPD GC–MS	20 $\mu g\ l^{-1}$	25
	$(DMDTP)^-$	86				
	$(DETP)^-$	59				
	$(DMTP)^-$	39				
	$(DEP)^-$	3				
	$(DMP)^-$	1				
50 mg GCB in cartridges 700 μl dichloromethane–methanol (60:40) 250 ml distilled, tap and surface water	Simazine	98.5	400	HPLC–UV GC–MS	2–4 ng l^{-1}	26
	Atrazine	97.9				
Double trap tandem system, 150 mg GCB, 150 mg SCX 5 ml dichloromethane–acetonitrile (60:40) 0.7 ml methanol–70 mmol/l KCl	Simazine	96.3–97.7	400	HPLC–UV	10 ng l^{-1}	29
	Simetryn	98.2–99.8				
	Atrazine	99.4–99.8				
	Prometon	98.6–100.3				
	Ametryn	97.3–99.4				
	Propazine	96.4–97.7				
	Prometryn	95.0–96.5				
	Terbutryn	95.7–97.2				
Same as above but 250 mg GCB eluted with 6 ml dichloromethane–methanol (95:5) 2 l drinking water	Fenuron Metoxuron Monuron Monolinuron Fluometuron Chlorturon	83–100	*ca.* 7000	HPLC–UV	1 ng l^{-1}	30

Compares with C_{18}						
	Metobromuron Difenoxuron Isoproturon Diuron Linuron Chlorbromuron Chloruxoron Neburon					
Granular activated carbon	Diazinon Azinphos-methyl Fenthion	55 60 >90	1	FIA–HPLC–UV	0.5 mg l^{-1}	27
Polysorb S	Aldrin γ-HCH Heptachlor Endrin DDE DDD DDT 2,4-D 2,4,5-T	94.0 98.7 97.4 95.2 96.0 97.0 96.8 99.3 98.8	20–40	GC HPLC	0.1–0.2 μg ml^{-1}	31
100 ml XAD-2 250 ml diethyl ether and 250 ml methanol Drinking and river water	Atrazine Simazine Linuron Metbromuron Monolinuron Chlorotoluron Buturon Carbaryl Phenmedipham Diuron Metoxuron Chloroxuron Methabezthiazuron Fenuron Cycluron	–	105	HPLC, FD, FAB	–	32
50 mg XAD-4 0.5 ml ethanol 100–500 ml water samples	Diazinon Malathion Parathion	75 97 72	1000	GC–FPD GC–FID	–	33
25–40 ml XAD-4 500 ml dichloromethane–hexane	1,2,3,4-TCDD 2,8-DCDBF 2,4-D 2,4-DME	53.3 66.5 21.5 –	1000	GC–ECD GC–NPD	0.25 ng l^{-1} 3 5 113	34

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TABLE 2 (*continued*)

Extraction	Pesticides[a]	Recovery (%)	Concentration ratio	Determination method	Detection limit	Ref.
16–19 l river water, agricultural drains (pH 8)	Amitraz	–			150	
	Aroclor 1232	51.4			–	
	Atrazine	71.2			20	
	Captan	–			–	
	Carbaryl	47.3			25	
	Diazinon	–			10	
	Diuron	51			10	
	Endosulfan	70.0			0.25	
	Ethion	77.6			10	
	Guthion	79.9			25	
	Molinate	68.0			25	
	Oryzalin	9.4			–	
	Tiobencarb	90.6			50	
100 ml XAD-2 500 ml acetone and 500 ml hexane 2 l sea water Compares with polyurethane foam and liquid–liquid extraction	PCB BHC	– –	–	GC–ECD	–	35
XAD-2, XAD-8 30 l distilled and river water 150 ml acetonitrile and 150 ml dichloromethane or 150 ml diethyl ether	Atrazine Methyl atraton	95–100	105	GC–MS	1 $\mu g\ l^{-1}$	36
XAD-4 5 ml ethanol 1 l sample	Malathion Parathion Phosalone	95 90 105	200	Spectrophotometric as phosphomolybdenum blue	150 $\mu g\ l^{-1}$	37
1.5 g XAD-4 2 ml diethyl ether and 10 ml hexane 1 l water Compares with C_{18}	α-HCH γ-HCH Aldrin Dieldrin *p,p'*-DDE *p,p'*-DDT α-Endosulfan β-Endosulfan Azinphos-ethyl	90–100 75–100 80–90 80–110 55–90 30–80 80–100 70–80 80–120	83	GC–ECD	–	38

