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Analysis of surface waters with different extractive procedures

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ABSTRACT

Solid phase extraction (SPE) techniques are now widely employed for analysis of pesticides and organic pollutants in water samples. We investigated the recovery of compounds belonging to different chemical classes through three extractive phases: Carbopack B, C-18 and XAD-2 columns, and C-18 membranes. A gas chromatography-mass spectrometry (GC-MS) method was used in the selected ion recording (SIR) mode. In order to set up a general-purpose extractive apparatus, we developed an all-glass system, to avoid the possibility of contaminants leaking from plastics. Contaminants can be released from the solid phase used for the extraction, and this point was investigated through GC-MS.

INTRODUCTION

The principal requirement of an extractive method is sufficient and reproducible extraction of the analyte. However, in environmental water analysis, mainly following the increasing importance of trace analysis, a further requirement is to avoid introducing interfering compounds. This is particularly important when a large spectrum of mainly unknown pollutants is considered. Other points in a modern analytical laboratory are the feasability of a method in terms of speed, cost and simplicity. Many of these variables are linked or related. Thus, for instance, the time required for an analysis is generally related to its cost, and the simplicity to the reproducibility.

For all these reasons SPE has gained in popularity[1-4], and we have been using this technique for several years to analyze pesticides and other pollutants in water[5-8]. Here we extend our studies to deal with some general points of SPE.

EXPERIMENTAL PART

Materials and chemicals

C-18 phase was obtained from Analytical International, Harbor City, CA. Carbopack B, 120-400 mesh size, was purchased from Supelco, Bellefonte, PA. Empore extraction membranes (C-18) were bought from J. T. Baker, Phillipsburg, NJ and XAD-2 phase was obtained from BDH Chem. Ltd, Pool (England).

Extraction

Carbopack B[9], C-18 phase[10,11], C-18 membranes[12] and XAD phase[13] were used as previously described. Modifications to the procedure are described in the Results and Discussion. Further details on the extractive apparatuses have been presented[6-7].

Instrumental analysis

For the instrumental analyses we used a VG TS-250 mass spectrometer, coupled to a gas chromatograph HP 5890. Alternatively, a HP 5971A mass spectrometer was used.

RESULTS AND DISCUSSION

Different apparatuses: characteristics and fluxes

We are interested in an all-glass extraction system in order to obtain more general applicability and because we adopt GC-MS as instrumental endpoint. This technology is sensitive to many chemical classes, with the "drawback" of greater sensitivity also toward interfering compounds released by the extractive system.

In the course of the last few years we have worked with four particular all-glass extractive apparatuses (fig. 1). Apparatuses A and B operate with a head pressure (we used a nitrogen cylinder); the first is a balloon, typically one liter in capacity, and the second one is a Mariotte bottle, more suitable for higher volumes - we have tested it up to ten liters. The head pressure forces the water through the extractive column.With the first apparatus the elution time for one liter of ground water is 45 min, and several samples can be extracted simultaneously by fitting "T" deviations of the flow from the cylinder, in a tree structure. We used these two devices for the analyses of pesticides in ground water[6-7].

