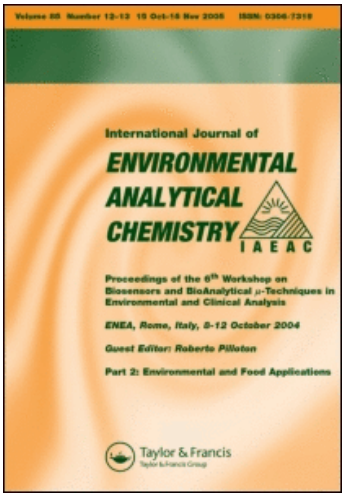

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LIQUID CHROMATOGRAPHIC DETERMINATION OF POLAR POLLUTANTS IN SURFACE WATER USING MEMBRANE EXTRACTION DISKS FOR ON-LINE TRACE ENRICHMENT

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Membrane extraction disks loaded with alkyl-bonded silica, copolymer or ion-exchange material have been tested for the on-line trace enrichment of polar pesticides from surface water. To this end, a new membrane extraction disk holder has been designed, which can be used in the forward flush and backflush mode. The basic compounds carbendazim, chloridazon, simazine and 4-chloroaniline were used as test compounds. They are preconcentrated from acidic solution using one or two membrane extraction disk holders in series (operated in the reversed-phase and ion-pair mode), and analysed by gradient liquid chromatography with polymer PLRP-S as the stationary phase and aqueous acetonitrile mixtures (pH 3) as the eluent. Data on the efficiency and repeatability of the on-line procedure are reported. Preconcentration of 30 ml of surface (river Rhine) water allows the UV detection of the four pollutants at the 0.1 $\mu g\ l^{-1}$ level.

KEY WORDS: Trace enrichment, liquid chromatography, membrane extraction disks, polar pollutants, surface water

INTRODUCTION

Today a major part of analytical problem solving is directed at the trace-level determination of organic constituents in environmental samples. Recently, much attention has been devoted to the determination of polar pesticides in surface, ground and tap water, which typically have to be carried out at the 0.1–5 $\mu g\ l^{-1}$ level. When such analyses have to be carried out on a routine basis, column liquid chromatography (LC) with UV absorbance detection will probably be the method of choice. However, in order to obtain the detection limits required, considerable trace enrichment will be necessary. Such trace enrichment still is often done by means of liquid–liquid extraction, and the advantages and disadvantages of this technique are well documented[1]. As an alternative, solid-phase extraction (SPE) on precolumns filled with different types of sorbents has recently gained widespread acceptance. Next

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to octadecyl- and octyl-bonded silicas, copolymers and ion-exchangers are frequently used sorbent materials.

Recently, Empore membrane extraction disks were introduced as an attractive tool for the trace enrichment of selected analytes from tap and surface water[2,3]. These membranes consist of a network of polytetrafluoroethylene (PTFE) fibrils in which sorbents (i.e., C-18, C-8, ion-exchange or polymeric material) are enmeshed. These disks can be used in the off-line[3] as well as the on-line[2] mode.

Hagen *et al.*[3] used C-18 and C-8-bonded silica Empore disks in the off-line mode. They were able to enrich several phthalates and pesticides from tap and ground water with acceptable recoveries; analysis was done by gas chromatography (GC). Kraut–Vass *et al.*[4] used 47 mm I.D. Empore disks in a micro-analysis holder for the determination of several pesticides, plasticisers and additives. After off-line trace enrichment, desorption, and evaporation, the compounds were analysed by means of GC with mass spectrometric detection.

The disadvantages of off-line SPE such as loss of sensitivity (injection of aliquot), losses due to evaporation or during transfer, and contamination are well known. On-line trace enrichment using membrane extraction disks in an adjustable membrane disk holder can eliminate these drawbacks. This has been demonstrated by Brouwer *et al.* who used small (4.6 mm I.D.) membrane extraction disks held in a disk holder coupled on-line to a LC system[2]. Polar pesticides were preconcentrated and determined by LC-UV.

