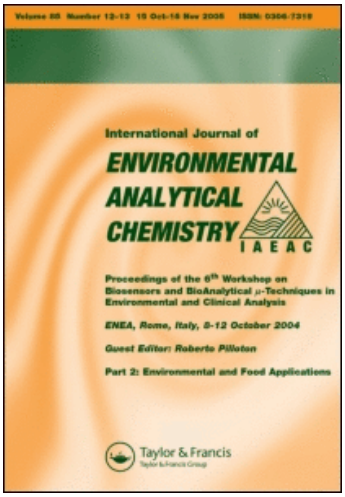

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On-Line Dialysis-Column Liquid Chromatography for the Determination of Polar Pesticides in Water Samples Containing Humic Substances

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ON-LINE DIALYSIS-COLUMN LIQUID CHROMATOGRAPHY FOR THE DETERMINATION OF POLAR PESTICIDES IN WATER SAMPLES CONTAINING HUMIC SUBSTANCES

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The potential of the on-line combination of dialysis, for the removal of interfering humic substances from environmental samples, and trace enrichment on a precolumn packed with C_{18}-bonded silica for the determination of polar pesticides by column liquid chromatography with UV detection is investigated, using six phenylurea herbicides as model compounds. The influence of the membrane material, thickness and molecular weight cut-off value, the configuration of the system - i.e. planar or hollow-fibre membranes - and, especially, the sample volume on analyte recovery and removal of humic substances is studied. Systems which allow the determination of the test compounds at the 1.0 µg/l level in river and lake water and at the 0.1 µg/l level in tap water are presented.

KEY WORDS: Column liquid chromatography, on-line dialysis, phenylurea herbicides, humic substances.

INTRODUCTION

The determination of trace amounts of polar organic pollutants in aqueous environmental samples is often complicated by the presence of humic substances in the water matrix. The term 'humic substances' is used to describe a large class of naturally occurring organic compounds that are found in all terrestrial and aquatic environments. These compounds represent an extremely heterogeneous mixture of molecules formed by the breakdown of all kinds of vegetational and animal matter. Their molecular weights range from about 500 to over 300,000 and the amount and nature of humic substances can vary considerably between different environmental matrices and even within one matrix[1]. In contrast to soil humic substances, relatively little is known about the occurrence and distribution of humic substances in aquatic environments. The average concentration in river water is about 5 mg/l, while in wetlands such as swamps and marshes concentrations of up to 100 mg/l are found[2]. Two major fractions of humic substances are distinguished in aqueous samples: fulvic acids,

the fraction that is water-soluble at all pH values and humic acids, which are not soluble below pH 2. In river water, fulvic acids (molecular weight up to 2,000) constitute about 90% of the total humic fraction and humic acids (molecular weight 2,000–10,000) about 10%. In wetlands these values are, on an average, 60% and 40%, respectively[2].

In the analysis of environmental aqueous samples by column liquid chromatography (LC), solid-phase extraction is often applied as a sample-pretreatment technique to enrich organic pollutants, which have to be determined at the low µg/l level or below. Since humic substances, which are present in the water matrix in much higher concentrations, are also concentrated to some extent, several problems may arise. Because of the polar nature of the humic substances and their UV absorbance and native fluorescence, an interfering matrix peak is often seen in the early part of the chromatogram, which complicates the quantification of polar analytes[3], this effect is most pronounced for acidified samples[4]. In addition, the recovery of some analytes tends to be lower than in standard solutions, which is ascribed to binding of the analytes to humic substances[5]. Finally, adsorption of the humic substances onto the stationary phase results in a reduced lifetime of the preconcentration column and the analytical column.

In order to reduce the amount of humic substances in the matrix of the analyte and, thus, circumvent the above problems, several approaches can be followed - the use of membrane-based techniques being the most important. To quote an example, reversed osmosis using membranes with a molecular weight cut-off value (MWCO) of 1,000 D has been applied for the removal of coloured humic substances from drinking water[6]. Sample pretreatment of natural waters using supported liquid membranes has been described for the LC determination of acidic herbicides[7]. The use of dialysis has never been reported so far, although it is a well-established technique for the removal of macromolecular compounds in the field of biomedical and food analysis. When coupled on-line to solid-phase extraction the dilution that is normally brought about by dialysis can be easily overcome. In this way, the pretreatment and analysis of large numbers of complex samples can be performed automatedly, as has been shown for, e.g., serum[8], plasma[9], whole blood[10], milk[11] and eggs and meat[12].

In the present study an evaluation is provided of the on-line combination of dialysis, solid-phase extraction and column liquid chromatography with UV detection for the analysis of different types of water samples. The influence of several membrane parameters - material, thickness and MWCO value - on dialysis is investigated. The effect of the configuration of the dialysis system is studied using a hollow-fibre and two planar units. The practicality of the approach for the LC-UV determination of six polar phenylurea herbicides at the 1.0 µg/l level in river and lake water and at the 0.1 µg/l level in tap water is shown.

