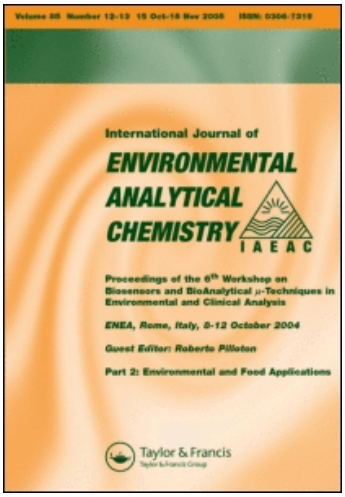

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Off-Line and On-Line Preconcentration Techniques for the Determination of Phenylureas in Freshwaters

M. -C. Hennion[a]; P. Subra[a]; R. Rosset[a]; J. Lamacq[b]; P. Scribe[b]; A. Saliot[b]
[a] Laboratoire de Chimie Analytique de l'Ecole Supérieure de Physique et Chimie de Paris, Paris, France
[b] Laboratoire de Physique et Chimie Marines de l'Université Pierre et Marie Curie, Paris, cedex 05, France

To cite this Article Hennion, M. -C. , Subra, P. , Rosset, R. , Lamacq, J. , Scribe, P. and Saliot, A.(1990) 'Off-Line and On-Line Preconcentration Techniques for the Determination of Phenylureas in Freshwaters', International Journal of Environmental Analytical Chemistry, 42: 1, 15 — 33
To link to this Article: DOI: 10.1080/03067319008028312
URL: http://dx.doi.org/10.1080/03067319008028312

Intern. J. Environ. Anal. Chem., Vol. 42, pp. 15–33
Reprints available directly from the publisher
Photocopying permitted by license only

OFF-LINE AND ON-LINE PRECONCENTRATION TECHNIQUES FOR THE DETERMINATION OF PHENYLUREAS IN FRESHWATERS*

M.-C. HENNION,* P. SUBRA and R. ROSSET

Laboratoire de Chimie Analytique de l'Ecole Supérieure de Physique et Chimie de Paris, 10, rue Vauquelin, 75005 Paris, France

J. LAMACQ, P. SCRIBE and A. SALIOT

Laboratoire de Physique et Chimie Marines de l'Université Pierre et Marie Curie, ERA CNRS 353, Tour 24–25, 4, place Jussieu, 75252 Paris cedex 05, France

(*Received 30 October 1989*)

Phenylurea herbicides are analysed by reversed-phase liquid chromatography using UV detection at 244 nm after a concentration step in order to determine ppb or sub-ppb levels in drinking and river waters. With an average UV detection limit of 5 ng, a 500 ml sample volume is necessary to reach the 10 ppt level for spiked LC grade water samples and enables easy determination of concentrations below the ppb level for river water samples. Off-line and on-line methods are compared for the concentration step. Off-line concentration consists in a liquid sorption on *n*-octadecyl silica (C18) and elution by a suitable organic solvent. Polar phenylureas have low retention volumes on C18 silica and consequently the length of the concentration column has to be 10 cm to concentrate them at the ppb level from 100 ml of water and longer for lower levels of detection. Nevertheless, we show that increasing the size of the concentration column does not improve the limits of detection because of the numerous interferences also concentrated when percolating high volumes of water. On-line technology can be used only with short precolumns and requires a sorbent with a great retention for phenylureas. The copolymer-based PRP-1 is found to be an excellent sorbent and it is then possible to apply on-line precolumn technology with preconcentration through two precolumns (10 × 21 mm ID) in series, the first one being packed with C18 silica and the other with the PRP-1 polymer. Interfering compounds are then trapped onto the first precolumn acting as a filter and common phenylurea-breakthrough volumes on the PRP-1 precolumn are higher than 500 ml. Knowing the amounts preconcentrated on both precolumns and using UV and electrochemical detection help the identification of phenylureas in river water.

KEY WORDS: Phenylurea herbicides, freshwaters, off-line preconcentration, on-line precolumn technology.

---

*Presented at the 18th International Symposium on Environmental and Analytical Chemistry, Barcelona, 5–8 September, 1988.

INTRODUCTION

Substituted phenylurea herbicides are widely used in agriculture and their determination in environmental media such as the natural fresh waters necessitates the development of analytical methods sensitive at the ppb level or below. Direct gas chromatography (GC) is unsuitable because of the rapid thermal decomposition of some compounds into their isocyanates.[1] Consequently, indirect methods, i.e. hydrolysis of herbicides to their anilines and subsequent derivatization for sensitive and selective detection by GC with electron capture detection, have been used.[2–7] Nevertheless, such procedures lack specificity because substituted anilines are also their main (bio)degradation products and are widely used bulk chemicals; they are also released into the environment via degradation of other products such as pesticides and aniline-based dyes.[3] De Kok *et al.*[1,3,8] have overcome this specificity problem by combining liquid chromatography (LC) for suitable group separation of anilines and herbicides before hydrolysis, and capillary GC.