As was mentioned above, today much attention is devoted to the development of multi-residue methods for the determination of a wide variety of pesticides—acidic, neutral, and basic—in environmental water samples. In order to preconcentrate all those compounds simultaneously, at least two precolumns appear to be necessary. In most cases on-line SPE is performed at low pH using a C-18-bonded silica or a polymer-based PRP-1 or PLRP-S precolumn in series with a cation exchanger[6]. However, the cation exchanger is rapidly overloaded when using samples of high ionic strength. In order to avoid this, calcium ions can be precipitated with oxalic acid and heavy metal ions complexed with EDTA prior to SPE and analysis.

In this paper, the potential of on-line SPE using one or more membrane extraction disk holders containing different types of membrane extraction disks is further explored. Since basic pollutants have been selected as test compounds, some of the disks are loaded with sodium dodecyl sulphate to improve retention at low pH. The optimised procedure is applied to the analysis of water samples from the river Rhine.

EXPERIMENTAL

Reagents and materials

Carbendazim, chloridazon and simazine were obtained from Riedel-de-Haën (Hannover, FRG). 4-Chloroaniline was purchased from Fluka AG (Buchs, Switzerland). HPLC-grade acetonitrile, methanol, phosphoric acid, sodium dihydrogen phosphate and perchloric acid were obtained from J. T. Baker (Deventer, The Netherlands);

sodium dodecyl sulphate was from Merck (Darmstadt, FRG). All aqueous solutions were prepared with demineralised water which was further purified with a Milli-Q (Millipore, Bedford, MA, USA) ultrafiltration system. Buffer solutions were prepared by mixing 1 M stock solutions of phosphoric acid, disodium hydrogen phosphate and/or sodium dihydrogen phosphate to the appropriate pH value and subsequent dilution to 10 mM.

Stock solutions of the analytes were prepared by dissolving 5 mg of the analyte in 5 ml of methanol and dilution with Milli-Q water to a concentration of 50 mg l^{-1}. Sample solutions were obtained by dilution of the stock solutions in surface (river Rhine) or Milli-Q water and acidifying to pH 3 with a 10 mM phosphate buffer.

Set-up and procedures

The LC system consisted of a Kontron (Zürich, Switzerland) Model 410 LC pump to deliver the aqueous sample, and a Hewlett Packard (Waldbronn, FRG) Model 1090 pump for delivering the mobile phase. Detection was performed with a HP 1040 diode-array detector, set at 230 nm. The analytical column was a 250 mm × 4.6 mm I.D. stainless-steel column containing 5 μm styrene-divinylbenzene copolymer PLRP-S (Polymer Laboratories, Church Stretton, UK) as the packing material. Empore disks containing AG 50W-X8 cation-exchange material were purchased from BioRad (Veenendaal, The Netherands). Disks containing the polystyrene-divinylbenzene copolymer Biobead SM-2 (XAD) were a gift from BioRad, and disks containing C-18 material were a gift from Sopar Biochem (Nieuwegein, The Netherlands). All membrane extractions disks had a thickness of 0.5 mm and a diameter of 47 mm. Glass fibre papers (F192-02), carboxylic acid modified, were a gift from Whatman (Fairfield, NJ, USA). The home-made stainless-steel membrane disk holder and the equipment for cutting the membranes will be discussed under 'Results and discussion'.

The LC system including one or two membrane disk holders is shown in Figure 1. In the system shown in Figure 1a, 30 ml of sample, adjusted to pH 3 with 10 mM phosphate buffer, were preconcentrated on one membrane disk holder filled with ten 4.6 mm diameter membrane extraction disks containing different packing materials. After switching of the valve the analytes were desorbed with an aqueous acetonitrile gradient (pH 8) to the PLRP-S analytical column, separated and detected at 230 nm. The same system was used for trace enrichment of the analytes as ion-pairs. Ten 4.6 mm diameter membrane extraction disks were loaded with 25 ml of a 2 mM sodium dodecyl sulphate (SDS) solution (5 ml min^{-1}). 30 ml of sample (pH 3) were preconcentrated (2 ml min^{-1}) on the SDS-loaded precolumn. After switching the valve, the analytes retained on the SDS-loaded precolum were desorbed with an aqueous acetonitrile gradient (pH 8) and transferred to the analytical column.