	Diclorphos	68–88				
	Disulfoton	24–45				
	Parathion	30–60				
XAD-2 and XAD-7	Alachlor	105.0	4000	GC–MS	0.005 $\mu g\ l^{-1}$	39
300 ml	Atrazine	83.0			0.005	
dichloromethane	Butylate	101.1			0.005	
2-l water sample	Captan	74.8			1.0	
	Carbaryl	97.9			0.05	
	Carbofuran	80.4			0.005	
	Chlorothalonil	90.9			1.0	
	Chlorpyriphos	86.7			0.005	
	Cyanazine	85.0			0.05	
	Diazinon	103.8			0.0005	
	Fenamiphos	113.0			0.05	
	Fonofos	108.6			0.005	
	Isofenphos	81.5			0.005	
	Linuron	98.7			0.05	
	Metolachlor	102.5			0.005	
	Metribuzin	91.3			0.005	
	Prathion	109.3			0.005	
	Pendimethalin	88.9			0.005	
	Simazine	81.0			0.005	
	Terbufos	84.3			0.05	
PRP-1 and Porapak Q	Propazine	90–100	250–1000	HPLC–UV	10–50 $\mu g\ l^{-1}$	40
1 ml acetonitrile	Atrazine					
250 ml water	Simazine					
	Prometryne					
	Prometone					
10 × 2 mm I.D. pre-column, PLRP-S	MCPA	>85	–	On-line HPLC–UV	0.05–0.1 $\mu g\ l^{-1}$	41
Acetonitrile–water	2,4-D					
25 ml tap water (pH 3)	MCPC					
	2,4-DP					
	Bentazone					
	2,4,5-T					
	MCPB					
	2,4-DB					
	2,4,5-TP					
15 mm PRP-1	Simazine	–	–	On-line HPLC–UV	–	42
2 ml water	Atrazine	–				
500 ml natural water (pH 6–8)	Propazine	25				
	Terbutylazine	50				
Completed with a cation exchanger						
0.22 g Separon SE	MCPA		100	GC–NPD		43

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TABLE 2 (*continued*)

Extraction	Pesticides[a]	Recovery (%)	Concentration ratio	Determination method	Detection limit	Ref.
0.5 ml acetone 50 ml river water	Propazine Simazine Ametryne Atrazine Prometryne Terbutryne Ametryne Desmetryne	 98.6–100.5 98.6–100.9 99.2–100.4 99.1–100.7 99.5–100.9	100	GC–NPD	8 $\mu g\ l^{-1}$	44
200 ml water	As above		400	GC–NPD HPLC–UV		45
Tenax GC 40 ml diethyl ether 1–10-l water samples	Diazinon Lindane Heptachlor Aldrin Methyl parathion Malathion Dieldrin Endrin Phenmedipham Carbaryl Promecarb Propham Dinobuton	72 90 63 10 75 80 72 98 98 71 77 100 79	105	GC–ECD GC–FID HPTLC	0.01 $\mu g\ l^{-1}$	46
0.75 g Tenax GC, two cartridges 15 ml light petroleum 1 l water	α-HCH γ-HCH *p,p'*-DDE *p,p'*-DDD Heptachlor	59–75 58–79 73–84 76–84 53–93	500	GC–ECD GC–MS	5 $\mu g\ l^{-1}$	47
0.11 g Tenax-GC cartridges Thermal on-line desorption for 5 min, 250°C 1-l water samples	α-HCH BHC *p,p'*-DDE Dieldrin	113 109 82 86	–	GC–MS	–	48

1 g polyurethane foam 50 ml acetone 0.5–3 l distilled or tap water	Dimethoate Azodrine Lannate	94–97 95–98 90–93	60	Spectro-photometry	–	49
0.2–10 g Wolfatit Y 77 25 ml methanol 1 l tap water	Methamidophos Dimethoate Trichlorfon Natrichlorfon acetate Fenuron Propachlor 2,4-D	74–93 90–96 84–98 22–100 79–94 98–100 68–99	40	Counting of ^{14}C	–	50

[a] ME = Methyl ester.

Desorption of the compounds from the concentration columns is mainly performed with a small volume of liquid. The partition coefficient in a given polymer–eluent system should favour the pesticide being studied shifted in favour of the eluent (hexane–diethyl ether [23,38], light petroleum–toluene [24,28], methanol–dichloromethane [25,26,29,30, 39], acetone [43–45,49], diethyl ether–methanol [32], dichloromethane–hexane [34], acetone–hexane [35], acetonitrile with dichloromethane or diethyl ether [36], diethyl ether [46], ethanol [33,37], acetonitrile [40], acetonitrile–water [41], water [42], light petroleum [47] and ethanol [50]).

Another system described is thermal desorption [48], which has been applied for the determination of some organochlorine pesticides. The extraction column is introduced inside the GC oven. The desorption process is similar to that in headspace analysis. Thermal desorption can fail as a result of the very strong interaction between the analyte and the sorbent, as a temperature sufficient to desorb the analyte might also destroy the sorbent, the analyte or both. If the analyte is thermally unstable, thermal desorption can invalidate quantification and introduce artefacts even if the analyte is only weakly adsorbed.

The use of supercritical carbon dioxide to accomplish the desorption can provide solutions to these last two problems. The application of this technique to desorb spiked γ-BHC, hexachlorobiphenyl and parathion from Tenax [51] and polymides [52] may become an attractive alternative to solvent and thermal approaches in the future.

