Disks versus columns in the solid-phase extraction of pesticides from water

E. Viana*, M.J. Redondo, G. Font, J.C. Moltó

Laboratory of Food Chemistry and Toxicology, Faculty of Pharmacy, University of Valencia, C/ Vicent Andrés Estellés s/n, 46100 Burjassot, Valencia, Spain

Abstract

Forty four pesticides including organochlorine, organophosphorus, carbamate, triazine and other pesticide structures were extracted from distilled water spiked at 0.4 μg l^{-1} level using octyl- (C$_8$) and octadecyl-silica (C$_{18}$) based supports which are fixed on a PTFE membrane disk or hand-packed in glass minicolumns. Determination was carried out by capillary gas chromatography with an electron capture detector and a nitrogen–phosphorus selective detector operating in parallel. The analytical behaviour of C$_8$ and C$_{18}$ Empore membrane disks and C$_8$ and C$_{18}$ preparative Bondapak in glass minicolumns was studied on the basis of the statistical differences. On the whole, the minicolumns provided better recoveries than the disks, whereas with the same kind of support (disk or column), the results obtained with C$_8$ were close to those obtained with C$_{18}$, except for carbamate and triazine pesticides in which the C$_8$ disks provided better recoveries than the C$_{18}$ ones. The theoretical and practical differences between the disks and columns were also examined.

Keywords: Membrane disks; Solid-phase extraction; Water analysis; Pesticides

1. Introduction

The protection of drinking water quality is one of the most important mandates of the Environmental Department of any government. Considerable progress has been made in recent decades in controlling the presence of organic chemical pollutants in water. The environmental impact of pesticides is increasing, and trace analysis of these substances requires techniques which allow detection of as many compounds as possible and which need few extraction and clean-up steps. Solid-phase extraction (SPE) has proved to be a useful tool for extracting pesticides from waters

[1], and some of the methods proposed by the US Environmental Protection Agency (EPA) include the use of chemically bonded silicas to isolate certain kinds of pesticides and other organic pollutants [2]. These alkyl-modified silica particles are usually enmeshed in an inert PTFE matrix (membrane disks) or enclosed in a packed-bed column made of glass or plastic materials. Recently a new SPE material based on a rigid glass fibre disk with a silica bonded phase has come into the market [3].

Extraction disks are usually composed of a membrane of PTFE (47 or 25 mm diameter) supporting ca. 500 mg of octyl- or octadecyl-silica with a particle diameter of approximately 8 μm and a pore size of 60 Å [4]. Commercial columns

* Corresponding author.

present a less uniform particle distribution than disks. In SPE columns, the phase is placed in a polyethylene PTFE or glass cartridge which contains from 100 to 500 mg of solid phase, with a particle diameter of nearly 40 μm (37–55 μm) and a pore size of 300 Å.

The main difficulties encountered with any kind of bonded silica phase are caused by the presence of suspended particles in the sample. The particles of the alkyl bonded silica act as a mechanical filter retaining particles of suspended sediment, thereby giving a loss in flow-rate [5,6]. This is very inconvenient when large volumes of sample are processed. To resolve this problem, acidification to pH 2 is widely applied because in this way the small particles of insoluble salts of magnesium, aluminium and calcium remain solubilized [4,7–9]. However, such extreme pH values are not recommended by the suppliers. Another way to solve the problem is by prefiltering the water samples prior to extraction [5,7,10].

C_{18} Empore disks have been reported to extract some fungicides [11], carbamates and herbicides [12] or polar pesticides and herbicides [13] from waters.

C_8 Empore disks were used to recover organochlorine pesticides, triazine herbicides and other contaminants from spiked water samples [9] and organochlorine, organophosphorus insecticides, triazine and neutral herbicides from drinking water [8].

SPE with columns, either of octyl- or octadecyl-silica, is a widely employed technique which has been applied to the extraction of a large number of pesticides like triazines [14], carbamates [15], organophosphorus and organochlorines [16,17] from water. Recently, recoveries obtained with C_{18} cartridges and C_{18} Empore disks have been compared for a few pesticides from ground water [18].