In the system shown in Figure 1b, 30 ml of sample (pH 3) were passed through two membrane holders in series, each containing ten membrane extraction disks. In some instances, the disks held in the second holder were loaded with 25 ml of a 2 mM solution of SDS. The various combinations of disk materials used in the two holders are discussed in the 'Results and discussion' section. By switching both valves the

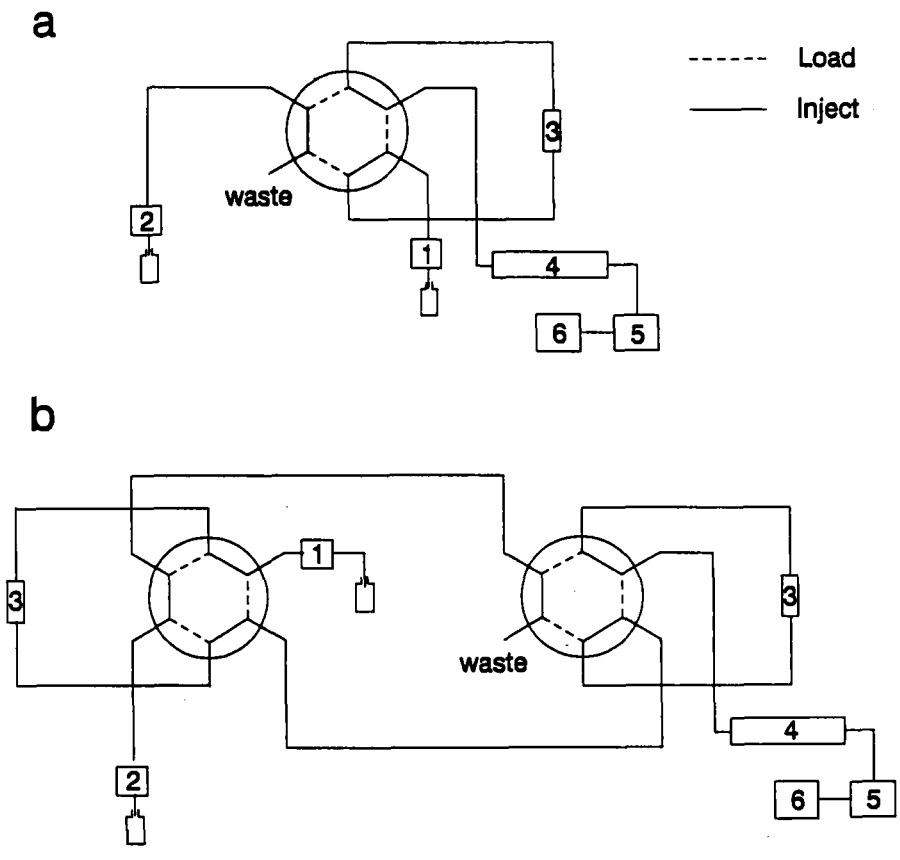

Figure 1 Set-up of analytical systems. (a) one-precolumn set-up; (b) two-precolumn set-up. 1, mobile phase pump; 2, sample pump; 3, membrane disk holder; 4, analytical column; 5, diode-array detector; 6, computer.

analytes were backflushed to the analytical column, separated by an aqueous acetonitrile (pH 8) gradient, and detected at 230 nm.

For gradient elution a binary solvent was used. Solvent A was 100% acetonitrile and solvent B was an aqueous 10 mM phosphate buffer (pH 8). The initial composition was 10% A and 90% B (v/v) and a linear gradient to 30% A and 70% B was applied in 17 min. This composition was held for 13 min. All LC experiments were performed at ambient temperature.