EXPERIMENTAL

Chemicals

The phenylurea herbicides metoxuron (Mx), monuron (Mo), diuron (Di), metobromuron (Mb), linuron (Li) and chlorobromuron (Cb) were a gift from Dr. A. de Kok

(Rijkskeuringsdienst van Waren, Alkmaar, The Netherlands). All other chemicals were of analytical-grade quality and were obtained from J.T. Baker (Deventer, The Netherlands). The water samples used were Amsterdam (The Netherlands) tap water, water from the River Rhine taken at Lobith (The Netherlands), and from De Braak, a small wetland lake in Amstelveen (The Netherlands).

Equipment

A Gilson (Villiers-le-Bel, France) ASTED was used in combination with an LC-UV system. The ASTED consisted of a Model 231 autosampler equipped with two 1 ml Model 401 dilutors in slave configuration, a Model 99/55 rack for 128 sample vials of 860 µl and five reagent vials of 25 ml, and a Model 7010 Rheodyne (Berkeley, CA, USA) six-port switching valve.

For the work with planar membranes two dialysis blocks, made of polymethylmethacrylate, were used. One block - referred to hereafter as 'the small block' - had a donor channel volume of 100 µl and an acceptor channel volume of 175 µl. The other - the large - block had donor and acceptor channel volumes of 1.2 and 1.0 ml, respectively. The properties of the planar membranes used in this study are summarized in Table 1. Two hollow-fibre membrane bundles (Spectrum, Los Angeles, CA, USA), each consisting of 176 fibres were used. The fibres of one bundle had an MWCO value of 6 kD, an I.D. of 215 µm and a membrane thickness of 18 µm and those of the other bundle had an MWCO value of 9 kD, an I.D. of 150 µm and a membrane thickness of 9 µm. In both cases the membrane material was regenerated cellulose. The bundles were fitted in a home-made holder and placed in a 250 ml sample vial equipped with a magnetic stirring bar. For solid-phase extraction a 10 × 2 mm I.D. stainless-steel precolumn was used which was slurry packed with 40 µm Baker C_{18}-bonded silica and held in a home-made precolumn holder.

The LC system consisted of a Gilson Model 305 high-pressure piston pump and a 140 × 3.1 mm I.D. stainless-steel analytical column packed with a 5 µm RoSil (Research Separation Laboratories, Eke, Belgium) C_{18} stationary phase. 20 mM sodium phosphate buffer (pH 7) - acetonitrile (60:40, v/v) at a flow rate of 0.5 ml/min was used as eluent. An Applied

Table 1 Properties of various planar dialysis membranes.

Membrane Number	*Supplier*	*Material*	*MWCO (kD)*	*Thickness (µm)*
1	Spectrum[a]	native cellulose acetate	1	85
2	Spectrum	native cellulose acetate	2	85
3	Spectrum	native cellulose acetate	5	85
4	Spectrum	regenerated cellulose	3.5	50
5	Spectrum	regenerated cellulose	12	35
6	Gilson[b]	cellulose acetate	15	20
7	Bran & Luebbe[c]	unknown	unknown	25

[a]: Los Angeles, CA, USA
[b]: Villiers-le-Bel, France
[c]: Maarssen, The Netherlands

Biosystems (Ramsey, NJ, USA) Model 759A UV spectrophotometer set at 245 nm and a Hewlett Packard (Waldbronn, Germany) Model 3396A integrator were used for detection.

Set-up

A schematic diagram of the system is shown in Figure 1. Dialysis with a planar membrane (Figure 1A) was performed at ambient temperature by introducing the sample into the donor channel of the dialysis block by means of dilutor 1, where it was kept stagnant, and continuously pumping the acceptor phase (HPLC-grade water) through the acceptor channel to the precolumn by means of dilutor 0 (1.5 ml/min). By switching the six-port valve, the enriched analytes were backflushed by the eluent to the analytical column. After each run, both channels were flushed with 5 ml of water.

The hollow-fibre unit was used, at ambient temperature, in the set-up shown in Figure 1B. The sample was put into a 250-ml vial and stirred and the acceptor phase was pumped through the fibres and to the precolumn by dilutor 0 (3.0 ml/min). Cleaning of the fibres took place after each run by rinsing them with water. To remove adsorbed compounds from the membranes, the bundle was immersed in methanol for a few minutes after every five analyses.

When not in use, both planar and hollow-fibre membranes were stored in an aqueous 0.05% sodium azide solution.