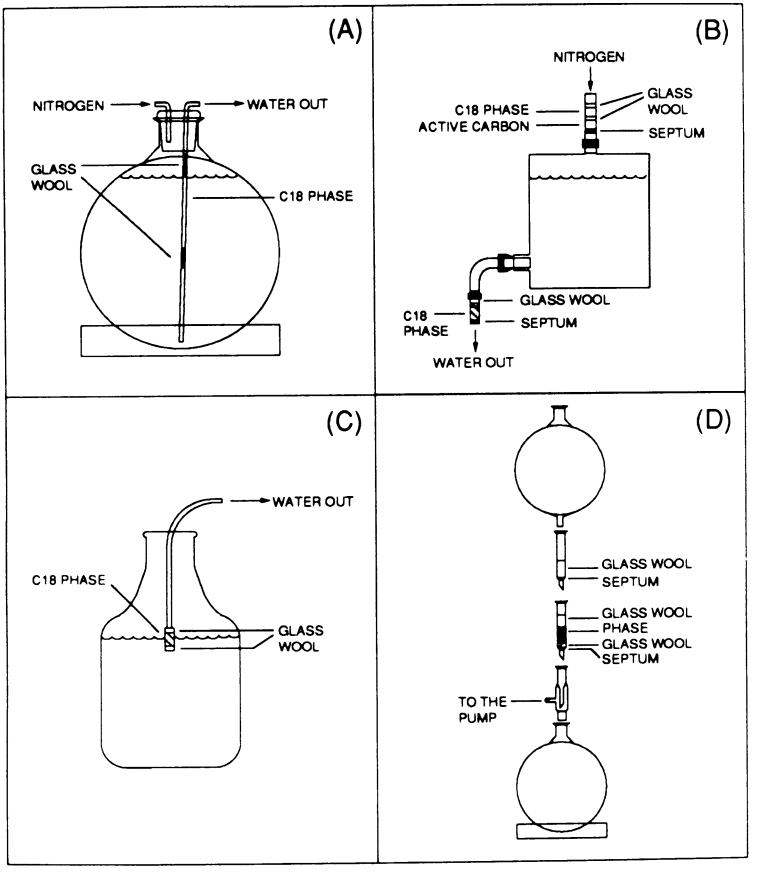

Figure 1. Four different all-glass extraction apparatuses (not in scale).

Apparatuses C and D shown in fig. 1 operate under vacuum. Apparatus C does not require the transfer of the water sample, because the extractive column can be placed directly in the bottle, containing the sample as received for analysis.

In order to shorten the extraction time, we developed apparatus D. With apparatuses B and C the extraction of a 5-l sample could take several hours and the worst conditions were with surface water with particulate suspension, since the suspended material may clog the column. Apparatus D offers a higher elution speed. For clean water the flux can easily reach 80 ml/min, with a vacuum

produced by a water pump; for surface water from the Lagoon of Venice the flux was 50 ml/min.

The membrane extraction apparatus was a standard, commercially available one. With samples from the Lagoon of Venice, using a glass-wool prefilter, the flux was low and dropped during elution.

Recovery of compounds

The recovery of the compounds depends on their chemical nature, on the phase, the water conditions[9,10,14,15] (such as pH, salts), the flux[13] and water volume[9,16]. Generally, for trace compounds, the amount is not a problem, since the quantity of the extractive phase is in large excess. However, in some cases recovery varies with the amounts of the spiked analytes[11,13,17].

A wide range of extracting phases has been used, but there are no all-purpose ones. Thus, compounds that are unpolar, of low polarity and not ionic can be generally extracted with C18 phases or membranes[3,4,7,12]. More polar compounds can be recovered better with a Carbopack B column[9,16]. As an example, Table 1 presents the recovery of five compounds from pure water (1μg/l, pH 7,3) with three different extractive systems. The five compounds, atrazine, fenantrene, pyrene, endosulfan and coprostanone, represent

Table 1: % recovery (±S.D.; n = 4) from water with different phases

	C18 membrane[a)]	C18 phase[a)]	Carbopack B[b)] neutral fraction
atrazine	91 ± 2	98 ± 1	90 ± 6
phenantrene	66 ± 8	77 ± 11	2 ± 1
pyrene	71 ± 4	87 ± 4	2 ± 0.1
endosulfan	79 ± 2	89 ± 5	103 ± 10
coprostanone	35 ± 12	62 ± 8	82 ± 9

a) washed with AcOEt, activated with MeOH and eluted with AcOEt.
b) used as in ref.[9].

different chemical unpolar classes. With AcOEt as eluting solvent the C18 phase shows good recovery, and the corresponding

membrane behaves similarly. Carbopack B also gives good recovery, but this phase is not satisfactory for the polycyclic aromatic compounds because they are adsorbed too strongly on the phase to be reversed by the eluting solvent. Similarly, in another experiment, we found that Carbopack B was not suitable for the extraction of 1-phenyldodecane.

We also studied the extraction of two pesticides, ethofumesate and fenamiphos from distilled water at high concentrations (0.1 mg/l) with C-18, Carbopack B and XAD-2 columns, and with liquid-liquid extraction (LLE). In all cases we used dichloro-methane/methanol 8/2 as extractive solvent since it has been reported to give good results for other pesticides[9]. The results (Table 2) confirm how a correct choise of the extraction phase allows to improve the recovery.