RESULTS AND DISCUSSION

Membrane disk holder and cutting device

The design of the new home-made stainless-steel membrane extraction disk holder is shown in Figure 2a. The membrane disk holder can contain one to ten disks with

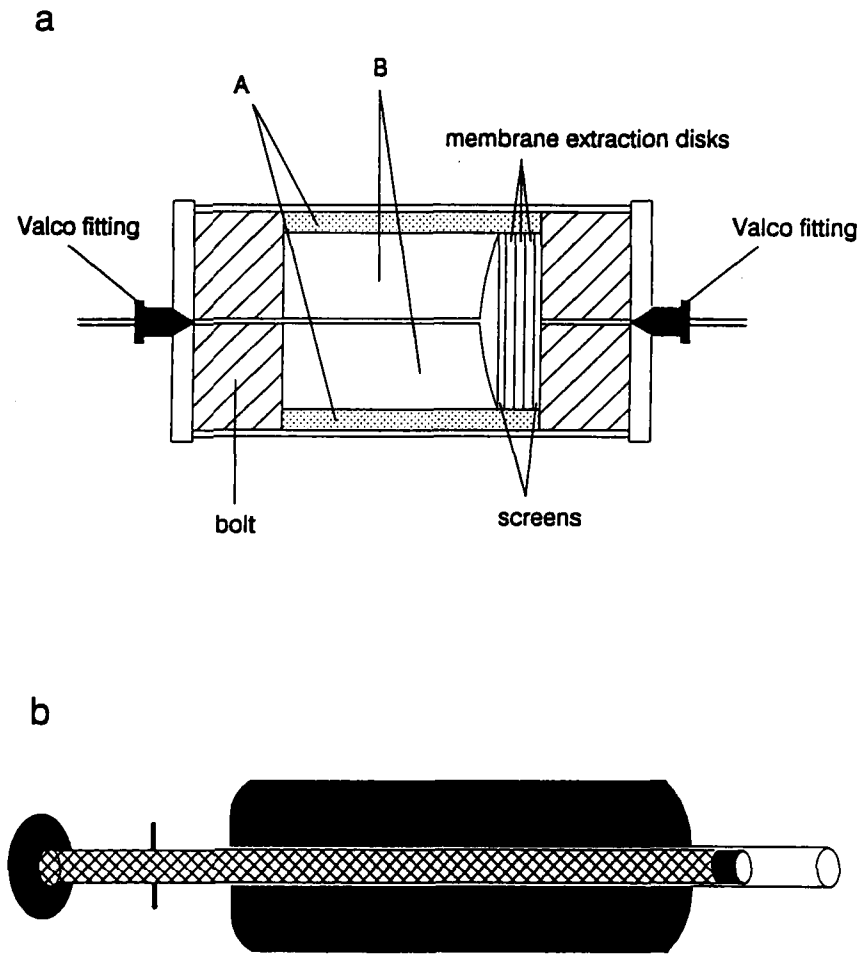

Figure 2 Design of (a) membrane disk holder and (b) cutting device. A, cylinder to adjust diameter, and B, cylinder to adjust length of holder.

a variable diameter. By changing the length of cylinder B the number of membranes in the holder can be adjusted. The screens inside the holder prevent the membrane disks from moving. The advantage of a holder which can contain more than one membrane disk will be obvious: unlike conventional precolumns the capacity of the holder can be adjusted for each individual analysis. This is important when analysing polar compounds, which normally have low breakthrough volumes. The inner diameter of the membrane holder can be adjusted by altering the inner diameter of cylinder A (Figure 2a). This means that when going from a 4.6 mm I.D. via a 3.1 or 2.0 mm I.D. to a narrow-bore analytical column, the membrane holder can be adjusted correspondingly in order to prevent extra band broadening.

Comparison of the design of the earlier described[2] and the present membrane disk holder reveals several improvements. Instead of a bolt on only one side of the holder,

in the new design two bolts are present. This makes it easier to remove a cylinder containing used membrane extraction disks. The second and most important improvement is the shape of cylinder B. In the previous model there was a relatively large dead volume when the holder was only partially filled. As a result it was not possible to use that holder in the backflush mode because of additional band broadening. In the new holder the hole inside cylinder B has the same diameter as the capillaries on both ends of the holder. Therefore this holder can be used in the forward as well as in the backflush mode. Cylinder B is now funnel-shaped at one side, which is necessary to provide an equal flow over the entire disk. A flat-ended cylinder B would provide a flow over only a small part of the membrane extraction disks resulting in a lower capacity. The disk holder is leak-tight up to at least 200 bar.