Liquid chromatographic methods are more attractive because they allow a direct determination but they require a concentration step for trace enrichment.[9] Nevertheless, it appears from the literature that the problem of discrimination between phenylureas and their anilines still exists because the separation is difficult. When one or two phenylureas are sought it is relatively easy to separate them from their corresponding degradation products.[6,10–13] But if many phenylureas are sought, phenylureas and corresponding anilines have close retention times both in normal-phase and in reversed-phase chromatography.[8,14–16] Goewie *et al.*[14] have shown that discrimination between phenylureas and anilines can be easily achieved with a platinum-loaded phase acting as an aniline filter. They used on-line precolumn technology for the concentration of phenylureas with two precolumns in series. The first one was packed with the platinum phase acting as an aniline filter and the second with a *n*-octadecyl (C18) silica permitting the preconcentration of intact phenylureas which were on-line transferred to and separated on a reversed-phase analytical column. As these compounds are relatively polar, their retention on C18 silica with water as mobile phase is not very high, and during the preconcentration the volume which can be percolated without breakthrough of the more polar herbicides is 10 ml.[14] For UV detection at 240–245 nm the detection limits reported in the literature are between 5 and 10 ng injected, which corresponds to a detection limit in water samples of about 1 μg/l (1 ppb). However, the said detection limit is obtained with spiked LC grade water and when real surface water samples are analysed, the detection limit is 10 times higher. Electrochemical detection allows a lower detection limit and a selective determination of 30 ppt of metoxuron and of 0.2–0.5 ppb of other phenylureas in surface waters.[17,18] Mass spectrometry coupled to LC and specific detection by derivatization reaction have also been used to improve detection limits.[20,21]

In the present study, we have attempted to increase the preconcentrated volume in order to use direct UV detection and to detect phenylureas at the 10–100 ppt level. The EEC limits for total herbicides, insecticides and fungicides are 0.5 ppb in drinking water and 0.1 ppb for individual species.[22] It is difficult to carry out accurate quantitative determinations when working right at the detection limit; in

fact, a detection limit of 10 ppt is necessary for a quantitative 0.1 ppb determination in natural samples. To reach the 10 ppt concentration level with an average detection limit of 5 ng injected, a sample volume of 500 ml and a complete recovery of each compound are necessary. As already mentioned, C18 silicas have been shown to be suitable sorbents for these compounds with a sample volume limited to 10 ml in an on-line procedure using precolumns of 1 × 0.2 cm ID. Increasing the sample volume without breakthrough of the analytes means increasing the size of the concentration column and therefore an off-line procedure because for an on-line procedure, the length of the precolumn cannot exceed 1 or 2 cm for coupling with a classical 15-cm-long analytical column.[23] An off-line procedure using C18 silica is described in the first part of this study and has been optimized in order to analyse nearly the whole concentrate. In the second part, an on-line procedure is carried out using another sorbent which shows higher retentions of phenylureas in water than those obtained with C18 silica sorbents. A previous study[24] has indicated a retention above 250 ml for linuron with a 1 × 0.2 cm precolumn packed with a divinylbenzene-styrene copolymer sorbent (PRP-1) and has also shown the advantages of coupling two precolumns in series, the first one packed with C18 silica acting as a filter to many interferents and the second packed with the copolymer PRP-1.[25] Knowing the amounts preconcentrated by each precolumn reinforces the identification of compounds. An electrochemical detector is used to further confirm the identity of the compounds.

EXPERIMENTAL

Apparatus

Off-line analysis was performed on a Waters HPLC liquid chromatograph equipped with a Lambdamax 481 variable-wavelength UV detector (Waters, Milford, MA, USA) and a Rheodyne valve with a 100-μl loop (Berkeley, CA, USA). On-line percolation of water was performed with a Milton Roy pump (LDC, Riviera Beach, FL, USA) and precolumn elutions and analyses were carried out with a Varian 5060 liquid chromatograph (Palo Alto, CA, USA) equipped with a variable-wavelength UV 200 spectrophotometer and a Coulochem model 5100 (ESA, Bedford, MA, USA) electrochemical detector. Precolumn and analytical column switching was done using two Rheodyne valves (Berkeley, CA, USA). Quantitative measurements of peak areas were provided by a CR3A integrator-computer from Shimadzu (Kyoto, Japan).

Stationary Phases and Columns

Off-line concentration columns were 10 cm × 4.6 mm ID and 50 cm × 10 mm ID stainless-steel columns home-packed with 0.9 and 22.7 g, respectively, of preparative-grade (55–105 μm) C18 silica from Waters. This silica was cleaned in a soxhlet apparatus with, successively, dichloromethane for 24 h and methanol during 24 h, and then dried at 40 °C overnight. The analytical column was a 25 cm × 4.6 mm ID stainless-steel column packed with 5 μm octadecyl silica Spherisorb ODS 2 from LDC (Staffordshire, UK). Using on-line technique,

samples were preconcentrated on 1 cm × 2.1 mm ID stainless-steel precolumns available from Chrompack (Middelburgh, the Netherlands) which were hand-packed with a thick slurry using a microspatula or with a thin slurry using a syringe. Stationary phases were 10 μm octadecyl silica RP-18 from Merck (Darmstadt, FRG) and the spherical 10 μm styrene-divinylbenzene copolymer PRP-1 from Hamilton (Reno, NV, USA). The analytical column was a 15 cm × 4.6 mm ID stainless-steel column prepacked with 5 μm octadecyl silica Spherisorb ODS 2 from LDC.

Chemicals

HPLC-grade acetonitrile was from Rathburn (Walkerburn, UK) and methanol from Prolabo (Paris, France). LC-quality water was prepared by purifying demineralized water in a milli-Q filtration system (Millipore, Bedford, MA, USA) or by evaporation in a quartz apparatus (Quartex, Paris, France). The phenylureas and anilines were supplied by Serva (Heidelberg, FRG). Other chemicals were from Prolabo, Merck or Fluka (Buchs, Switzerland).

Procedure

Stock solutions of selected solutes were prepared by weighing and dissolving them in methanol. LC-grade water samples were spiked with these solutions at the parts-per-billion level and adjusted to pH 3 with perchloric acid. Final standard solutions did not contain more than 0.5% methanol. River water samples were filtered over a glass fiber filter (Whatman GF/F).

Off-line methodology

Concentration of phenylureas was performed by percolating 100 ml of water samples (spiked LC-grade or river water) through the 10 × 0.46 cm ID column at a flow rate of 6 ml/min. After flushing with 10 ml of milli-Q water, the concentrated species were eluted with 6 ml of methanol at a flow rate of 1 ml/min. The extract was then evaporated to 500 μl using a speed vacuum type concentrator (Savant, Paris, France), then transferred to a 3 ml vial for a further concentration to 200 μl under nitrogen. 100 μl were then injected onto the analytical column. Recoveries were calculated by comparing peak areas after concentration with those obtained with direct injection of standard solutions.