Nowadays the number of uses reported for columns are higher than those reported for disks. This fact must not be understood as an analytical preference but can be explained by the fact that the use of solid phases as hand packed columns or cartridges has been known since the late 70s, whereas disks have been introduced more recently. Commercial cartridges can also be used to extract samples in situ avoiding the transport of

large amounts of samples [6]. On the other hand, bulk packing material can be applied to solid samples performing solid-phase microdispersion [19] and glass minicolumns can be easily packed for research purposes with any kind of new solid phases which do not need to be presented as cartridges or membrane disks.

The purpose of this work is to compare the analytical properties and theoretical and practical considerations of the use of C_8 and C_{18} packed-bed glass minicolumns and membrane disks, on the basis of the statistically significant differences between recoveries of a large number of pesticides extracted from water samples.

2. Experimental

2.1. Reagents and standards

Pesticides given in Table 1 were purchased from Dr. Ehrenstorfer Laboratory (Promochem, Wesel, Germany), with purities between 95–99%. Acetone, ethyl acetate, n-hexane and methanol (nanograde quality) were also purchased from Promochem. Washed glass wool from Panreac (Montcada i Reixac, Barcelona, Spain) was treated with DM/DCS. Stock solutions of 1000 μg l^{-1} of each pesticide were prepared in ethyl acetate.

2.2. Apparatus

A KONIK KNK 2000C gas chromatograph (Sant Cugat del Vallés, Barcelona, Spain) was equipped with a ^{63}Ni electron capture detector (ECD), a nitrogen–phosphorus selective detector (NPD) and a Spectra-Physics SP 4290 integrator.

The working fused-silica capillary column was a DB-5 (5% phenyl-methylsiloxane), 0.25 μm film thickness, 30 m × 0.25 mm I.D., provided by J&W Scientific (Folsom, CA, USA).

2.3. Gas chromatographic conditions

The injector temperature, operating in splitless mode (0.7 min), was set at 285°C, ECD and NPD

Table 1
Mean recoveries (R) and R.S.D. ($n = 4$) for the extraction of selected pesticides from spiked waters using C_8 and C_{18} hand-packed glass minicolumns and C_8 and C_{18} Empore[TM] disks

Pesticide	C_8 column		C_8 disk		C_{18} column		C_{18} disk	
	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)	R (%)	R.S.D. (%)
Organochlorine								
Aldrin	67	10	56	12	63	8	49	11
Dieldrin	86	5	71	6	98	7	67	10
α-Endosulfan	88	5	76	7	97	4	70	10
β-Endosulfan	85	8	81	6	101	7	79	8
Endosulfan sulfate	85	5	90	4	98	8	86	6
Endrin	90	7	82	6	95	7	80	9
α-HCH[a]	84	6	66	8	85	8	64	11
β-HCH	87	6	89	6	89	9	83	10
δ-HCH	90	7	77	14	87	8	68	9
HCB[b]	75	8	76	14	72	8	65	10
Heptachlor	75	10	51	8	68	9	48	14
Heptachlor epoxide	87	9	69	6	96	9	64	10
Isodrin	85	7	48	8	81	8	45	13
Lindane	85	9	79	10	100	7	69	12
Methoxychlor	90	6	85	10	96	7	90	6
Organophosphorus								
Chlorfenvinphos	72	10	64	10	79	9	64	10
Chlorpyriphos	82	9	69	10	91	9	70	11
Diazinon	86	4	83	7	85	9	68	7
Disulfoton	67	10	75	4	69	10	62	5
Ethion	85	9	68	7	96	8	73	4
Ethoprophos	71	4	37	13	67	7	19	15
Heptenophos	90	8	96	7	86	9	83	10
Malathion	89	7	95	4	98	9	95	6
Parathion-ethyl	84	10	83	10	94	9	71	14
Parathion-methyl	88	8	90	10	94	8	84	10
Phenthoate	72	9	79	8	89	10	77	4
Pyridaphenthion	89	6	86	9	88	9	69	9
Quinalphos	86	4	88	9	88	8	72	8
Sumithion	94	6	89	5	98	11	83	6
Trithion	90	10	42	10	97	10	50	10
Carbamates								
Carbaryl	71	10	76	9	51	11	58	9
Molinate	82	10	77	10	83	9	59	8
Pirimicarb	84	10	86	9	83	8	56	5
Thiobencarb	89	4	92	4	90	9	72	10
Triazines								
Atrazine	72	7	87	9	67	5	66	9
Prometryne	95	6	93	5	87	9	67	7
Propazine	68	9	97	5	66	9	67	7
Other structures								
Fenarimol	87	7	84	10	97	10	81	9
Iprodione	91	4	73	10	95	6	70	8
Procymidone	95	9	86	7	97	11	81	7
Propiconazole	86	8	59	8	81	6	68	11
Tetradifon	65	10	67	4	75	10	72	8
Triadimefon	82	10	81	7	80	5	81	8
Vinclozolin	85	9	80	10	96	8	85	5