In order to prevent manual handling of the membrane disks which may result in contamination, a cutting device was developed in our workshop (Figure 2b). With the plunger in the backward position small membrane disks can be cut from the original 47 mm diameter disks by means of a sharp punch. By moving the plunger forward the small membrane disk can be pushed into cylinder A of the disk holder without any manual handling at all.

Sorption capacity of membrane extraction disks

In order to study the sorption capacity of several types of Empore membrane extraction disks, four polar basic pesticides were selected as test compounds, viz. a carbamate, carbendazim, a nitrogen-containing heteroaromatic, chloridazon, a triazine, simazine, and an aromatic amine, 4-chloroaniline. The structures and UV absorption diode-array spectra of the compounds are given in Figure 3.

The test solutes were preconcentrated at pH 3 on Empore extraction disks or on SDS-loaded extraction disks, and subsequently on-line desorbed in the backflush mode and separated on a PLRP-S analytical column using gradient elution with an aqueous acetonitrile solvent mixture. This column was chosen because coupling of a hydrophobic preconcentration module with a less hydrophobic analytical column will easily cause additional band broadening. At pH 3 all test compounds are protonated so that an interesting comparison can be made of the sorption efficiency of the C-18, XAD and cation-exchange membrane extraction disks.

Preliminary experiments showed that when using the cation-exchange extraction disks, no proper chromatograms were obtained. Since earlier off-line experiments in our laboratory with the same extraction disks had shown their sorption capacity to be quite good, desorption of the analytes obviously is the limiting factor in the present procedure. No further attempt was made to solve the problem. In all further work, ten (the maximum number) 4.6 mm diameter extraction disks—either C-18, SDS-loaded C-18, XAD or SDS-loaded XAD—were inserted in the holder, and the per cent recovery, i.e. analyte sorption, was determined for each of the four test solutes. Since rapid trace-level analysis is the primary aim of our studies, 30-ml sample volumes were taken which were loaded at 2 ml min^{-1}. The results were calculated by comparison with conventional 10-μl loop injections. The data reported in Table 1 show that with carbendazim, simazine and, especially, 4-chloroaniline, loading of the