On-line methodology

The experimental set-up is described in Ref. 24. A water sample was percolated through the two precolumns in series; the precolumns were flushed with 4 ml of 10^{-3} M perchloric acid. Each precolumn was then separately coupled to the analytical column by switching a valve and backflush-eluted by an acetonitrile gradient via the LC pump. Precolumns in series were cleaned with pure acetonitrile and regenerated with 25 ml of 10^{-3} M perchloric acid.

Table 1 Extrapolated capacity factors of phenylureas and calculated retention volumes in litres on (a) the 10 × 0.46 cm and (b) the 50 × 1 cm concentration column

Solute	*Capacity factor*	*Retention volume*	
		a	*b*
Metoxuron	265	0.1	2.5
Monolinuron	360	0.4	10
Metabromuron	731	0.9	22.5
Chlortoluron	800	1	25
Diuron	966	1.2	30
Buturon	1050	1.3	32
Linuron	2320	2.8	70

RESULTS AND DISCUSSION

Off-Line Methodology

Relation between the sample volume and the retention of phenylureas

Concentration of phenylureas by liquid-solid extraction is in fact a simple LC process with water as the mobile phase. Solutes will be trapped only if they are not eluted by the water itself. To prevent any breakthrough of analytes during the extraction procedure one must choose a sample volume lower than the breakthrough volume; it can be measured in the following manner: a solution of LC-grade water is spiked with a very small amount of solute (in order to avoid any overloading of the column capacity) and is fed through the concentration column. When the solute is retained, the liquid leaving the precolumn is free from it and has no UV absorbance; when breakthrough occurs a percolation front (or a breakthrough curve) is observed and the breakthrough volume is read at the beginning of the front. Under ideal Gaussian conditions the inflexion point of the curve corresponds to the retention volume of the solute in water. In practice, it is difficult to measure breakthrough volumes with a 10-cm-long concentration column because they are often higher than 100 ml, at least if conditions for concentration have been correctly chosen. That is the reason why breakthrough volumes are considered, in a first approximation, to be equal to the retention volumes. These can be extrapolated from capacity factors measured with water-methanol mobile phases thanks to the linear relationship between the logarithm of the capacity factor and the eluent water content.[26]

Experimental capacity factors of phenylureas were measured using an eluent containing between 20% and 60% water with the 10-cm-long concentration column and excellent linear relations were obtained. Extrapolated values of capacity factors in pure water and the corresponding retention volumes for the 10 cm and the 50 cm columns are reported in Table 1. Metoxuron has the lowest capacity factor and if this compound is to be determined, the sample volume has to be limited to 100 ml for a "theoretical" recovery of 100%. For a higher sample volume, breakthrough of this solute occurs and the preconcentration recovery is

Table 2 Mean experimental recoveries (%) and standard deviation (s.d.) from 100 ml concentrations of spiked milli-Q and spiked river water ($n=4$)

Solute	*Concentration (ppb)*	*Milli-Q water*		*River water*	
		Recovery	*s.d.*	*Recovery*	*s.d.*
Metoxuron	0.83	65	0.1	64	0.7
Monolinuron	0.51	66	1.4	75	1.4
Buturon	0.82	73	1.4	86	3.5
Chlortoluron	0.88	71	2.1	76	10.4
Diuron	1.09	70	1.1	68	0.1
Linuron	1.18	72	0.7	84	1.4

below 100%. With the 50-cm-long concentration column, sample volumes up to 2.5 litres can be handled without any breakthrough. Table 1 shows that the ratios of retention volumes between the two columns are approximately equal to the ratio of stationary phase volumes in the two columns (≈ 25).

Experimental recoveries

Even if the sample volume is chosen in order to have a 100% "theoretical" recovery, in an off-line procedure containing transfer and evaporation steps, it is difficult to avoid any loss; therefore it is important to measure experimental recoveries and their reproducibility. Recoveries were calculated by the ratio between peak areas obtained by injecting 100 μl of the concentrate from 100 ml of water spiked with a known amount of phenylureas and peak areas obtained by direct injection of 100 μl of a standard phenylureas solution. Table 2 shows that an average recovery of 65–70% is obtained for spiked LC-grade water samples. These recoveries are similar for natural riverwater samples spiked with phenylureas, owing to a dissolved organic carbon content of 9 mg per litre. In both cases reproducibility is satisfactory. The 30% loss is due to evaporation and transfer: concentrated analytes are eluted from the concentration column by 6 ml of methanol, evaporated to 500 μl, and then transferred to a suitable vial for a further evaporation to 200 μl This loss may be higher than that generally reported, but by evaporating down to 200 μl and injecting 100 μl, about 35% of the initial amount is analysed, and this value is high for an off-line procedure where frequently only a small aliquot is injected into the analytical system. One important result of this study is that reproducible recoveries were obtained when working under strictly reproducible conditions.