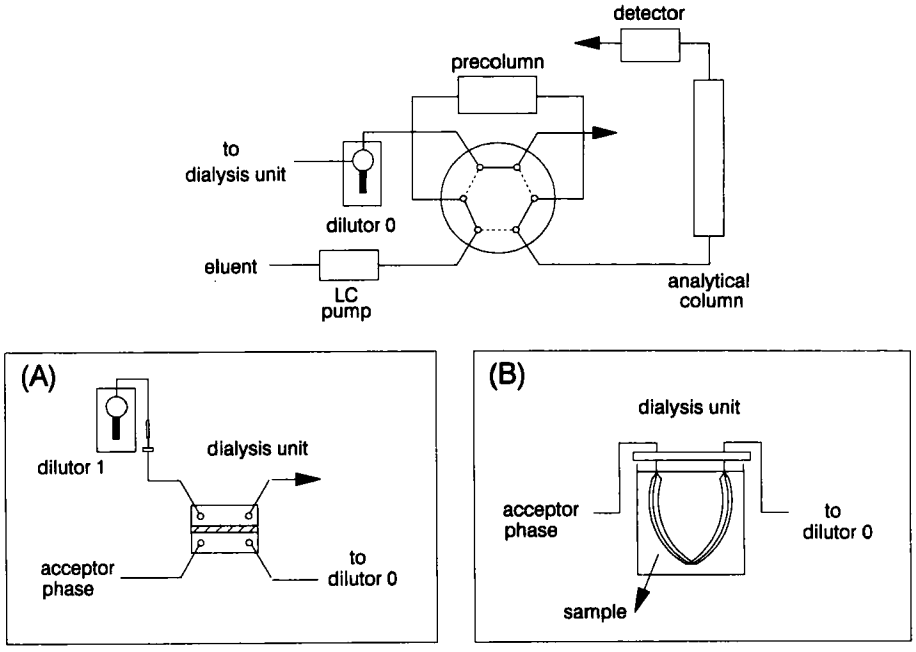

Figure 1 Schematic set-up of the dialysis system using a planar membrane (A) or a hollow-fibre unit (B).

RESULTS AND DISCUSSION

Influence of membrane parameters

In general, the separation of a series of compounds by a porous dialysis membrane is based on the difference in their diffusion rates through this membrane. These diffusion rates, in their turn, depend on the ratio between the size of the molecule and the pore width of the membrane. The membrane material is supposed to be inert and not to be involved in the separation process. To obtain an optimum separation between macromolecular matrix components and the analytes of interest, the pore width has to be carefully optimized to find an acceptable compromise between a high membrane flux of the analytes and a sufficient removal of the interfering compounds. Another important membrane parameter is the thickness, because the membrane transport rate decreases with increasing thickness. For a more fundamental discussion of membrane transport see e.g.[13].

Seven different planar membranes (cf. Table 1) were examined using the small dialysis block and aqueous 1 mg/l solutions of the phenylureas as test compounds. The membranes Nos. 1–3, all made of so-called native cellulose acetate, were found to be unsuitable for analytical purposes - regardless of their MWCO value - because of the very bad reproducibility of the analyte recovery. With these membranes, the analyte recovery was virtually zero in the first experiment and gradually increased to 100% in subsequent runs. In addition, a strong memory effect of up to 15% was observed. Obviously, a strong interaction takes place between the analytes and the membrane material. A possible explanation for this phenomenon can be found in the polymer structure of the membrane. Cellulose and cellulose acetate are known to exist in two forms which differ in crystal structure[14]. The native form, or form I, has a highly regular structure, in which the glucose units are arranged in such a way that cavities are formed throughout the polymer which allow the formation of inclusion complexes with aromatic compounds and, thus, give rise to a strong interaction. The regenerated form, or form II, has a distorted polymer structure in which inclusion cavities are scarce. Interaction with small molecules is due to adsorption rather than to inclusion and is, as such, much weaker. The planar membranes Nos. 4 and 5 and the hollow fibres were manufactured from regenerated cellulose and, in agreement with the theory described above, showed good reproducibility and virtually no memory effect (typically less than 1% for all test compounds). The same results were found for membranes Nos. 6 and 7. Although the suppliers could not provide detailed data on their polymer structure, one can safely conclude that both membranes consist of a regenerated form of cellulose or cellulose acetate.

The influence of the MWCO value and the membrane thickness on the recovery of diuron is shown in Figure 2. The highest dialysis rate - i.e. analyte recovery per unit time - was found for membranes Nos. 6 and 7, which have the smallest thickness and the highest MWCO value. Here, a recovery of 100% is reached after about 15 min. An increase in membrane thickness and a decrease in MWCO leads to a smaller recovery per unit time, because of slower diffusion through the pores. This is observed for membrane No. 5 and, more distinctly, for membrane No. 4. The maximum recovery that can be obtained within 20 min is now significantly lower (60–80%).