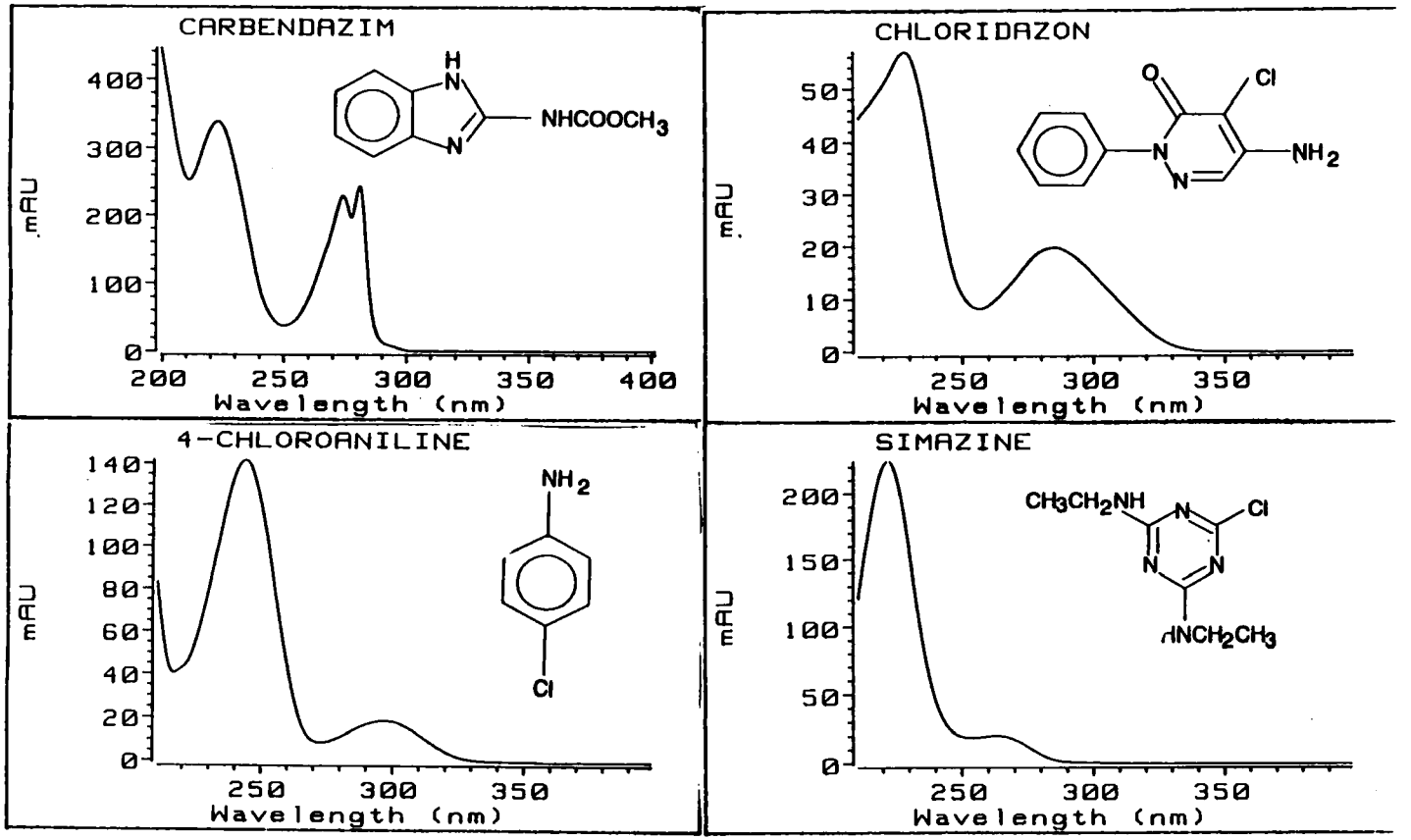

Figure 3 Structures and diode-array spectra of analytes.

Table 1 Recovery (%) of test compounds on various membrane extraction disks ($n = 2$)[a].

Compound	*Membrane extraction disks*			
	C-18	*C-18 +SDS*	*XAD*	*XAD +SDS*
Carbendazim	53	100	21	89
Chloridazon	86	32	56	36
Simazine	98	98	77	84
4-Chloroaniline	10	86	17	73

[a] For conditions, see text.

disks with SDS considerably increases the sorption efficiency. Somewhat surprisingly, the opposite behaviour is found for chloridazon. Probably, active sites present on the C-18 and (the backbone of) the XAD material which can interact with the (protonated) chloridazon, are shielded by the SDS excess.

In order to preconcentrate all four compounds efficiently, the final system contained two membrane disk holders in series. The first holder was loaded with C-18 or XAD extraction disks, and the second one with SDS-loaded C-18 or XAD extraction disks, respectively (cf. Figure 1b). The recoveries obtained upon preconcentration of 30-ml surface water samples are in good agreement with the data of Table 1: all compounds display recoveries of over 70% and 80% in the XAD- and C-18-based preconcentration system, respectively.

Application and validation

The final experiments were carried out using the combined C-18/SDS-loaded C-18 (10 extraction disks each) preconcentration system. A typical chromatogram for river Rhine water is shown in Figure 4. All compounds are nicely separated without serious interference from the matrix peak which is mainly caused by humic and fulvic substances present in surface water. The peak at $t_{ret} = 20$–21 min is due to desorbed SDS. During ten consecutive 30-ml trace-enrichment analyses, the back pressure over the membrane extraction disks gradually increased from about 10 bar to 30 bar. Because the disks slowly become yellow-coloured, sorption of humic substances is an obvious explanation. The increased back pressure had, however, no negative influence on the performance of the total analytical system.