Detection limits

Detection limits have been studied by injecting 100 μl of diluted standard phenylureas solutions into the analytical column using UV detection at 247 nm. Detection limits are defined as the injected amounts giving a signal-to-noise ratio of 3. Experimental results are reported in Table 3. About 1.5 to 3 ng of the phenylureas can be detected. That is, when preconcentrating a 100 ml sample, one can detect at the 30–50 ppt level. In fact, this level can only be reached with spiked

Table 3 Detection limits (ng) of phenylureas (UV at 247 nm) obtained from injection of 100 μl of a diluted standard solution (a) and injection of 100 μl of the concentrate from a 100 ml sample of spiked river water (b)

Solute	*Detection limit (ng)*	
	a	*b*
Metoxuron	1.2	12
Monolinuron	1	7
Buturon	1.2	12
Chlortoluron	1.5	16
Diuron	1.4	10
Linuron	3	11

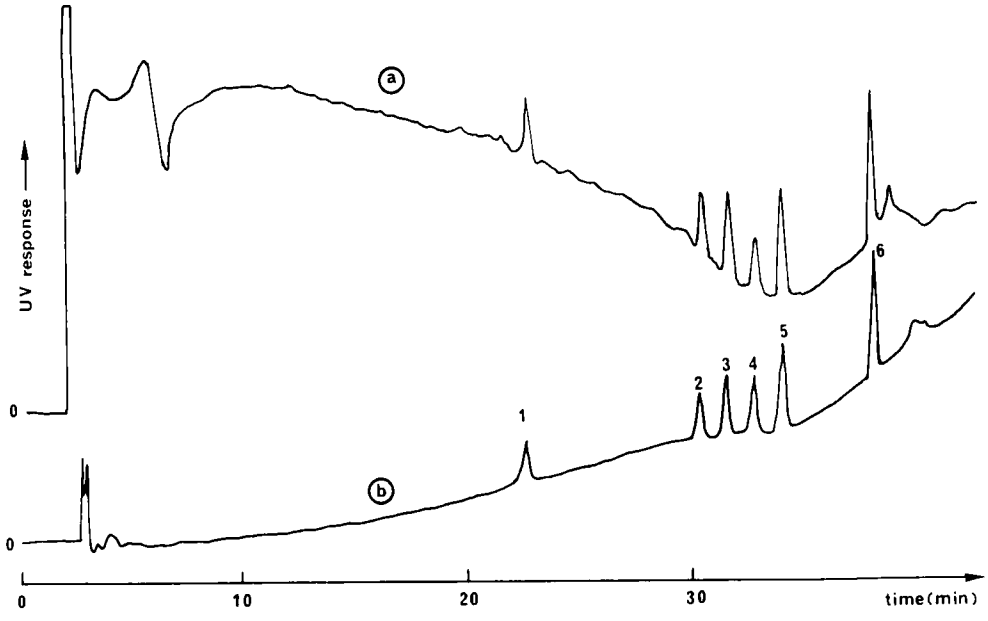

Figure 1 Analysis of the extract obtained from 100 ml of (a) a LC-grade water sample and (b) a river water sample spiked with the same amount of phenylureas. Solutes: 1 = metoxuron, 2 = monolinuron, 3 = buturon, 4 = chlortoluron, 5 = diuron, 6 = linuron. Column: (250 × 4.6 mm ID) packed with 5 μm Spherisorb ODS-2. Mobile phase: water–methanol gradient: 25% of methanol at time 0, 60% at 24 min, 64% at 30 min and 100% at 45 min. Volume injected: 100 μl; UV detection at 247 nm, sensitivity: 0.1 a.u. f.s.

LC-grade water solutions and the second column of Table 3 shows that detection limits are 10 times higher with a 100 ml sample of spiked river water; this is explained by the presence of many interferents also concentrated with the phenylureas (Figure 1). A lot of interfering compounds are found at the beginning

of the chromatogram, during the first 20 minutes; the water–methanol gradient had been selected in order that analytes have long retention times to avoid a strong influence of interferents. However, due to this precaution, it is impossible to detect a concentration lower than 300 ppt in river water from a 100 ml sample. The sample volume has to be increased, but it then becomes necessary to increase the concentration column dimensions as well, specially if metoxuron is to be determined. Results obtained from a 5 litre sample concentrated on the 50×1 cm ID column are presented in the last part of this study.

On-Line Methodology

In on-line methodology, a preconcentration step similar to the above is performed in the so-called precolumn. The basic difference with the previous methodology consists in the elution step of the concentrated organics; after the sample percolation, in on-line techniques, the precolumn is coupled to a reversed-phase analytical column via switching valves. The concentrated analytes are then directly transferred to the analytical column and their desorption is performed by the water-acetonitrile gradient also used for their analysis. This technique has many advantages, especially when applied to trace analysis: no contamination risk occurs since there is no transfer, evaporation or manual handling of the concentrate; the whole concentrated amount is analysed which allows a lower sample volume. Selectivity can be increased during the preconcentration step by coupling several precolumns packed with different specific sorbents in series. Nielen *et al.*[27] applied on-column technology to the determination of many different pollutants in waste water; combination of three precolumns gives satisfactory group separation prior to chromatographic analysis: a C18 silica sorbent, a styrene-divinylbenzene copolymer and a cation exchanger trap the non-polar, the moderately polar and the more polar solutes, respectively. On-column technology requires the dimension of the precolumn to be adapted to the dimension of the analytical column in order to avoid band broadening of analytes during their transfer from the precolumn to the analytical column.[23] For a classical analytical column of 15×0.46 cm ID, the precolumn dimension should not exceed 1×0.46 cm ID. We have seen earlier that capacity factors of phenylureas are relatively low and with a 1-cm-long precolumn breakthrough will rapidly occur, thus limiting the sample volume. A previous study[24] has shown that retention properties of the copolymer-based sorbent PRP-1 are higher than those of silica sorbents for moderately polar aromatic solutes. A single precolumn packed with PRP-1 could be used alone to concentrate phenylureas, but as shown by the off-line procedure there are many interferents in natural waters. For this reason, two precolumns are coupled in series for the preconcentration step. The first one, packed with a C18 sorbent, is intended to trap the non-polar interferents, whereas phenylureas will be trapped by the second one packed with PRP-1.