2.2. Partitioning

The development of surface-modified materials for LC has opened up a new technology for applied research [53]. The bonded phases were originally introduced for use in LC to obviate the limitations of silica gel when used to separate mixtures of highly polar and ionic sustances [54,55]. These phases can be prepared by reacting silica gel with an appropriate organic mono-, di- or trichlorosilane, producing a surface coating of organic material that replaces the surface hydroxyl groups as the interacting moieties of the stationary phase. The interacting organic groups can be simple hydrocarbon chains, as with a reversed-phase material, a hydrocarbon chain with a terminal polar functional group, as with a polar bonded phase, or an ion-exchange moiety, as with an ion-exchange bonded phase [56]. The first attempts to use them as preconcentration media date back to 1971 [57], but the modern technique had its beginning in 1978 with the commercial introduction of Sep-Pak cartridges (Waters, Milford, MA, USA) [58].

Today, SPE has blossomed into a widely applied technique: more than 30 suppliers offer phases ranging from conventional HPLC phases, such as C_{18}, C_8, cyano and amino, to reactive particles that users can derivatize with a ligand of their choice [59]. The bonded silica mostly used is that with the octadecyl group [60–63].

Table 3 presents procedures for the preconcentration of various types of pesticides from water samples on bonded silicas.

It is well known that simple extraction, evaporation and other similar techniques share the disadvantage of a high risk of contamination from containers, solvents and laboratory surroundings, and also the risk of degradation on evaporation to dryness. Octadecyl-bonded SPE has been proposed by the US Environmental Protection Agency (EPA) in Method 525 [114].

Although an off-line SPE procedure usually shortens the time of sample handling, a certain amount of tedious labour remains. The means for reducing this time-consuming work is to automate the entire procedure as much as possible. The use of precolumns makes it possible to employ on-line concentration techniques on C_{18} or C_8 in conjunction with HPLC [66–69,71,74,75,103, 106–108] but also with GC [70].

Automation of sample preparation for pesticide analysis is essential when large water samples are required. Manufacturers have met the needs of residue chemists for sampling automation by offering laboratory robots with bonded silica cartridges. The Varian AASP (advanced automated sample processor) system has been proposed for pesticide analysis of water [115,116].

A new generation of SPE devices have recently emerged. Borrowing the disc configuration of membrane filters, these devices include flat discs with large cross-sectional areas that provide advantages for on-line preconcentration and clean-up methods with respect to sorption, capacity, back-pressure

TABLE 3

DETERMINATION OF TRACES OF PESTICIDES IN WATER BY PARTITIONING ON BONDED SILICAS

Extraction	Pesticides	Recovery (%)	Concentration ratio	Determination method	Detection limit	Ref.
200 mg C_8	α-HCH	105	200	GC–ECD	–	64
0.5 ml ethyl	δ-HCH	105				
acetate	β-HCH	104				
100 ml	Heptachlor	79				
distilled, tap	Aldrin	86				
and sea water	Endosulfan	102				
Compares with	Dieldrin	92				
C_{18}, diphenyl,	Zoolone	104				
cyclohexyl, C_2,	DDT	79				
C_4, cyano, amino,						
benzenesulphonic						
acid and silica						
500 mg C_{18}	TMF	99.2	20	HPLC–UV	$<5\ \mu g\ l^{-1}$	65
1.5 ml methanol	CDPA	85.3				
30 ml river, lake	Bayer 73	91.8				
and distilled						
water (pH 4.0)						
ACDA-Pt and C_{18}	Fenuron	–45	6	On-line	–	66
precolumn	Metoxuron	92–98		HPLC–UV		
combination	Monuron	98–102				
1.7 ml methanol–	Fluometuron	92–103				
water (60:40)	Monolinuron	96–100				
10 ml river and	Buturon	0–				
distilled water	Chlortoluron	93–96				
	Metobromuron	93				
	Isoproturon	95				
	Difenoxuron	90				
	Diuron	91				
	Linuron	90				
C_{18} precolumn of	Fenuron	<90	6	On-line	–	67
11 × 2 mm I.D.	Monuron			HPLC–MS		
only	Diuron					
As above	Metobromuron					
	Linuron					
	Chlorbromuron					

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TABLE 3 *(continued)*

Extraction	Pesticides[a]	Recovery (%)	Concentration ratio	Determination method	Detection limit	Ref.
11 × 2 mm I.D. with 10-μm LiChrosorb RP-18 2.4 ml 0.02 *M* phosphate buffer (pH 7)–methanol (45:55) 10 ml of water Methanol–0.02 *M* phosphate buffer (pH 7)(45:55) 1 ml water	Fenuron Metoxuron Monuron Monolinuron Diuron Chlorbromuron Linuron	44 98 98 94 98 94 96	4	On-line HPLC–EC	0.01 μg l^{-1} 0.02 0.02 0.04 0.05 0.4 0.3	68
20 × 2 mm I.D., 40 μm C_8 Analytichem As above	Monuron Monolinuron Chlorotoluron Diuron Chlorobromuron	89–95 89–104 94–97 95–96 96–97	4	On-line HPLC–UV	–	69
LC micro-precolumn with C_8 85 μl *n*-hexane 1 ml water	α-HCH HCB γ-HCH Heptachlor epoxide Aldrin Heptachlor *o,p'*-DDE Endosulfan *p,p'*-DDE Dieldrin *o,p'*-DDE Endrin *p,p'*DDD *o,p'*-DDT *p,p'*-DDT Aroclor 1254	97 99 94 95 97 107 97 97 104 68 52 – 44 44 28 95–106	12	On-line LC with GC–ECD	0.3–0.5 ng l^{-1} 1 ng l^{-1} for a single component	70
Membrane extraction discs, C_{18}	Atrazine Simazine 2,3,4-Trichlorophenol	84 81 89	4	On-line HPLC–UV	0.1 μg l^{-1} 1 μg l^{-1} 0.1 μg l^{-1}	71