Table 2: % recovery (±S.D.; n = 4) from water with different phases

	LLE[a)]	phase C18[b)]	C.B.n[c)]	C.B.a[c)]	XAD 2[d)]
ethofumesate	50±34	11±3	81±6	-	26±19
phenamiphos	23±15	12±7	74±28	-	4±2

a) Extracted with dichlorometane/MeOH = 8/2 and dried on natrium sulfate column.
b) Washed with dichlorometane/MeOH = 8/2, activated with MeOH and eluted with dichlorometane/MeOH = 8/2.
c) Used as in ref.[9] C.B.n= Carbopack B neutral fraction; C.B.a.= Carbopack B acid fraction.
d) Washed with dichlorometane/MeOH = 8/2; activated with MeOH and water; eluted with dichlorometane/MeOH = 8/2

We also used Carbopack B to extract salicylic acid and recovery was acceptable (54%); but the salicylic acid was eluted part in the first fraction and part in the second one; thus we preferred a single common fraction.

The water volume may affect the recovery of the compounds. In a previous study we considered the recovery of 50 pesticides from 1 l of water using a C18-Phenyl mixed phase[7]. We then studied the recovery of 46 of them using a 10 L-sample and the same procedure. The average recovery was 67.0 ± 35.6 with a 10-l sample, compared with 85.0 ± 23.1 for a 1-L sample. The lower recovery is due to the elution properties of the water, and indeed recoveries are lower for compounds with higher water solubility.

Another point to be considered is the performance of different apparatuses in terms of water flux. The water flux can be increased with some techniques, but this is not always desirable. Higher fluxes could lead to lower recoveries[13]. We studied this aspect with apparatus D and recovery was the same at fluxes of 40 and 80 ml/min.

The salt content in the water sample may influence the extraction; in some cases it does not change the recovery[9,16], while in other it increases or reduces it[15,17]. We studied fecal steroid recovery with the Carbopack B column in distilled and salted (3.5% of NaCl) water: the average recovery was 48% in distilled water and 37% in salted water.

Interfering peaks

In the qualitative analysis (but in some quantitative analysis too) it is better to avoid peaks due to substances released by the extraction system and by the analytical procedure, since these may cause interfering peaks. These compounds stem from impurities in the solvent, leaching from the plastics used during the extraction procedure, such as the plastic tube containing ready-to-use columns or a plastic syringe used to elute the solvents or, finally, leakage of impurities in the extractive phase.

Impurities in the solvent are minimized with the SPE technique. Spurious peaks may originate from silicone caps; these contaminants are mainly silicone derivatives.

Attention must be paid to peaks produced by the plastics or the extractive phase. Peaks from plastics may be present in samples extracted with other techniques, but SPE generally enhances this problem. That is why we preferred to eliminate plastics from our procedures as far as possible (Teflon and similar fluorinated material are safe enough).

We considered contaminants present in C-18 and Carbopack columns and by C-18 membranes, used with all-glass apparatuses. We found contaminants for all the extractive materials. The most common were 2,6-di-*ter*-butyl-4-methylphenol (BHT, a common plastic additive, usually present only in the washing solvent), phthalates (also common plastic additives), silicone derivatives (also from the Carbopack B phase), alcanes and the 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester of 2-methyl-propanopic acid.

Since most of these compounds have also been found in surface and ground water[18], care must be taken to avoid wrong assignment of the origin of the peaks in water extracts.

In any case, as a common rule, the phase has to be washed before extraction with the same solvent used for the elution of the compounds of interest. The volume of the washing solvent has to be checked by appropriate blanks. Blanks have to be done using unpolluted water for elution.