[a] Hexachlorocyclohexane.
[b] Hexachlorobenzene.

temperatures were set at 300°C and the oven temperature was programmed as follows: the initial temperature 50°C (0.8 min) was increased at 30°C/min to 140°C which was held for 2 min, then increased at 5°C/min to 280°C, the final temperature being held for 12 min. Helium was used as a carrier gas at a flow-rate of 2.8 ml min^{-1}.

Parallel detection was performed by splitting the effluent from the DB-5 column to both detectors by a steel splitter from SGE (Austin, TX, USA).

2.4. Extraction apparatus

A glass extraction minicolumn (100 × 9 mm I.D. with coarse frit No. 3) containing 0.5 g octyl- or octadecyl-silica Bondapak (37–55 μm) as bulk packing material (Millipore Corporation Waters, Chromatography Division, Milford, MA, USA), and covered with a plug of silanized glass wool.

A standard Millipore 47-mm filtration apparatus equipped with 47-mm disks, of octyl- or octadecyl-bonded silica Empore™ (Varian, Harbor City, CA, USA).

2.5. Extraction procedures

2.5.1. Column extraction

A volume of 0.5 l of distilled water was spiked with 0.5 ml of 0.4 μg ml^{-1} pesticide standard mixtures in ethyl acetate, and transferred to a separatory funnel connected by means of glass joints to the chromatographic glass minicolumn, which contained 0.5 g of C$_{18}$ or C$_8$ bonded porous silica. The minicolumn was conditioned with 5 ml of methanol and 10 ml of distilled water. The water sample was then passed through the glass minicolumn at a flow-rate of 30–40 ml min^{-1} with aid of vacuum, allowing it to drain for ca. 1 min. After percolation, the column was detached from the separatory funnel and the adsorbed analytes were eluted with 5 ml of ethyl acetate and 5 ml of hexane. The residual water was manually discarded with aid of a Pasteur pipette and the organic layer was concentrated to 0.2 ml at 45°C using a gentle stream of nitrogen. A 2-μl aliquot of this organic layer

was injected onto the gas chromatographic system.

2.5.2. Disk extraction

A volume of 0.5 l of spiked water samples (0.4 μg l^{-1}) was passed through a C$_{18}$ or C$_8$ preconditioned membrane disk (all types of disks were activated by passing 10 ml of methanol and 10 ml of distilled water through them). In the analysis of organochlorine pesticides, spiked water samples were added with 2.5% methanol before the extraction step. Reduced pressure was applied to obtain an appropriate flow-rate. The adsorbed pesticides were then slowly eluted with 5 ml of ethyl acetate and 5 ml of hexane. The organic phase was concentrated to 0.2 ml at 45°C using a gentle stream of nitrogen, and 2 μl of the organic phase were injected onto the gas chromatographic system.

3. Results and discussion

Quadruplicate analysis of selected pesticides carried out with a C$_8$ column, a C$_8$ disk, a C$_{18}$ column and a C$_{18}$ disk gave the recovery means (R) and relative standard deviations (R.S.D.) shown in Table 1.

The results as a whole confirm that all the phases tested are suitable to extract a large variety of low- and intermediate-polarity pesticides.

It must be noted that the extraction of organochlorine compounds with disks (C$_8$ and C$_{18}$) from unmodified distilled water was very poor (results not reported) and the recoveries shown in Table 1 for C$_8$ and C$_{18}$ disks correspond to 2.5% methanol added to distilled water prior to the extraction. The practice of adding a low proportion of methanol to the water sample as a solid-phase wetting agent is well known: it was applied to extract organochlorine [4,20] and other pesticides besides the organochlorine [7,8,10]. In a previous report, the addition of 5% acetone only improved the recovery of pp'-DDD among another 17 organochlorine pesticides which were extracted with C$_8$ SPE cartridges [21].