Validation was performed using the same set-up. For all compounds calibration curves were constructed over the range 0.2–10 $\mu g\,l^{-1}$; the analyses were done in duplicate. The square of the regression coefficient was over 0.999 in all cases. The UV detection limits at 230 nm—which is close to the wavelength of maximum absorbance in all cases—were about 0.1 $\mu g\,l^{-1}$ for all four compounds. Diode-array spectra (200–400 nm; cf. Figure 4) which were useful for identification confirmation, were typically obtained at the 0.5 $\mu g\,l^{-1}$ level. In order to determine the precision and accuracy of the system, river Rhine water spiked with the analytes at the 2 $\mu g\,l^{-1}$ level

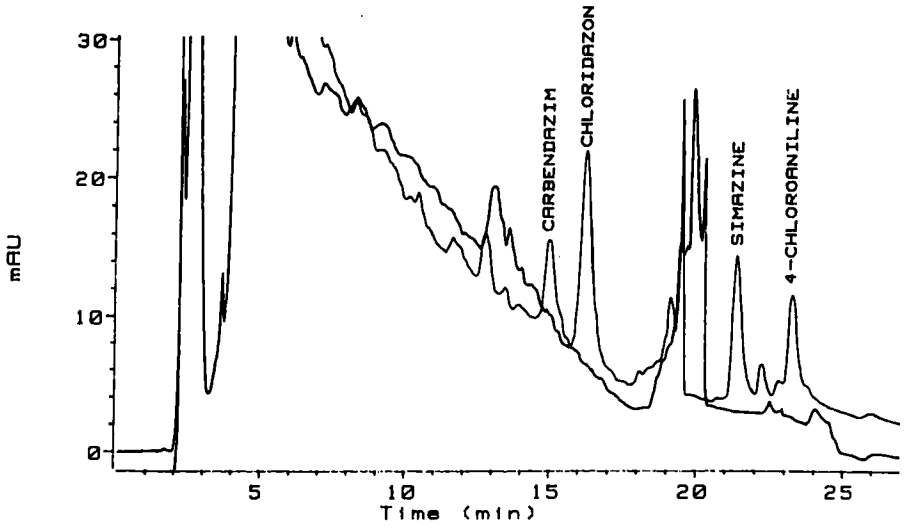

Figure 4 LC-UV chromatogram of blank and spiked (1 $\mu g\,l^{-1}$) Rhine water after preconcentration of 30 ml of sample on C-18 and SDS-loaded C-18 membrane extraction disks. For details, see Figure 1b and text.

was analysed ($n = 6$). The results are given in Table 2. The mean within-day precision was about 5%, while the accuracy (comparison with loop injections) was ca. 8%, which is certainly acceptable at these concentration levels in surface water.

CONCLUSIONS

A new leak-tight membrane extraction disk holder has been constructed which can contain one to ten disks of varying size. The membrane disk holder can be used in the forward flush and the backflush mode and is leak-tight to at least 200 bar. As an example four basic compounds have been preconcentrated at pH 3 on membrane

Table 2 Preconcentration recovery and validation of total analytical system[a].

Analyte	*Preconcentration recovery*		*Validation*	
	I	*II*	*Accuracy (%)*	*Precision (%)*
Carbendazim	98	90	4.0	5.0
Chloridazon	92	82	−5.5	4.0
Simazine	100	99	11	6.0
4-Chloroaniline	86	76	12	6.0

[a] LC-UV system with preconcentration module consisting of ten C-18 (I) or XAD (II) membrane disks in series with ten SDS-loaded C-18 (I) or SDS-loaded XAD (II) membrane disks coupled with the PLRP-S analytical column. Analyte concentration: 10 $\mu g\,l^{-1}$ (preconcentration) or 2 $\mu g\,l^{-1}$ (validation). Sample, river Rhine water.

extraction disks containing different packing materials and either loaded or not loaded with SDS. Trace enrichment from 30 ml of surface water with subsequent on-line desorption and separation on a polymer LC column with aqueous acetonitrile as eluent yields detection limits of 0.1 $\mu g\,l^{-1}$ (UV absorbance at 230 nm) for all compounds. Although the back pressure over the membrane disk holders gradually increases with an increasing number of analyses, a single set of membrane extraction disks can be used for at least ten 30-ml analyses without any loss in performance.

Future research will involve the use of membrane extraction disks for the determination of larger numbers of compounds. Besides, their use in an on-line LC-GC system will be evaluated. Finally, because of promising preliminary results obtained with relatively soft materials, the usefulness of, e.g., glass fibre paper[5], cellulose and polyurethane foam disks will be evaluated.

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