2 ml acetonitrile–water (pH 3) (60:40) 10 ml water						
Sep-Pak C_{18} cartridges 4 ml diethylether and 8 ml methanol	Propachlor Alachlor Cycloate	–	–	TLC/^{14}C	–	72
Sep-Pak C_{18} cartridges 5 ml methanol 25 ml water (pH 4)	$(DMP)^-$ $(DMTP)^-$ $(DMDTP)^-$ $(DEP)^-$ $(DETP)^-$ $(DEDTP)^-$ Phosalone Azinphos-ethyl Azinphos-methyl Ultrazide Metasistox	2 29 14 15 85 64 76 91 77 98 96	4	GC–NPD derivatization by diazotation	2–3 $\mu g\ l^{-1}$	73
Sep-Pak C_{18} cartridge 8 ml *tetrahydrofuran*	*p,p'*-DDT 1,3,6,8-T_4CDD 1,3,6,7-T_4CDD 1,2,3,4,7-P_5CDD 1,2,3,4,7,8-H_6CDD 1,2,3,4,6,7,8-H_7CDD O_8CDD	–	–	On-line HPLC with scintillation counting	–	74
0.4 g C_{18} 0.1 *M* acetic acid–methanol (50:50) 2 ml water	2,4-D MCPA Dichlorprop Mecoprop	74–100 75–100 84–100 85–100	–	On-line HPLC–UV	5–10 $\mu g\ l^{-1}$	75
J. T. Baker 6 ml C_{18} 4 ml methanol 250 ml creek, river and pond water	Atrazine Simazine 2,4-D Silvex 2,4,5-T	70–88 70–88 93–100 93–100 93–100	2500	TLC–UV	1 $\mu g\ l^{-1}$	76

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TABLE 3 *(continued)*

Extraction	Pesticides	Recovery (%)	Concentration ratio	Determination method	Detection limit	Ref.
J. T. Baker C_{18} 500 mg 0.5 ml ethyl acetate 100–1000 ml water sample	Aldrin *p,p'*-DDE *o,p'*-DDT *p,p'*-DDT Dieldrin α-Endosulfan β-Endosulfan Endrin Heptachlor Heptachlor epoxide *p,p'*-Metoxychlor	Average 92%	2000	TLC–UV	0.06 μg l^{-1}	77
As above	Azinphos ethyl Diazinon Ethyl parathion Fonofos Malathion Carbofenothion Methyl parathion	83.5–96	2000	TLC–UV	0.4 μg l^{-1}	78
100 mg C_{18} 100 μl of ethyl acetate 100 ml water sample	Alachlor Atrazine Chlordane Cyanazine *p,p'*-DDE Endrin Fonofos Heptachlor epoxide Lindane Metolachlor Metribuzin Trifluoralin	91 80 82 92 81 106 96 88 98 88 88 90	1000	GC–MS	0.01 μg l^{-1}	79
Same as above Compares with XAD-2	Carbaryl Carbofurane Chlorpyrifos Ethyl parathion	83 92 82 95	1000	GC–MS	0.01 μg l^{-1}	80
500 mg RP-C_{18} 1 ml eluent 500–1000 ml water sample	Simazine Atrazine Propazine Terbutylazine	90–106 92–114 93–114 93–120	500–1000	GC–NPD HPLC–diode array	10–40 ng l^{-1}	81

	Promethyne	93–106				
	Cyanacine	96–104				
	Metolachlor	94–104				
	Metazachlor	97–112				
500 mg C_{18} 1 ml water–methanol mixtures 1 l river water sample	Benodanil Bentazon Bromacil Chlorflurenol Ethidiuron Hexacinon Napropamid Thiazafluron	–	1000	HPLC–UV and fluorescence	270–700 $\mu g\ l^{-1}$	82
100 mg C_{18} 2 ml *n*-hexane 100–500 ml water	PCB No. 149 PCB No. 153 PCB No. 151 PCB No. 137 PCB No. 187 PCB No. 174 PCB No. 180 PCB No. 170 PCB No. 196	110.9 95.4 97.8 97.9 94.9 95.8 92.7 91.1 80.0	5000	GC–ECD	–	83
1 g and 0.5 g C_{18} column, J. T. Baker 9.5 ml methanol for eluted AC 243,997 and 4.5 ml for the others 500 ml water (pH 2) for AC 243,997 and (pH) 4.5 for the others	Sulfometuronmethyl Chlorsulfuron AC 243,997	97.7 108 87.5	100	HPLC–UV	–	84
As above	Picloram 2,4-D	98.2 91.9	100	HPLC–UV	–	85
C_{18} columns 2 ml *n*-hexane 100–1000 ml river and distilled water sample Compares with C_8	α-HCH α-BHC Lindane *p,p'*-DDE *p,p'*-DDT	94.7 94.6 75.9 77.3 85.5	500	GC–ECD	–	86