Table 1 shows that mean recoveries were higher than 70% for 40 pesticides when using C_8 columns, for 37 pesticides when using C_{18} columns, for 32 pesticides when C_8 disks are used and for 22 pesticides using C_{18} disks. Based on these results, general analytical preference must be in the decreasing order: C_8 columns, C_{18} columns, C_8 disks and C_{18} disks.

Individually, C_8 columns gave mean recoveries higher than 65% for all the selected pesticides; C_{18} columns gave low mean recoveries for Carbaryl (51%); C_8 disks gave low mean recoveries for Isodrin (48%), Ethoprophos (37%) and Trithion (42%); and C_{18} disks gave low mean recoveries for Aldrin (49%), Heptachlor (48%), Isodrin (45%) and Ethoprophos (19%). Extraction of Ethoprophos with disks was irregular and extremely low.

Estimation of mean confidence intervals at $(1 - \alpha)$ 95% level were represented graphically for organochlorine pesticides in Fig. 1, for organophosphorus pesticides in Fig. 2 and for triazine, carbamate and other pesticide structures in Fig. 3.

Most recoveries for the selected pesticides reported in the literature fall within the mean confidence intervals provided in this paper, even when some differences exist within bulk packing, phase weight or supplier.

In this study, recoveries found for Atrazine were slightly lower than most values reported in the literature [1,14]. Also when propazine is extracted with a C_{18} column [22,23], when Aldrin is extracted with a C_8 disk [9] or a C_{18} column [17] and when Carbaryl is extracted with a C_{18} column [24–26], the recoveries found in the literature were higher than those reported here.

Kraut-Vass and Thoma [9] report several recoveries above 100%. This difference can be explained because the present technique was not optimized to extract selectively one kind of pesticide such as carbamates or triazines.

The revised literature lacks data of recoveries for the SPE of several pesticides, thus, no comparison can be made.

Statistical analyses of the results were made, and when differences were statistically significant, the mean difference intervals $(1 - \alpha)$ 95%
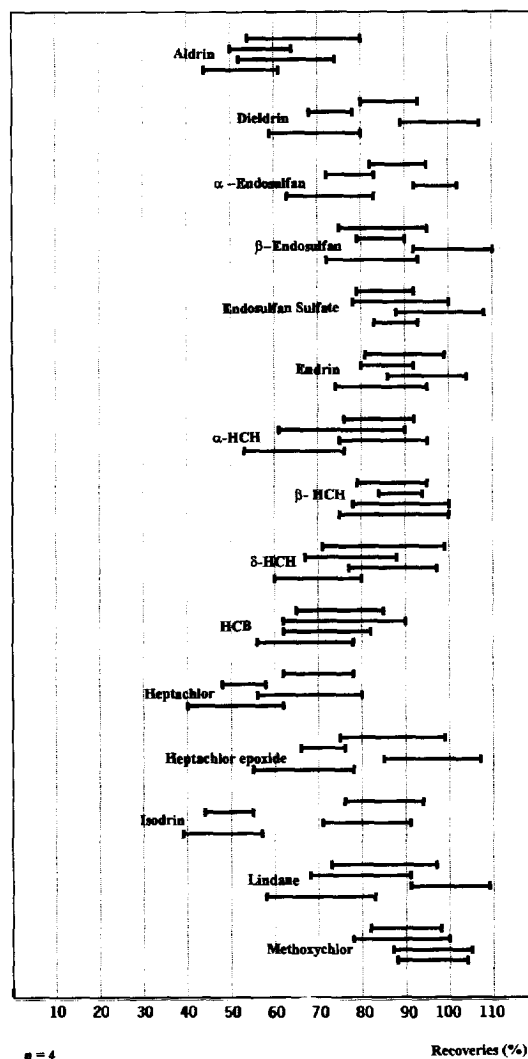

Fig. 1. Mean interval estimation with a confidence level of 95% for the extraction of organochlorine pesticides from spiked waters using C_8 and C_{18} hand-packed glass minicolumns and C_8 and C_{18} Empore™ disks. For each pesticide: top line, interval of recoveries for C_8 column; upper-middle line, interval of recoveries for C_8 disk; lower-middle line, interval of recoveries for C_{18} column; bottom line, interval of recoveries for C_{18} disk.

were estimated. These results are presented in Table 2 (comparing disks and columns) and in Table 3 (comparing C_8 and C_{18} disks).