The effect of exchanging membranes on the repeatability of the total analytical procedure

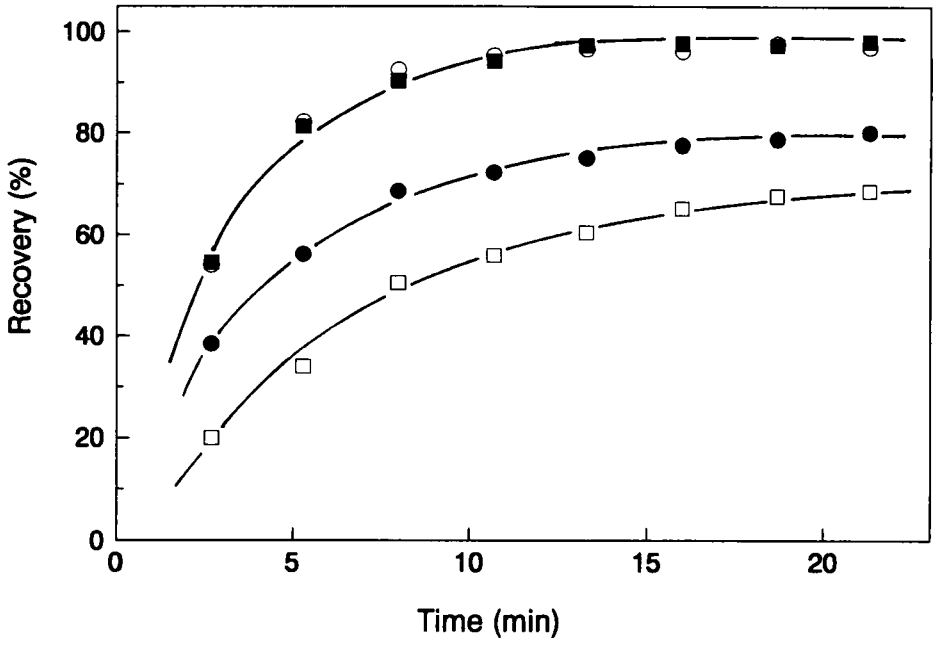

Figure 2 Per cent recovery of a 1.0 mg/l aqueous solution of diuron vs. dialysis time for the small dialysis block equipped with different planar membranes: membrane 4 (□), membrane 5 (●), membrane 6 (■) and membrane 7 (○). Acceptor phase flow rate, 1.5 ml/min.

was shortly investigated. Only membrane No. 6 is supplied premounted, the other membranes had to be placed in the dialysis block by stretching them by hand. The relative standard deviation (RSD) of the response typically was less than 3% for all test compounds at the 1 mg/l level, both when a single membrane (n=6) or two membranes (n=3 plus n=3) were used.

Influence of the configuration of the dialysis system

In order to meet the requirements of the Dutch National Policy Document on Water Management[15], it should be possible to detect 1–3 µg/l of individual organic pesticides in surface water and 0.1 µg/l in tap water.

In general, the lower limit of detection (expressed in concentration units) is determined by several chromatographic parameters, the detectability (UV response) of the analyte and the amount of analyte injected onto the analytical column. The latter parameter is governed by (i) the analyte recovery of the total analytical procedure, (ii) the sample volume processed and (iii) the analyte concentration in the sample. In other words, the limit of detection can be improved - i.e. the detector response can be enhanced - by increasing the recovery and/or the sample volume. In the present study, these parameters are directly related to the configuration of the dialysis system, provided that no breakthrough occurs on the precolumn.

Table 2 Properties of different dialysis units.

Unit	*Membrane area (cm^2)*	*Donor volume (ml)*	*Ratio (cm^2/ml)*
Small block	4	0.1	40
Large block	12	1.2	10
Hollow fibres	210	250	0.8

A large donor volume allows the pretreatment of large sample volumes and a high membrane area/sample volume ratio leads to a high recovery. To quote an example, despite a quantitative recovery for all compounds when using the small dialysis block, the limit of detection was only 3 µg/l for aqueous standard solutions. This result, obtained after 8 min of dialysis using the 15 kD membrane (No. 6) or 20 min using the 3.5 kD membrane (No. 4), is due to the very small sample volume of only 100 µl.

In order to improve the detection limits, two other configurations were tested which differed from the small block in donor volume and membrane area/sample volume ratio(Table 2). Figure 3 shows the results obtained with an aqueous 1 mg/l solution of diuron, a 15 kD planar membrane (No. 6) and a 9 kD hollow-fibre membrane bundle. Here, it should be added that no analyte breakthrough occurred since the breakthrough volumes of all analytes were larger than 60 ml on the precolumn used, while the acceptor phase volumes were below 60 ml in all cases. As expected, the recovery was highest for the system with the largest area/volume ratio (Figure 3A). After 15 min of dialysis, 100% recovery was found for the small block (ratio, 40 cm^2/ml), while for the large block (ratio, 10 cm^2/ml) this value was 60% and for the hollow fibres (ratio, 0.8 cm^2/ml) a mere 5%. In the latter two cases, complete recovery can only be reached at the expense of an unduly long dialysis time. However, the detection limits that can be achieved depend on both the recovery and the sample volume. This is demonstrated in Figure 3B. Despite the lower recovery, the response is highest for the system with the largest sample volume (note the logarithmic scale). With the hollow-fibre system (250 ml sample) the response is about 10-fold higher than with the large block (1.2 ml) and 100-fold higher than with the small block (0.1 ml). When using aqueous standard solutions, detection limits were about 0.2 µg/l for the large block (8 min of dialysis, 15 kD) and about 0.02 µg/l for the hollow fibres (8 min of dialysis, 9 kD) for all six test compounds. Therefore, if the sample volume is not a limiting factor, the hollow-fibre system is to be preferred to obtain low detection limits.