On-line method with two precolumns in series

The set-up is described in Ref. 24. When two precolumns are used, sorption can be appreciated by determining breakthrough volumes on each precolumn. Retention

volumes of very apolar solutes on the C18 precolumn are high and these solutes are recovered only on the first C18 precolumn; polar solutes not retained by the C18 sorbent but by the PRP-1 sorbent are recovered only on the second precolumn. These two types of solutes are selectively retained, but there are many moderately polar solutes which are slightly retained by the C18 precolumn and to a greater extent by the PRP-1 precolumn. These solutes are recovered on both precolumns and the respectively preconcentrated amounts depend on the sample volume as shown in Figure 2. When the sample volume percolated through the two precolumns in series is 50 ml, only two compounds are recovered from the second one and it can be concluded that the breakthrough volumes of these solutes are lower than 50 ml (Figure 2a); when the sample volume is 500 ml, breakthrough occurs for all six phenylureas on the C18 precolumn; they are, however, well retained by the PRP-1 precolumn. Solute concentrations are 20 ppb in the 50 ml sample and 2 ppb in the 500 ml sample. The chromatograms show clearly that it is necessary to increase the sample volume up to 500 ml for detection at the low ppb level and that because of breakthrough volumes close to 50 ml on the C18 precolumn, the amounts preconcentrated on it are low. But it can be also observed in Figure 2b that the amounts preconcentrated on PRP-1 are much higher than those on C18, indicating high breakthrough volumes on this precolumn. Another important result is that, depending on the sample volume, there is a fixed ratio between the amounts preconcentrated on both precolumns. This provides supplementary information for identification of solutes.

Amounts preconcentrated and recoveries on each precolumn

A direct experimental method of recovery measurement has been reported in Ref. 24; it consists of measuring peak areas obtained on analysis of 10 ml of spiked LC-grade water. One has only to be sure that no breakthrough occurs from the C18 precolumn with a 10 ml sample volume. Then the sample volume is increased but the solute concentration is decreased in order to have a constant amount in each sample. For each percolation, peak areas are measured on the chromatograms corresponding to the elution of each precolumn as for those represented in Figure 2. Dividing these values by the peak area values obtained for the first 10 ml percolation represents an experimental measurement of recovery which has the advantage of taking into account the transfer and the desorption processes. Breakthrough value of a solute on the C18 precolumn starts when its recovery decreases on this precolumn. If no breakthrough occurs from the PRP-1 precolumn the sum of recoveries from C18 and PRP-1 is 100%, and each recovery represents the part of solute preconcentrated on each precolumn. Breakthrough on the PRP-1 column starts when the sum of the recoveries begins to fall below 100%. Table 4 represents experimental recoveries calculated by this method. When the sample volume increases, the recovery decreases on the C18 precolumn and increases on PRP-1. With a sample volume up to 500 ml the sum of the recoveries measured on both precolumns is still 100%, indicating that the breakthrough volume of each phenylurea is higher than 500 ml on the PRP-1 sorbent. Table 5 reports the estimated breakthrough volumes obtained with the 1×0.21 cm ID precolumns packed with C18 silica and PRP-1, respectively. The copolymer-based