(Continued on p. 150)

TABLE III (*Continued*)

Extraction	Pesticides	Recovery (%)	Concentration ratio	Determination method	Detection limit	Ref.
500–800 mg C_{18} 1 ml methanol 1 l water sample (pH 3)	Simazine Atrazine Propazine Bentazon	94.4–97 102.8-103.5 100.0-102.8 97.3-102.4	1000	HPLC GC	0.01 $\mu g\ l^{-1}$	87
As above	Molinate	94.4–97.3	1000	HPLC	–	88
500 mg Sep-Pak C_{18} 1 ml ethyl acetate 1-l tap water samples Compares with liquid–liquid partitioning	Lindane Methyl parathion Malathion Metoxichlor	102.7 93.1 94.7 85.0	1000	GC–ECD	5 ng l^{-1} 40 20 20	89
As above Tap, lake and sea water samples	Heptenophos Fonofos Disulfoton Methyl parathion Malathion Sumition Ethyl parathion Phentoate Ethion Trithion	83–88 78–96 72–95 90–108 92–103 95–102 92–97 75–91 90–93 79–101	1000–10 000	GC–NPD	52 ng l^{-1} 20 15 39 78 15 52 31 18 52	90
500 mg C_{18} in glass column 5 ml light petroleum 1–10 l surface water samples	HCB Lindane Heptachlor Aldrin Heptachlor epoxide *o,p'*-DDE *p,p'*-DDE *o,p'*-DDD Endrin *p,p'*-DDD *p,p'*-DDT Metoxychlor	82 105 84 80 101 85 85 94 100 95 88 98	5000–50 000	GC–ECD	21 ng l^{-1} 18 37 39 26 65 47 93 71 47 69 92	91

As above	Dichlobenil	77	5000	GC–ECD	3–60 ng l^{-1}	92
	Trifluoraline	94				
	Vegadex	74				
	Chloranil	60				
	Methyl-clorpyrifos	95				
	Propanil	80				
	Chlorpyrifos	91				
	Dacthal	99				
	Captan	104				
	α-Endosulfan	97				
	Folpet	102				
	Profenofos	104				
	Dieldrin	98				
	β-Endosulfan	101				
	Captafol	93				
	Tetradifon	105				
	Dicofol	99				
	Mirex	68				
	Dialifor	104				
As above but eluted with ethyl acetate	Prometryne	96.4–99.6	5000–50 000	GC–NPD	52 ng l^{-1}	93
	Propazine	95.2–98.3			37	
	Simazine	59.9–71.4			92	
	Cumaphos	82.4–98.4			45	
	Diazinon	89.1–90.4			89	
	Dimethoate	6.4–10.2			1	
	Formothion	60.9–64.2			16	
	Phorate	46.0–61.9			1	
	Piridafenthion	80.7–87.6			24	
	Pyrazophos	92.0–97.2			7	
	Quinalphos	81.3–90.0			2	
	Triazophos	84.0–87.0			48	
	Tetrachlorvinphos	84.7–88.7			10	
	Trichlorfon	5.5–6.3			729	
As above but eluted with *n*-hexane	2-PCB	91.8	5000–50 000	GC–ECD	0.6-53 ng l^{-1}	94
	2,2′-PCB	94.7				
	2,4-PCB	99.8				
	4,4′-PCB	92.6				
	2,4,5-PCB	108.5				
	3,3′,4,4′-PCB	91.9				
	2,2′,4,5,5′-PCB	85.7				
	2,2′,4,4′,5,5′-PCB	86.8				
	Decachlorobiphenyl	83.7				

(Continued on p. 152)

TABLE III (*Continued*)

Extraction	Pesticides[a]	Recovery (%)	Concentration ratio	Determination method	Detection limit	Ref.
Sep-Pak C_{18}	Ramrod	83.8	5	GC–ECD	0.38 $\mu g\ l^{-1}$	95
2 ml acetonitrile–isooctane	2,4-D methyl ester	75.0			0.22	
	CIPC	83.6			2.6	
10 ml water	Silvex methyl ester	83.8			0.032	
Compares with Florisil	2,4,5-T methyl ester	95.1			0.064	
	2,4-DB methyl ester	70.6			0.039	
	DEF	71.3			0.081	
200 mg C_{18}	TEPT	94.0	70	GC–FPD	–	96
1.0 ml of MTBE	Dichlorvos	56.9				
70 ml water	Ethoprop	92.0				
Compares with C_8	Phorate	54.6				
	Diazinon	89.3				
	Dimethoate	5.0				
	Methyl parathion	96.3				
	Parathion	94.3				
	Tokuthion	70.4				
	Fanphur	99.9				
	EPN	86.3				
	Azinphos-methyl	97.2				
200 mg C_{18} cartridges	Dicamba	62	1000	HPLC–diode array	–	97
1 ml methanol	2,4-D	101			10 $\mu g\ l^{-1}$	
1-l water samples	2,4,5-T	95			2 $\mu g\ l^{-1}$	
	Silvex	91			8 $\mu g\ l^{-1}$	
	Dinoseb	65			–	
C_8 cartridges	Malathion	–	450	GC–ECD	–	98
3 ml diethyl ether–isooctane	α-Endosulfan					
450 ml sea water	α,β-Endosulfan					
	β-Endosulfan					
	Fenvalerate					
6 ml C_{18} high-capacity cartridges	Carbofuran	85.9-105.3	50	HPLC–UV	0.4 mg l^{-1}	99
	3-hydroxy-7-phenol carbofuran	101.7-110.0				
2 ml methanol–water (60:40), acidified		103.8-112-9				
	3-Hydroxy carbofuran	104.7-109.7				
	3-Keto-7-phenol carbofuran	98.2-109.9				
	3-Ketocarbofuran	98.9-107.6				