Analysis of natural waters

The potential of the different membranes to retain humic substances from tap and surface water was tested with the large dialysis block and the hollow-fibre system. To obtain low detection limits, the obvious choice is to use the hollow fibres since there is, in principle, no limitation to the sample volume. Firstly, the analysis of Amsterdam tap water, which contains a relatively low concentration of humic substances, was studied. The hollow fibres with an MWCO of 9 kD were found not to retain enough of the matrix components to allow

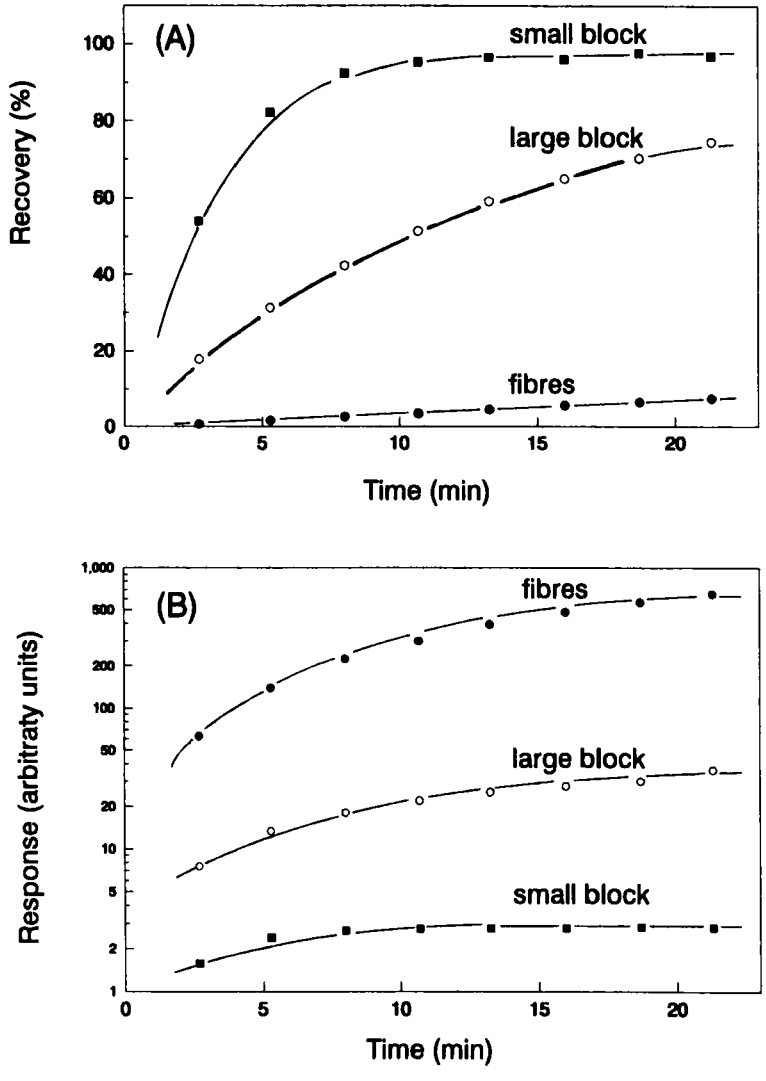

Figure 3 Per cent recovery (A) and response (B) of a 1.0 mg/l aqueous solution of diuron vs. dialysis time for different dialysis configurations: small block (■), large block (○) and hollow fibres (●). Acceptor phase flow rate for planar system (15 kD), 1.5 ml/min, for hollow fibres (9 kD), 3.0 ml/min.

the determination of the two most polar compounds at a level of 0.1 μg/l (Figure 4A). Replacing them by the 6 kD fibres caused the removal of a sufficiently large portion of the humic substances to permit quantitation of all analytes (Figure 4B). In principle, fibres with a lower MWCO should be applied to remove even more of the humic substances. However, to our knowledge, these are not commercially available. For the rest, one should note that the peak areas in Figure 4B are about 35% smaller than those in Figure 4A because of slower