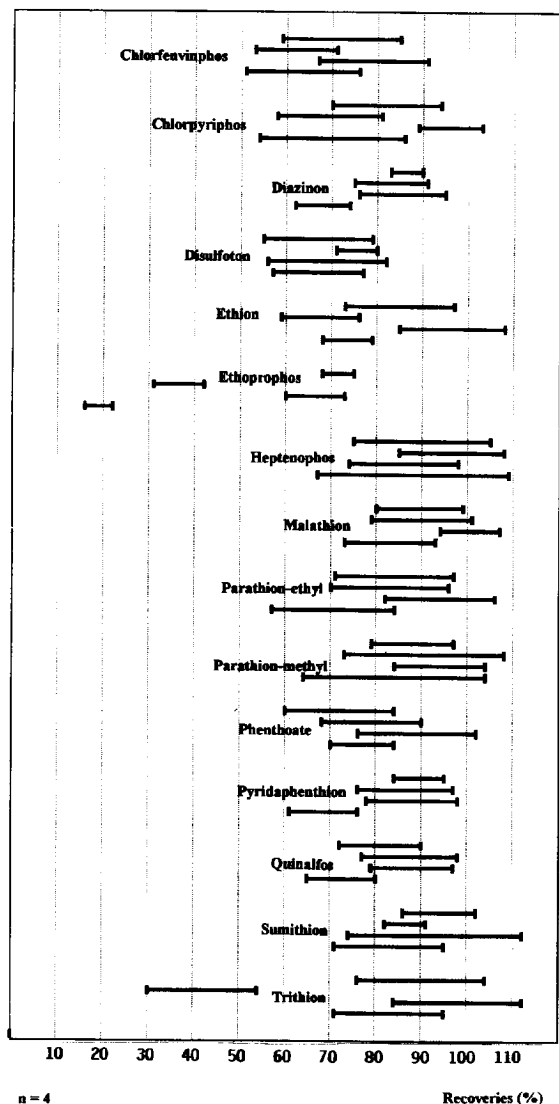As shown in Table 2, results obtained with columns were generally better than those ob-

n = 4   Recoveries (%)

Fig. 2. Mean interval estimation with a confidence level of 95% for the extraction of organophosphorus pesticides from spiked waters using C_8 and C_{18} hand-packed glass minicolumns and C_8 and C_{18} Empore™ disks. For each pesticide: top line, interval of recoveries for C_8 column; upper-middle line, interval of recoveries for C_8 disk; lower-middle line, interval of recoveries for C_{18} column; bottom line, interval of recoveries for C_{18} disk.

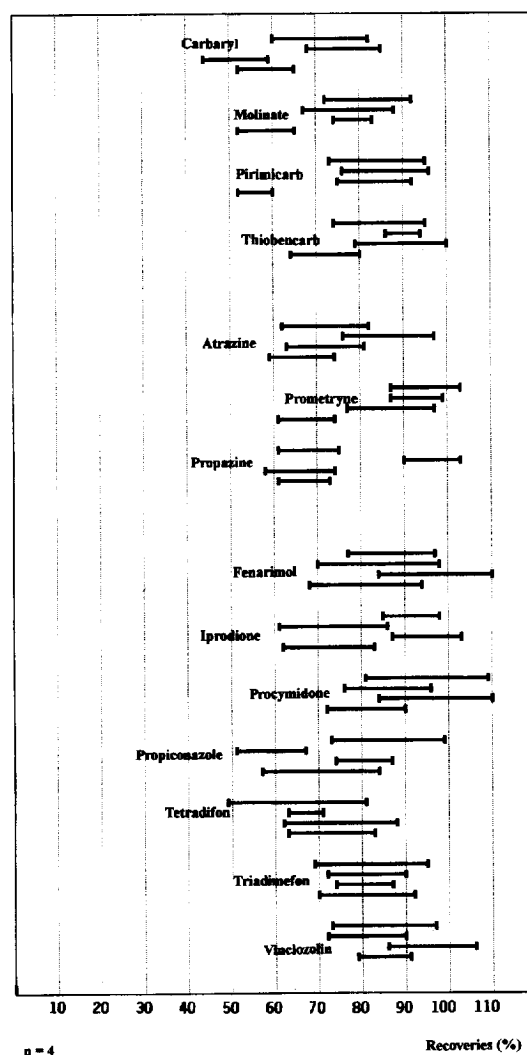

n = 4   Recoveries (%)