100 ml distilled and rice water	7-Phenolcarbofuran					
C_8	2,4-D	93.8	50	HPLC–UV	6 $\mu g\ l^{-1}$	100
2 ml methanol	2,4-DP	103.0			6	
100 ml water	2,4-D IOE	92.0			20	
Compares with C_{18}	2,4-DP BEE	100.0			10	
	Dicamba	82.2			2.4	
	Pendimethalin	91.5			5	
	Chlorpyrifos	93.7			5	
500 mg Bond-Elut C_{18}	Atrazine	99–103	125	GC–NPD	–	101
	Alachlor	96–105				
2 ml ethyl acetate–isooctane (1:9)	Metolachlor	95–99				
250 ml groundwater						
500 mg C_{18}	Chlorpyrifos	96	1000	GC–NPD		102
5 ml dichloromethane	Isofenphos	96			0.1 ppb	
	Carbaryl	106			0.1	
1 l groundwater	Triadimefon	107			1	
	Iprodione	102			1	
ODS column	*p,p'*-DDT	59–63	–	On-line	4 $\mu g\ l^{-1}$	103
methanol–water (75:25)	Aldrin	60–64		HPLC–UV	16	
	Dieldrin	64–77			7	
100 ml water	Heptachlor	63–69			10	
1 g C_{18}	Alachlor	95	500	GC–MS	–	104
2 × 3 ml dichloromethane	Atrazine	96				
	Cyanazine	97				
500 ml water samples	Metolachlor	95				
	Simazine	97				
330 mg C_{18} Sep-Pak plus cartridges	Propoxur	92	182	HPLC–UV	130 $ng\ l^{-1}$	105
	Carbofuran	91			140	
0.75 ml acetonitrile	Carbaryl	93			20	
	Propham	92			100	
100-ml water sample	Captan	88			920	
	Chloropropham	89			60	
	Barban	89			80	
	Dibutylate	84			300	

Continued on p. 154)

TABLE III (*Continued*)

Extraction	Pesticides[a]	Recovery (%)	Concentration ratio	Determination method	Detection limit	Ref.
3 cm ODS pre-column Acetonitrile–water 100 ml tap, distilled, deionized, commercial spring and HPLC-grade waters	As above	–	–	On-line HPLC–UV	Half the above values	106
C_{18} pre-column, 3 cm × 4.6 mm I.D. Water (pH 6.8)–acetonitrile 100 ml water Compares with C_8	Carbedazin Aminocarb Propoxur Carbofuran Carbaryl Propham Captan Chloropropham Barban Benomyl Butylate	–	–	On-line HPLC–UV	100 ng l^{-1} 65 65 70 10 50 460 30 40 500 150	107
C_8 precolumn Water–acetonitrile 10 ml water	Aldicarb Aldicarb sulphoxide Aldicarb sulphone MBC Benomyl	104 92 102 95 94	–	On-line HPLC–UV	2.5-11 $\mu g\ l^{-1}$	108
C_8 Empore membrane disc, 47 mm diameter 10 ml methanol 1 l groundwater Compares with C_{18}	Vernam Atrazine Diazinon Dyphonate Metribuzim Alachlor Sulprofox Heptachlor Aldrin Endosulfan	78.8-86.8 86.2–88.4 90.2–97.0 86.6–88.0 17.0–25.2 87.9–97.0 62.5–115.8 55.2–95.1 51.0–55.2 66.8–99.2	100	GC–NPD GC–ECD		109