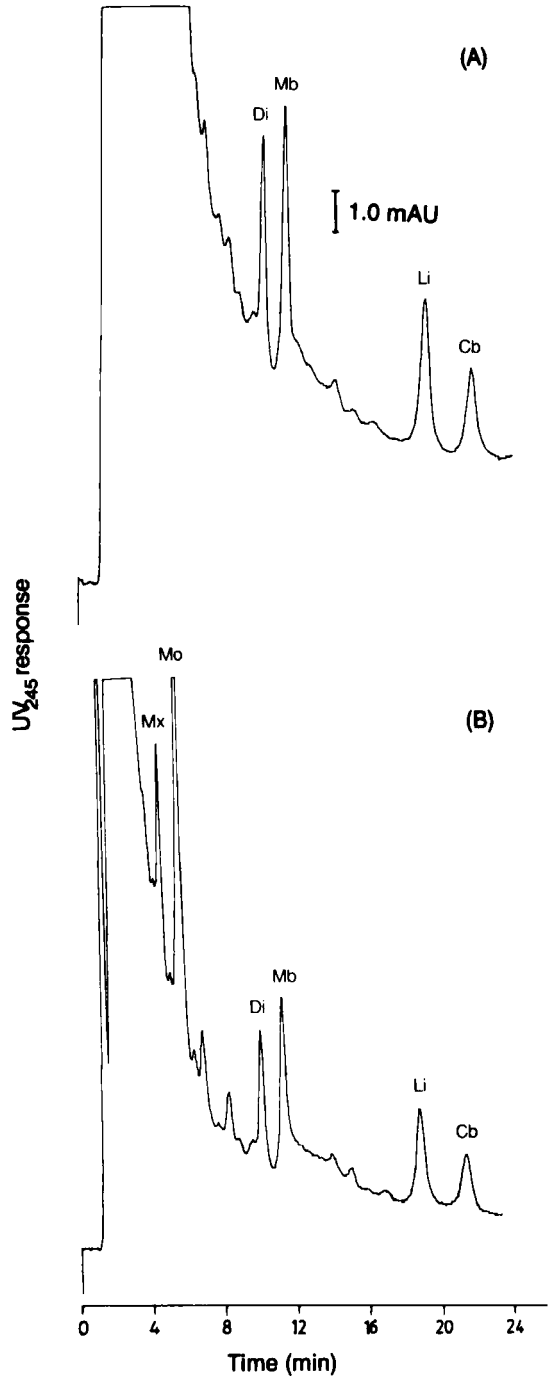

Figure 4 Hollow-fibre dialysis of 250-ml tap water samples spiked with 0.1 µg/l of the six phenylurea herbicides. Acceptor phase, 25 ml of HPLC-grade water (3.0 ml/min). Mx: metoxuron, Mo: monuron, Di: diuron, Mb: metobromuron, Li: linuron, Cb: chlorobromuron. MWCO values: 9 kD (A) and 6 kD (B).

diffusion of the analytes through the smaller pores and the thicker membrane wall (18 μm against 9 μm).

The river and wetland lake waters were found to contain much more interfering compounds with molecular weights smaller than 6 kD; the matrix peak found with these samples impeded the accurate determination of metoxuron and monuron, even at the 1.0 μg/l level. As an alternative, the large dialysis block provided with the planar 3.5 kD membrane was therefore used instead of the hollow fibres. Although the response with this system is lower than with the hollow-fibre unit, enough of the humic substances were now removed to allow the determination of all analytes in both river and wetland lake water at a concentration of 1.0 μg/l (Figures 5B and 6B, respectively).

Figures 4–6 illustrate several other aspects of sample pretreatment of aqueous samples by means of dialysis. The humic substances present in the water samples only interfere with the determination of the two most polar compounds, metoxuron and monuron. The other phenylureas can also be quantified without removal of the matrix components (Figures 5A and 6A). In fact, lower detection limits can be obtained without dialysis, because the procedure with the large block leads to a loss in recovery (cf. Figure 3A). This means that the application of dialysis for the pretreatment of natural waters is only worthwhile if the advantage - removal of matrix constituents - balances the inherent disadvantage - a lower recovery -, in other words in the case of polar analytes.

As stated before, the fulvic acid fraction accounts for ca. 90% of the total humic substances in river water. Comparison of Figures 5A and 5B - which show the result of direct enrichment and on-line dialysis of river water, respectively - demonstrates that a major part of the interfering matrix peak is removed by using a 3.5 kD membrane. This suggests that the matrix peak predominantly consists of compounds larger than 3.5 kD. It, therefore, lies at hand to conclude that the humic acid fraction rather than the, much larger, fulvic acid fraction is responsible for the interference in the chromatogram. Probably, the more polar fulvic acids break through the precolumn to a large extent. The fact that a 6 kD membrane does not sufficiently retain the humic substances suggests that the molecular weights of a major part of the humic acids range between 3.5 and 6 kD.

Comparison of the LC-UV chromatograms of direct enrichment of the lake water and the river water sample shows the presence of a larger matrix peak in the former case (Figures 5A and 6A), whereas the opposite is true when using dialysis (Figures 5B and 6B). Obviously, the concentration of humic substances smaller than 3.5 kD is higher in the river water sample, which is in agreement with the present theory of the origin of humic substances in different aquatic environments[1]. Rivers are thought to contain the smallest and most polar humic substances from among those present in soil that have leached into the water. In wetlands degradation of all forms of life takes place in the water itself giving rise to a higher concentration of high-molecular-weight humic acids. Therefore, the application of dialysis is most useful for matrices such as wetland and other stagnant waters. The larger lake water matrix peak observed after direct enrichment is probably due to the higher concentration of humic acids. The concentration of humic substances in the Dutch part of the river Rhine has been determined to be about 5 mg/l[2], 10% of which are humic acids. The exact concentration of humic substances in the wetland lake water is unknown, but because of the yellow-brown colour of the water it has to be at least 15 mg/l[1], 40% of which are humic acids.