Fig. 3. Mean interval estimation with a confidence level of 95% for the extraction of carbamate, triazine and other pesticides from spiked waters using C_8 and C_{18} hand-packed glass minicolumns and C_8 and C_{18} Empore™ disks. For each pesticide: top line, interval of recoveries for C_8 column; upper-middle line, interval of recoveries for C_8 disk; lower-middle line, interval of recoveries for C_{18} column; bottom line, interval of recoveries for C_{18} disk.

tained with disks. As an example, recoveries for Dieldrin using C_8 columns were between 6% and 19% higher than those obtained with C_{18} disks.

The most important differences were for Trithion (between 34–63% better with a C_8 column

than with a C_8 disk, and between 36–58% better with a C_{18} column than with a C_{18} disk), Ethoprophos (between 42–53% better with a C_{18} column than with a C_{18} disk, and between 28–41% better with a C_8 column than with a C_8 disk), Isodrin (between 27–43% better with a C_8

Table 2
Mean difference interval estimation with a confidence level of 95% for compounds for which recoveries using disks and columns are statistically different

Pesticide	Mean difference interval estimation (%)
C_8 *columns produced better recoveries than* C_8 *disks*	
Dieldrin	6–19
Ethoprophos	28–41
α-Hexachlorocyclohexane	8–24
Heptachlor	12–32
Isodrin	27–43
Propiconazole	15–39
Trithion	34–63
C_{18} *columns produced better recoveries than* C_{18} *disks*	
Diazinon	8–27
Dieldrin	18–39
α-Endosulfan	15–33
Ethoprophos	42–53
Heptachlor epoxide	17–43
Iprodione	13–32
Isodrin	21–46
Molinate	15–34
Lindane	17–41
Pyridaphenthion	9–30
Pirimicarb	19–35
Prometryne	10–29
Trithion	36–58
C_8 *disks produced better recoveries than* C_8 *columns*	
Propazine	19–38

* $n = 4$.

Table 3
Mean difference interval estimation with a confidence level of 95% for compounds for which recoveries obtained using C_8 disks are better than those obtained with C_{18} disks

Pesticide	Mean difference interval estimation (%)
Atrazine	10–31
Carbaryl	9–27
Diazinon	7–24
Disulfoton	9–17
Ethoprophos	12–33
Molinate	9–29
Pirimicarb	21–39
Prometryne	18–33
Propazine	22–37
Thiobencarb	11–28

* $n = 4$.

column than with a C_8 disk, and between 21–46% better with a C_{18} column than with a C_{18} disk), Heptachlor epoxide (between 17–43% better with a C_{18} column than with a C_{18} disk), Pirimicarb (between 19–35% better with a C_{18} column than with a C_{18} disk) and Propiconazole (between 15–39% better with a C_8 column than with a C_8 disk). The recoveries were significantly better with C_8 disks than with C_8 columns, only for the extraction of Propazine.

When the groups of pesticides were compared, it was expected to find better recoveries for intermediate-polarity pesticides, like carbamates or triazines, using the intermediate-polarity C_8 phases, rather than when the most apolar C_{18} phases are used. As shown in Table 3, this was only true for disks. In the case of columns, the differences were not significant. The extraction of some organophosphorus pesticides such as Diazinon, Disulfoton and Ethoprophos was also better with C_8 disks than with C_{18} disks.

When disks versus columns for the same kind of phase were compared, the differences found could not be correlated with the structure of the selected pesticides.

Other statistical differences between disks and columns could be found by increasing the number of assays, but in practice they would be of low magnitude, given that they were not detected with four assays.

With respect to the performance of the SPE using the different types of phases, it has been verified that the cited advantages of disks over columns, i.e. the more restricted flow-rates and the presence of channelling effect in columns [3,4], have little effect. This is because disks allow faster sample flows than columns but the elution of disks must be done very slowly and the disk requires wetting with the eluting solvent for several minutes [7]. The channelling of columns has a negligible effect on the recoveries and the small influence of sample flow on the recoveries has been demonstrated with both membranes and columns [3,7,8].