C_8 Empore membrane disc, 47 mm diameter 10 ml ethyl acetate and 10 ml dichloromethane 1 l water sample (pH < 2)	Alachlor	103	1000	GC–MS	–	110
	Aldrin	99–114				
	Atrazine	129–139				
	α-Chlordane	68–82				
	γ-Chlordane	82–85				
	trans-Nonachlor	18–37				
	Endrin	126–128				
	Heptachlor	116–131				
	Heptachlor epoxide	122–141				
	BHC	27–60				
	Lindane	113–122				
	Metoxychlor	48–95				
	2-PCB	78–112				
	2,3-PCB	101–125				
	2,4,5-PCB	90–108				
	2,2′,4,4′-PCB	97–144				
	2,2′,3′,4,6-PCB	106–118				
	2,2′,4,4′,5,6′-PCB	95–131				
	2,2′,3,3′,4,4′,6-PCB	15–30				
	2,2′,3,3′,4,5′,6,6-PCB	45–102				
	Simazine	110–112				
	Toxaphene mixture	304				
Sep-Pak C_{18} cartridge 2 ml ethyl acetate–isooctane 250 ml groundwater	Atrazine Alachlor Carbofuran	–	625	HPLC–UV Immunoassay	0.04–0.1 μg l^{-1} 0.1 μg l^{-1}	111
C_8 Empore disc, 47 mm diameter 15 ml ethyl acetate 1 l water	α-HCH	65	–	GC–NDP	0.02–0.5 μg l^{-1}	112
	HCB	92				
	β-HCH	73				
	γ-HCH	75				
	δ-HCH	68				
	Endosulfan ether	90				
	heptachlor	113				
	Aldrin	65				
	Heptachlor epoxide	85				
	o,p′-DDE	82				
	α-Endosulfan	86				
	Dieldrin	103				
	p,p′-DDE	87				
	o,p′-DDD	80				
	Endrin	82				
	β-Endosulfan	87				
	p,p′-DDE	74				
	o,p′-DDT	80				

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TABLE III (*Continued*)

Extraction	Pesticides	Recovery (%)	Concentration ratio	Determination method	Detection limit	Ref.
	p,p'-DDT	75				
	Metamidophos	46				
	Dichlorvos	60				
	Trichlorfon	48				
	Heptenophos	85				
	Phorate	75				
	Diazinon	95				
	Dimethoate	52				
	Chlorpyrifos-methyl	84				
	Parathion-methyl	75				
	Chlorpyrifos-ethyl	87				
	Parathion-ethyl	72				
	Quinalphos	72				
	Profenofos	75				
	Ethion	75				
	Vanmidothion	34				
	Phosalone	50				
	Azinphos-methyl	75				
	Azinphos-ethyl	62				
	EPTC	54				
	Molinate	78				
	Cycloate	67				
	Trietazine	78				
	Alachlor	70				
	Propazine	78				
	Terbutylazine	83				
	Atrazine	82				
	Prometryn	75				
	Terbutrine	75				
	Simazine	68				
	Ametryn	78				
	Propachlor	60				
	Trifluoraline	65				
	Benfluoraline	75				
	Propyzamide	95				
	Metribuzin	72				
	Metolachlor	85				
	Chlorthal-dimethyl	92				
	Isopropalin	50				
	Pendimethalin	60				
	Dichlofop-methyl	63				

Sep-Pak C_{18} cartridges	α-HCH	81.1	1000	GC–ECD	0.5 μg l^{-1}	113
10 ml ethyl acetate–10 ml dichloromethane	β-HCH	79.8		GC–NPD	0.3	
1 l water	Lindane	82.3			0.2	
	δ-HCH	81.0			0.3	
	Endrin	79.2			0.4	
	Dieldrin	78.1			0.4	
	Aldrin	80.0			0.04	
	Heptachlor	82.2			0.05	
	Heptachlor epoxide	78.8			0.2	
	Endosulfan A	80.3			0.4	
	Endosulfan B	78.2			0.3	
	p,p'-DDT	83.4			0.3	
	p,p'-DDE	82.2			0.4	
	p,p'-DDD	80.5			8	
	Chlorbenside	75.2			15	
	Chlorfenson	78.9			1	
	PCND	81.4			0.3	
	HCB	79.5			20	
	PCB2	83.2			9	
	PCB7	78.2			3	
	PCB28	78.3			0.3	
	PCB52	79.3			0.2	
	PCB101	81.2			0.1	
	PCB138	82.1			0.08	
	PCB153	80.7			0.05	
	PCB180	79.4			0.01	
	PCB209	81.9			0.002	
	Fenitrothion	83.2			2	
	Parathion-ethyl	85.6			4	

Abbreviations: ACDA = 2-amino-1-cyclopenteno-1-dithiocarboxylic acid; IOE = isooctyl ester; BEE = butoxyethanol ester.

and stability after repeated use [71,109,110,112].

Immobilized liquid membranes for separations have been developed in recent years. They have most frequently been used for separations of metal ions by facilitating transport mechanisms [117], but also for separations of organic molecules [118]. Audunsson [119] used immobilized liquid membranes in a flow system for the determination of amines in aqueous samples. A similar system was used by Nilve and co-workers [120,121] for enriched phenoxyalkanoic acids and sulphonyl urea herbicides prior to on-line determination by HPLC. With the liquid membrane technique sample preparation is performed in a flow system, which is easily automated.

3. FACTORS AFFECTING SOLID-PHASE EXTRACTION

The extraction recovery of pesticides from water samples depends on a number of factors such as the type of water samples (presence of particulate matter, ionic strength of the water), pH and sorbent treatment.