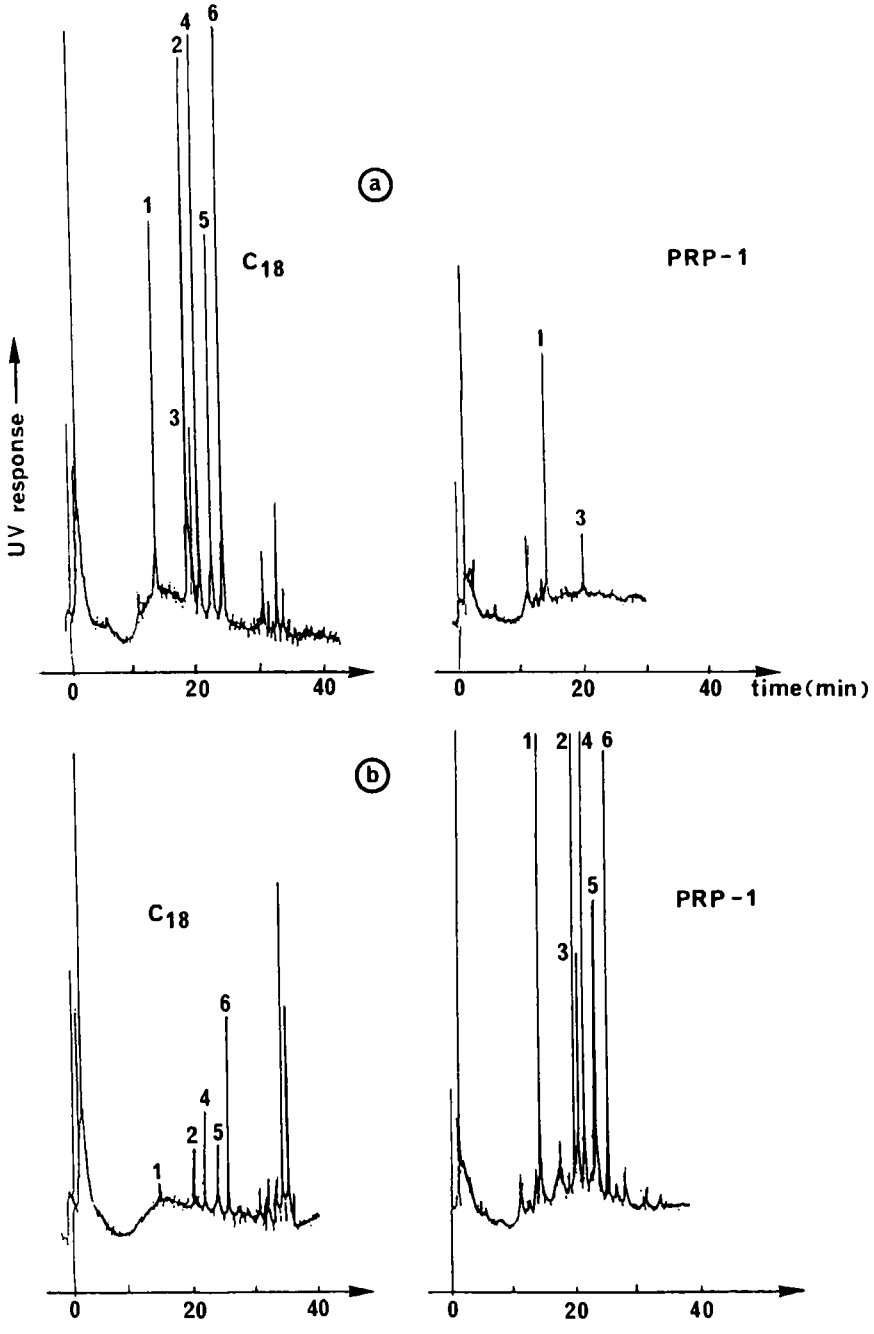

Figure 2 On-line preconcentration of a standard solution of phenylureas: (a) preconcentration of 50 ml spiked at a concentration of 20 ppb for each compound; (b) preconcentration of 500 ml spiked at a concentration of 2 ppb for each compound. Solutes numbered as in Figure 1; preconcentration through two precolumns in series packed with 10 μm RP-18 silica and with 10 μm PRP-1 copolymer at a flow rate of 3 ml/min; elution of each precolumn to the 150 × 4.6 mm ID analytical column packed with 5 μm Spherisorb ODS-2, at a flow rate of 1.5 ml/min. Mobile phase: acetonitrile gradient with a solution of potassium acetate/acetic acid 0.1 M at pH 6; gradient: 15% of acetonitrile from 0 to 5 min, 20% at 8 min, 50% at 25 min and 80% at 30 min; UV detection at 248 nm, sensitivity: 0.01 a.u. f.s.

Table 4 Dependence of recoveries (%) obtained on (a) a C18 and (b) a PRP-1 precolumn on percolated sample volume

Solute		*Recovery (%) for sample volume (ml)*						
		10	*25*	*50*	*75*	*100*	*200*	*500*
Metoxuron	a	100	96	60	37	30	15	4
	b	0	4	40	64	70	84	96
Monolinuron	a	100	100	100	78	65	33	13
	b	0	0	0	22	35	67	86
Buturon	a	100	97	68	42	35	18	4
	b	0	3	32	58	65	83	96
Chlortoluron	a	100	100	100	90	79	40	15
	b	0	0	0	10	21	60	85
Diuron	a	100	100	100	100	97	56	25
	b	0	0	0	0	3	44	75

Table 5 Estimated breakthrough volumes (ml) on (a) C18 and on (b) PRP-1 precolumns

Solute	*Breakthrough volumes (ml)*	
	C18	*PRP-1*
Metoxuron	20	> 500
Monolinuron	60	> 500
Buturon	20	> 500
Chlortoluron	70	> 500
Diuron	95	> 500

is an excellent sorbent for these compounds compared to alkyl-bonded silica. Taking the detection limit of 5 ng injected into account, one can detect phenylureas in LC-grade water samples at a concentration of 10 ppt.

Application to Determination of Phenylureas in River Water

A comparison between the off-line and on-line procedures has been made by determining phenylureas in water of the river Yerres, running through an agricultural area (near Paris). This water was sampled in March 1988 just after several days of rain.

Off-line procedure

Figure 3 represents the chromatogram for the analysis of an extract obtained by concentrating 100 ml on the 10 cm-long-column. Many interfering compounds are seen not to be resolved in the large peak during the first 8 min of the gradient and two resolved peaks appear near 30 min. The first of them has the same retention time as chlortoluron. Figure 4a represents the analysis of an extract of another, 5 litre, sample of the river concentrated on the 50-cm-long column; in Figure 4b the river water sample had been spiked with the five phenylureas at an average

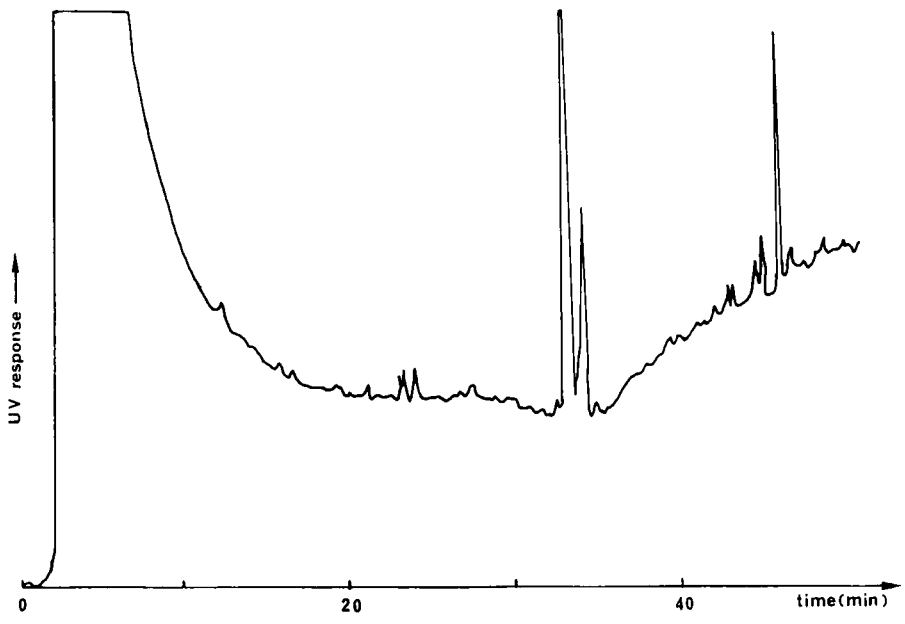

Figure 3 Analysis of an extract obtained from preconcentration of 100 ml of a river Yerres sample. UV detection at 247 nm, sensitivity: 0.05 a.u. f.s. Other conditions as in Figure 1.

concentration of 0.2 ppb. The total extract after evaporation was 390 μl and the amount injected 20 μl, which was the highest volume that could be injected because of the numerous interferents. With a 20 μl injection, a 22-min-long peak appears and when injecting more than 40 μl, this peak is observed throughout the gradient. Comparing Figures 3 and 4a clearly shows that increasing the sample volume and the dimensions of the precolumn does not improve the detectability of analytes because many other compounds are also concentrated and interfere. Figure 4b indicates also that spiking the samples does not allow reliable conclusions to be drawn as to the presence of phenylureas except for the absence of linuron.