It is known that SPE with disks or glass minicolumns produces clearer extracts than liquid–liquid extraction methods [8]. In this study no differences in the chromatographic profiles

were found between any kind of phase (C_8 or C_{18}) or between disks and columns, because spiked distilled water was utilized. However, in a previous study, C_8 cartridges provided clearer chromatographic profiles than C_{18} cartridges in the analysis of organochlorine pesticides in medicinal plants [21].

4. Conclusions

C_8 or C_{18} disks and columns can be used in residue water analysis of organochlorine, organophosphorus, carbamate, triazine and other pesticides, but the analytical data indicates that recoveries should be expected in the decreasing order: C_8 column, C_{18} column, C_8 disk and C_{18} disk. The differences between C_8 and C_{18} columns are small and not significant, however the use of C_8 disks provides better recoveries than the use of the C_{18} disks in extracting intermediate-polarity pesticides like triazine, carbamate and some organophosphorus pesticides.

To extract organochlorine pesticides efficiently with C_8 and C_{18} disks, the addition of 2.5% methanol to the water is recommended as a wetting agent of the phases. This practice is not necessary with columns.

Acknowledgements

References

[1] G. Font, J. Mañes, J.C. Moltó and Y. Picó, J. Chromatogr., 642 (1993) 135.

[2] C.J. Koester and R.E. Clement, Crit. Rev. Anal. Chem., 24 (1993) 263.

[3] D.D. Blevins and S.K. Schultheis, LC·GC Int., 7 (1994) 70.

[4] R.E. Hendrinks, LC·GC Int., 6 (1993) 296.

[5] T. McDonnell and J. Rosenfeld, J. Chromatogr., 629 (1993) 41.

[6] J.J. Richard and G.A. Junk, Mikrochim. Acta, I (1986) 387.

[7] D.F. Hagen, C.G. Markell and G.A. Schmitt, Anal. Chim. Acta, 236 (1990) 157.

[8] L.M. Davi, M. Baldi, L. Penazzi and M. Liboni, Pestic. Sci., 35 (1991) 63.

[9] A. Kraut-Vass and J. Thoma, J. Chromatogr., 538 (1991) 233.

[10] S. Bengtsson, T. Berglöf, S. Granat and G. Jonsäll, Pestic. Sci., 41 (1994) 55.

[11] J.S. Salau, R. Alonso, G. Batlló and D. Barceló, Anal. Chim. Acta, 293 (1994) 109.

[12] S. Chiron and D. Barceló, J. Chromatogr., 645 (1993) 125.

[13] E.R. Brouwer, H. Lingeman and U.A.Th. Brinkman, Chromatographia, 29 (1990) 415.

[14] A. Balinova, J. Chromatogr., 643 (1993) 203.

[15] A. De Kok, M. Hienstra and U.A.Th. Brinkman, J. Chromatogr., 623 (1992) 265.

[16] J.C. Moltó, Y. Picó, G. Font and G. Mañes, J. Chromatogr., 555 (1991) 137.

[17] J.L. Bernal, M.J. Del Nozal, J. Atienza and J.J. Jimenez, Chromatographia, 33 (1992) 67.

[18] J. Beltran, F.J. López and F. Hérnandez, Anal. Chim. Acta, 283 (1993) 297.

[19] A.R. Long, M.M. Soliman and S.A. Barker, J. Assoc. Off. Anal. Chem., 74 (1991) 493.

[20] P.R. Loconto, LC·GC Int., 4 (1991) 10.

[21] J.C. Moltó, B. Lejeune, P. Prognon and D. Pradeau, Int. J. Environ. Anal. Chem., 54 (1994) 81.

[22] U. Oehmichen, F. Karrenbrock and K. Haberer, Fresenius' Z. Anal. Chem., 327 (1987) 715.

[23] F. Moja, E. Suigo, M.L. Roveda, C. Bezzi, G. Vignanti, U. Pellegatta and R. Rosso, Giorn. Ital. Chim. Clin., 13 (1988) 145.

[24] G.A. Junk and J.J. Richard, Anal. Chem., 60 (1988) 451.

[25] M.W. Brooks, D. Tessier, D. Soderstrom, J. Jenkins and J.M. Clark, J. Chromatogr. Sci., 28 (1990) 487.

[26] C.H. Marvin, I.D. Brindle, C.D. Hall and M. Chiba, Anal. Chem., 62 (1990) 1495.