3.1. Type of water

Unfortunately, experiments are usually carried out on aqueous samples with low ionic strength and free from colloidal particles, such as distilled, deionized, tap or finished waters, representing a matrix that is different from natural waters and particularly from sea water [122]. Significant losses in recovery tests on pesticides have been observed with SPE when water samples with high contents of organic matter have been analysed owing to competition for the actives sites of the adsorbent between the chlorinated hydrocarbons and other hydrophobic groups present in the sample [64,92,94,99].

On analyses of marine and surface waters containing solid particles forming suspensions, the recoveries from unfiltered waters were found to be substantially lower than expected for some pesticides [48]. Humic substances in water can increase the apparent solubility of these compounds, bind organic compounds either with covalent bonds, as charge-transfer complexes, by hydrogen bonding or by Van der Waals interactions. These substances are adsorbed on the suspended solid particles [123–125].

Detergents diminish the retention of the pesticides in the solid phase, an effect probably due to an increase in the solubility of the pesticides in water [64,92–94].

An increase in the ionic strength of aqueous samples leads to weakening of the interaction between undissociated molecules and water, resulting in an increase in the extraction efficiency. A positive salting-out effect on adsorption on octadecylsilica has been observed for some herbicides [75,104] and pyrazone [126] and on Wolfatit Y77 for organophosphorus compounds [50]. In another report [126], an increase in ionic strength improved the retention for hydrophobic organic solutes in the water–Amberlite XAD-8 system [127]. However, the addition of NaCl or KCl had no significant effect on the extraction of a wide range of organic compounds on C_{18} [64,90,92].

3.2. Sample volume

The effect of sample volume on SPE recovery is of crucial importance for samples of environmental interest. Extraction of a sample volume of 200 ml–1 l is necessary in order to determine low levels of pollutants. In SPE, the solvent in which the solute is dissolved (*i.e.*, water for environmental samples) is capable of eluting the solute from the column; the solute of interest has some finite capacity factor in the sample solvent itself. If the number of column volumes of water required to elute the solute from the column, plus one column volume (the volume in the column when the sample was introduced), is exceeded, then the solutes begin to elute from the column as more sample is being continuously added to the head of the column; this results in decreased recoveries. The maximum sample volume from which 100% recovery can be achieved and beyond which the solute of interest begins to elute from the column is called the breakthrough volume. The breakthrough volume is determined by the capacity factor of the solute in the sample solvent, that is, the sample solvent strength. For reversed-phase sorbents, the breakthrough volume is a function of the hydrophobicity of the solute and the mass of sorbent used [45,84].

3.3. pH

The effect of pH on the retention of compounds on a solid phase can only be studied with stable and non-ionic pesticides [45,49,84,90,94]. In addition, it may be necessary to adjust the pH of the sample to ensure that the compound is in the appropiate form to achieve the efficient retention by the solid phase [41–43,73,82–84,87].

Most synthetic polymers are unaffected by extreme pH values, but some acrylates may be hydrolysed at high pH. Extreme pH values can change the nature of bonded phases; the recommended pH values are between 2 and 8.

3.4. Sorbent treatment

A typical sorbent treatment sequence involves the following steps: activation of the sorbent (wetting); washing for bonded phases; elution of concentrated pesticides; and regeneration of the column.

3.4.1. Activation

A requirement for effective adsorption is perfect mutual contact between the solid and liquid phases. The type of carbon generally used for pesticide enrichment is granular activated carbon with a large surface area (300–2000 m^2 g^{-1}) and a wide pore diameter distribution, which does not require previous treatment. As more than 99% of the surface area of a polymer sorbent is the internal area of the pores, the need for penetration of liquid phase into the pores is obvious. Complete permeation of the water into all these pores of the hydrophobic polymer is usually ensured by wetting the polymer first, with an organic water-miscible solvent, which is then replaced with water. Prewetting of chemically bonded silicas causes opening of the hydrocarbon chains, thus increasing its surface area.

3.4.2. Washing

After the sample has been extracted, potential interferents can be removed by washing the column with solvents of various strengths. For most non-polar phases, water can be used to remove many of the polar constituents of water samples without eluting pesticides. Less polar contaminants may be removed by adding relatively weak solutions of methanol or acetonitrile in water. However, to ensure that no breakthrough or loss of analytes occurs during washing steps, preliminary analyses should be carried out.

3.4.3. Desorption

Desorption is usually accomplished by the use of solvents. When the extraction is finished, a small volume of a liquid for which the partition coefficient in a given solid phase–eluent system favours the eluent is allowed to pass through the column [90–92,95,110]. Experimental results from adsorption and partitioning TLC and LC can be applied to the selection of the appropiate eluent [64].

The SPE column can be used more than once, provided that it is regenerated with the solvent used for its activation.

Preliminary studies with C_{18} SPE columns revealed the presence of interferents that co-eluted with the analytes of interest. Plasticizers have been reported to be frequent interferents [91,94,128]. Although the size of the interferent peaks was reduced by the precleaning procedure, they could not be completely eliminated. This phemomenon has also been observed with other polymeric sorbents [129].

4. ACKNOWLEDGEMENTS

The authors thank the CICYT (NAT 91 1129) for financial support for this study and the Science Ministry (Spain) for a grant for Y. P.

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