On-line procedure

Figure 5 represents the UV chromatograms obtained by eluting C18 and PRP-1 precolumns after percolation of 100 ml (Figure 5a) and 450 ml (Figure 5b) of the same river water sample (corresponding to the sample analysed off-line in Figure 3) through the two precolumns in series as described above. For the 100 ml sample, four peaks (A, B, C and E) show up in the chromatogram from the C18 precolumn and three peaks in that of the PRP-1 precolumn (B, C and D). Peaks A and E are recovered from the C18 precolumn only, D from PRP-1 only and B and C from both, but with a higher amount from the C18 precolumn. This indicates breakthrough values just below 100 ml on the C18 precolumn for these two solutes (the two peaks near 10 min also occur in the blank from the chromatographic

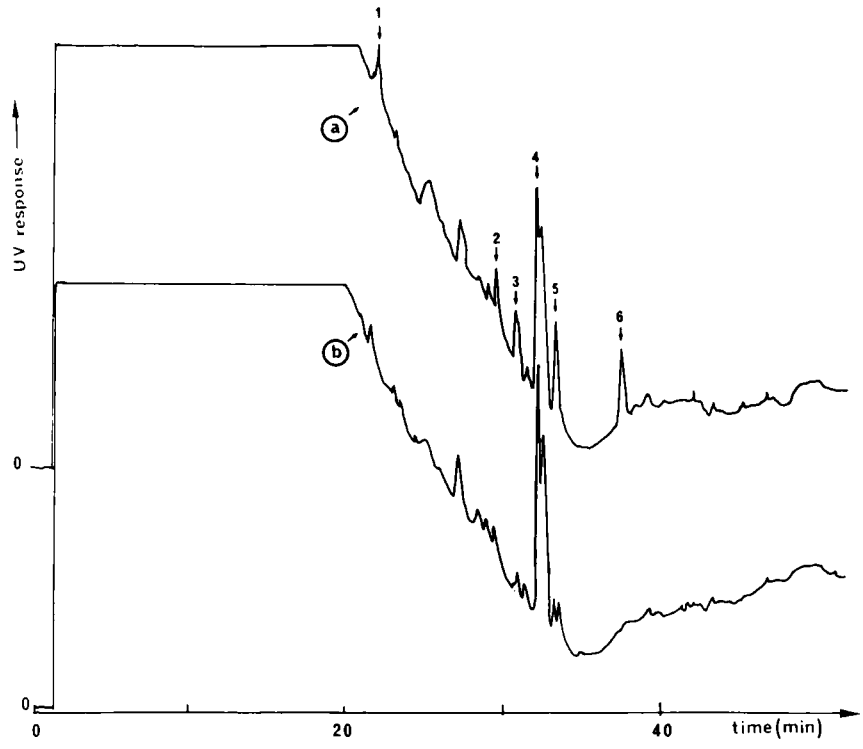

Figure 4 Analysis of an extract obtained from preconcentrating 5 l of river Yerres sample, (a) non-spiked and (b) spiked with phenylureas at concentration of: 1 = metoxuron (0.17 ppb), 2 = monolinuron (0.10 ppb), 3 = buturon (0.17 ppb), 4 = chlortoluron (0.18 ppb), 5 = diuron (0.22 ppb), 6 = linuron (0.24 ppb). The total extract was evaporated to 390 μl; the chromatograms represent an injection of 20 μl. Other conditions as in Figure 1.

system). The five peaks are also found with the 450 ml sample (Figure 5b) but, of course, with different ratios. The same four peaks are recovered from the C18 precolumn, and peaks A, B and C have about the same heights as those obtained with 100 ml, which confirms breakthrough values below 100 ml on the C18 precolumn. Peaks A, B and C are much higher on the PRP-1 precolumn. Solute E has increased in the C18 fingerprint and is not found in the PRP-1 fingerprint; its breakthrough value obviously is above 450 ml which indicates a very apolar solute. That is, one can collect information about the polarity of solutes from breakthrough volumes on two known sorbents.

Another important point is the elimination of interfering compounds which are mainly trapped by the C18 precolumn, especially when the sample volume is 450 ml, as shown by the large amount of non-resolved peaks during the first 40 min: C18 acts as a filter for many apolar compounds and therefore renders the reading of the PRP-1 fingerprint more efficient.