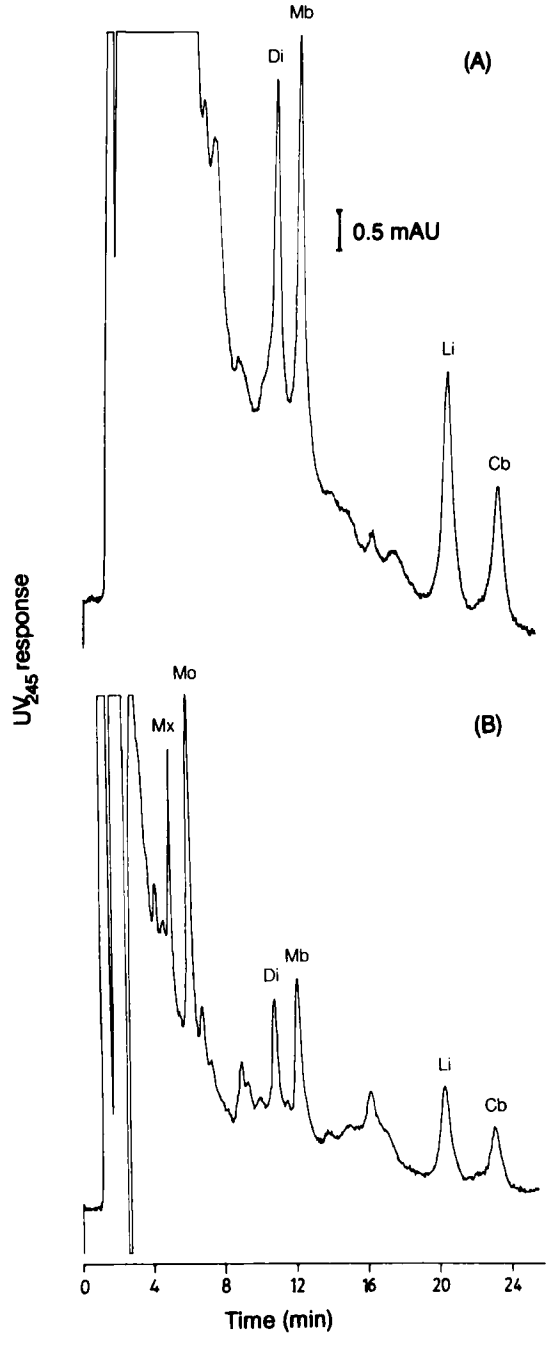

Figure 5 Direct enrichment (A) and dialysis with a planar 3.5 kD membrane (B) of 1.2-ml Rhine water samples spiked with 1.0 µg/l of the phenylurea herbicides. Acceptor phase, 20 ml of HPLC-grade water (1.5 ml/min). Abbreviations as in Figure 4.