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REFERENCES

1. MacCarthy, P., Klusman, R.W. and Cowling, S.W. 'Water Analysis' *Analytical Chemistry* , Vol.63, pp.301R - 342R, 1991
2. Sherma, J., 'Pesticides' *Analytical Chemistry*, Vol.63, pp. 118R - 130R, 1991
3. Liska, I., Krupcik, J. and Leclercq, P.A. 'The Use of Solid Sorbent for Direct Accumulation of Organic Compounds from Water Matrices -A Review of Solid-Phase Extraction Techniques' *Journal of High Resolution Chromatography*, Vol.12, pp. 577 - 590, 1989
4. Barcelò, D. 'Occurrence, Handling and Chromatographic Determination of Pesticides in the Aquatic Environment' *Analyst*, Vol.116, pp. 681 - 689, 1991
5. Davoli, E., Benfenati, E., Bagnati, R. and Fanelli, R. 'Analysis of Atrazine in Underground Waters at Part per Trillion Levels as an Early Warning Method for Contamination and for Soil Distribution Studies' *Chemosphere*,Vol.16, pp. 1425 - 1430, 1987
6. Bagnati, R., Benfenati, E., Davoli, E. and Fanelli, R. 'Screening of 21 Pesticides in Water by Single Extraction With C18 Silica Bonded Phase Columns and HRGC-MS' *Chemosphere*, Vol.17, pp. 59 - 65, 1988
7. Benfenati, E., Tremolada, P., Chiappetta, L., Frassanito, R., Bassi, G., Di Toro, N. Fanelli, R., Stella, G. 'Simultaneous Analysis of 50 Pesticides in Water Samples by Solid Phase Extraction and GC-MS' *Chemosphere*,Vol.21, pp. 1411 - 1421, 1990
8. Benfenati, E., Di Toro, N., Fanelli, R., Lualdi, G., Tridico, R., Stella, G., Buscaini, P. and Stimilli, L. 'Characterization of Organic and Inorganic Pollutants in the Adige River (Italy)' *Chemosphere*,Vol.25, pp. 1665 - 1674, 1992

9. Di Corcia, A. and Marchetti, M. 'Multiresidue Method for Pesticides in Drinking Water Using a Graphitized Carbon Black Cartridge Extraction and Liquid Chromatographic Analysis' *Analitical Chemistry,* Vol.63, pp. 580 - 585, 1991
10. Moltò, J.C., Picò, Y., Font, G. and Manes, J. 'Determination of Triazines and Organophosphorus Pesticides in Water Samples Using Solid-Phase Extraction' *Journal of Chromatography,* Vol.555, pp. 137 - 145, 1991
11. Geissler, A., Schöler, H.F. 'The Analysis of Chloropesticides and PCB in Water. A Statistical Evaluation of Four Enrichment Methods' *Chemosphere,* Vol.23, pp. 1029 -1041, 1991
12. Hagen, D.F., Markell, G.C. and Schmitt, G.A. 'Membrane Approach to Solid-Phase Extractions' *Analytica Chimica Acta,* Vol.236, pp. 157 - 164, 1990
13. Mallet, V.N., Brun, G.L., MacDonald, R.N. and Berkane, K. 'A Comparative Study of the Use of XAD-2 Resin and the Conventional Serial Solvent Extraction Procedure for the Analysis of Fenitrothion and some Derivatives in Water-Preservation Techniques' *Journal of Chromatography,* Vol.160, pp. 81 - 88, 1978
14. Mallet, C. and Mallet V.N. 'Conversion of a Conventional Packed-Column Gas Chromatograph to Accomodate Megabore Columns. II. Determination of Organophosphorus Pesticides in Environmental Water' *Journal of Chromatography,* Vol.481, pp. 37 - 44, 1989
15. Chladek, E. and Marano, R.S. 'Use of Bonded Phase Silica Sorbents for the Sampling of Priority Pollutants in Wastewaters' *Journal of Chromatographic Science,* Vol.22, pp. 313 - 320, 1984
16. Di Corcia, A., Marchetti, M. and Samperi, R. 'Extraction and Isolation of Phenoxy Acid Herbicides in Environmental Waters Using Two Adsorbents in One Minicartridge' *Analytical Chemistry,* Vol.61, pp. 1363 - 1367, 1989
17. Rostad, C.E., Pereira, W.E. and Ratcliff, S.M. 'Bonded-Phase Extraction Column Isolation of Organic Compounds in Groundwater at a Hazardous Waste Site' *Analytical Chemistry,* Vol.56, pp. 2856 - 2860, 1984
18. Commission of the European Communities. *Organic Micropollutants in the Acquatic Environment* (COST 641) Addendum to the 4th Edition, 1987