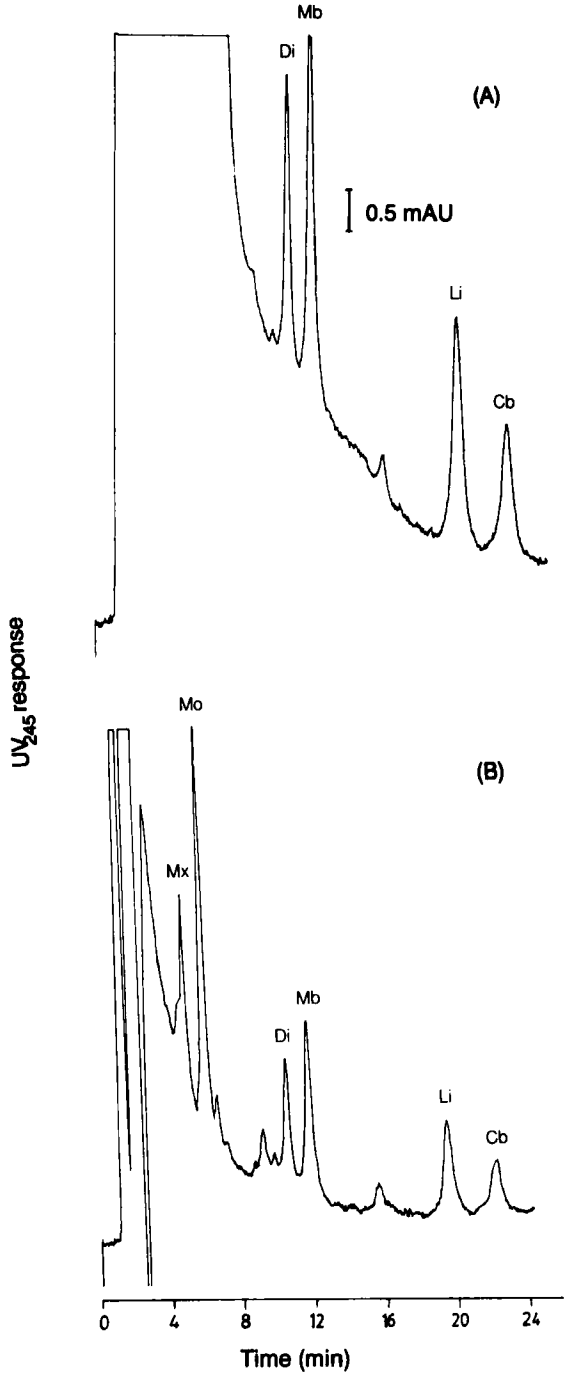

Figure 6 Direct enrichment (A) and dialysis with a planar 3.5 kD membrane (B) of 1.2-ml wetland lake water samples spiked with 1.0 µg/l of the phenylurea herbicides. Acceptor phase, 20 ml of HPLC-grade water (1.5 ml/min). Abbreviations as in Figure 4.

Table 3 Analytical data on the automated determination of phenylurea herbicides in Rhine water using on-line dialysis-LC-UV.

Analyte	*Limit of detection (µg/l)*[a]	*Recovery (%)*	*Linearity*[b]			*Precision (RSD, %)*[c]
			Slope (± RSD)	*Intercept (± RSD)*	R^2	
Metoxuron	0.5	36	12.6±0.5	5.9±3.0	0.9870	4.1
Monuron	0.3	37	37.4±0.4	3.1±2.0	0.9991	1.7
Diuron	0.5	35	20.3±0.2	0.9±1.1	0.9991	4.1
Monobromuron	0.5	34	25.4±0.3	2.6±2.1	0.9978	3.4
Linuron	0.3	32	21.8±0.3	2.4±1.8	0.9983	5.9
Chlorobromuron	0.3	32	13.9±0.3	1.9±1.9	0.9953	5.2

[a]: S/N = 3.
[b]: Range, 0.5–10 µg/l, seven data points in duplicate.
[c]: Level, 1 µg/l, n = 10.

Performance of the total system

Based on the above results, a method for the determination of the six phenylurea herbicides in river and lake water was set up. The large dialysis block equipped with a 3.5 kD membrane was used and 1.2-ml samples were processed by holding the sample stagnant in the donor channel and pumping 20 ml of HPLC-grade water through the acceptor channel to the precolumn at a flow-rate of 1.5 ml/min. After valve switching the enriched analytes were desorbed and LC-UV was carried out on the analytical column with 20 mM sodium phosphate buffer (pH 7) - acetonitrile (60:40 v/v) as eluent. The dialysis time, including cleaning of the membrane, was 17 min; the LC separation took 24 min. The total procedure could be performed fully automatedly and by parallel performance of dialysis and chromatography two samples could be analysed per hour. Relevant data on the analysis are summarized in Table 3. Calibration curves (0.5–10 µg/l) were constructed by using river Rhine water spiked with a mixture of the six analytes. The within-day precision at the 1 µg/l level was quite satisfactory: the relative standard deviation (RSD) was less than 6% for all compounds - even for the most polar ones. Detection limits of 0.3–0.5 µg/l were found for the present analytes - whose ε values range between 18,000 and 25,000 $M^{-1}.cm^{-1}$ - despite the fact that the absolute recoveries were below 40%.

CONCLUSIONS

The column liquid chromatographic determination of polar organic pollutants in natural waters, which is often hampered by the interference of humic substances, can be improved by applying dialysis as an on-line sample-pretreatment technique. The applicability of a dialysis membrane depends on the material used, and the thickness and molecular-weight cut-off (MWCO) value of the membrane. To prevent strong interactions of organic analytes with the membrane regenerated cellulose or cellulose acetate should be used as the membrane material. Rapid analyte transport through a membrane and, consequently, a high recovery per unit time requires membranes with a low thickness and a high MWCO value.

However, in order to effect an adequate removal of interfering matrix components - i.e. humic and fulvic acids - the MWCO value should be small and in practice a compromise has to be found. In the case of natural waters an MWCO of 3.5 kD proved to be optimal. As regards the dialysis module, the detection limit of analytes (expressed in concentration units) is determined by the configuration of the dialysis system: a high membrane area/sample volume ratio leads to a high recovery and a large sample volume to a high response.

By using a planar dialysis membrane with an MWCO of 3.5 kD and a sample of 1.2 ml, interfering humic substances were sufficiently removed to allow the automated determination of the six phenylureas selected as test compounds at the 1.0 µg/l level in natural waters. The method is especially advantageous for the most polar analytes, since these can not be quantified without the removal of the humic substances. In order to obtain lower detection limits, one can utilize hollow-fibre membranes which permit the use of larger sample volumes. However, hollow fibres with MWCO values lower than 6 kD are not commercially available and membranes with a 6-kD cut-off value do not retain a sufficiently large proportion of the humic substances to guarantee quantitation of the most polar analytes. However, such hollow fibres are suited for the analysis of tap water, which contains much less humic substances. Using 250 ml of sample, determination of the analytes is possible down to the - officially required - 0.1 µg/l level, even for metoxuron, the most polar compound tested.

Acknowledgement

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