A first identification of solutes is made by their retention times. Many solutes and about fifteen of the most commonly used herbicides (phenylureas and *s*-

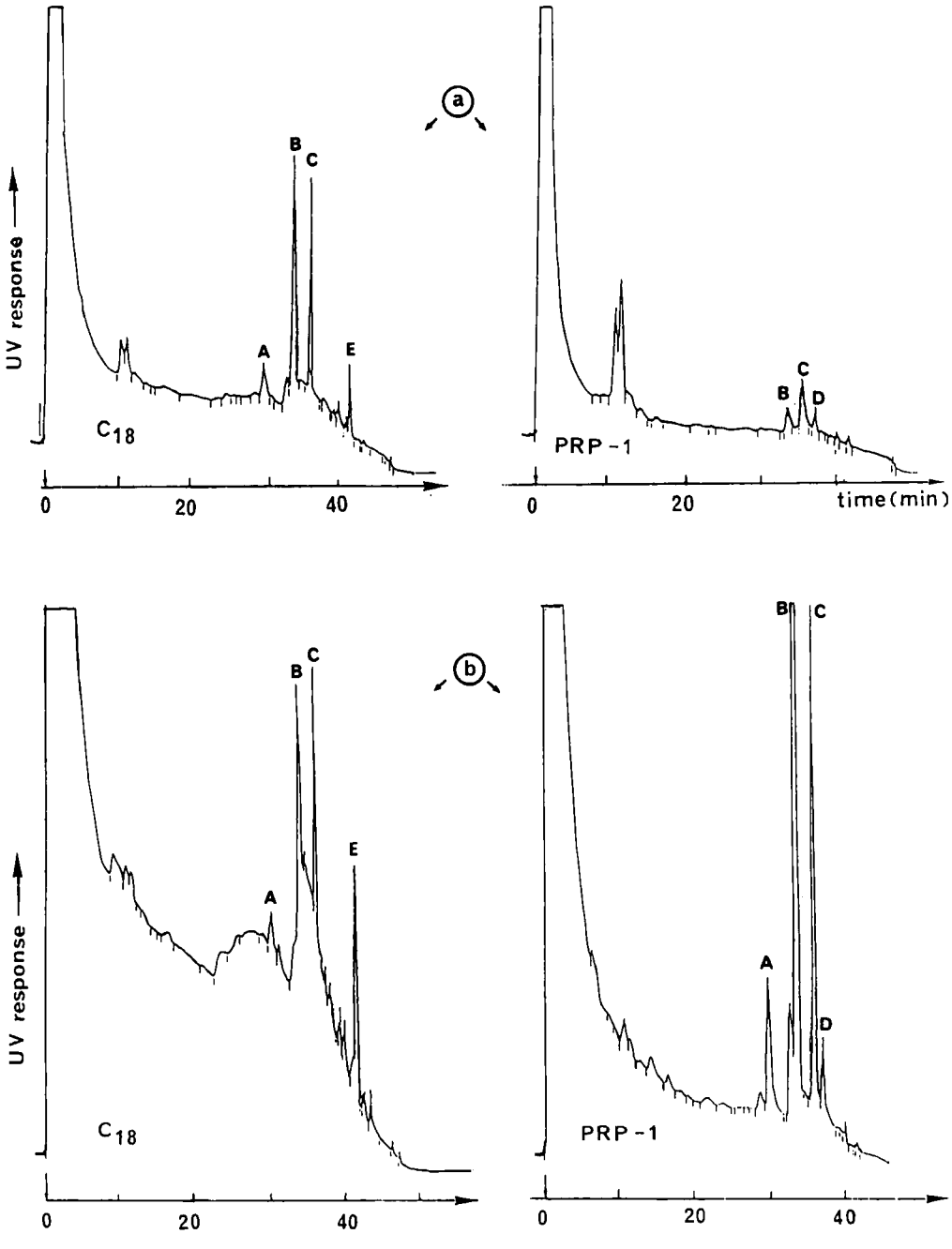

Figure 5 On-line preconcentration of (a) 100 ml and (b) 450 ml of a river Yerres sample (same sample as in Figure 3). UV detection at 244 nm, sensitivity: 0.1 a.u. f.s. Same conditions as in Figure 2 except the gradient profile: 15% of acetonitrile from 0 to 5 min, 20% at 20 min, 30% at 30 min and 100% at 45 min.

Table 6 Retention times, t_r of unknown peaks in Figure 5 and of selected phenylureas and atrazines having closely similar retention times

Peak	t_r *(min)*	*Solutes*	t_r *(min)*
		Atrazine	29.8
A	30 ±0.2	Monolinuron	30.1
		Buturon	30.2
B	33.8 ± 0.2	Chlortoluron	34
C	36.1 ± 0.2	Diuron	35.9
D	37.3 ± 0.2	Linuron	37.4
E	41.6 ± 0.2	Butylbenzylphthalate	41.4

Table 7 Comparison between experimental amounts of solute (%) preconcentrated on PRP-1 measured for river water samples (see Figure 5) and for LC-grade water samples spiked with the selected herbicides (see Tables 4 and 6)

Peak	*River water*		*Selected herbicides*	*LC-grade water*	
	100 ml	*450 ml*		*100 ml*	*450 ml*
			Monolinuron	35	83
A	0	62	Buturon	65	90
			Atrazine	4	64
B	7	78	Chlortoluron	21	82
C	23	70	Diuron	3	72
D	100	–	Linuron	0	–
E	0	0	Butylbenzylphthalate	0	3

triazines) have been injected using the same analytical gradient as in Figure 5. Table 6 reports the retention times of peaks A to E and the retention times of some solutes which could correspond to these peaks since they have closely similar retention times. Another means for identification of the solutes is provided by the amount preconcentrated on each precolumn. For each fingerprint represented in Figure 5 the percentage preconcentrated on PRP-1 has been calculated by dividing peak areas from PRP-1 by the sum of the peak areas from the PRP-1 and C18 precolumns. For the two volumes preconcentrated, the experimental values are reported in Table 7, while similar experimental values obtained with spiked LC-grade water samples are also reported. A comparison between these values indicates: (i) monolinuron, buturon and linuron do not correspond with peaks A and D, (ii) atrazine can correspond with peak A and butylbenzylphthalate with E, (iii) chlortoluron may correspond with peak B and diuron with C, even if the excellent agreement for 450 ml is not confirmed for 100 ml. Taking the interferents and the unstable baselines of the chromatograms into account, accurate results cannot be expected for the amounts preconcentrated on both precolumns.

It is clear that identification is not the easiest step (in the absence of expensive mass spectrometry coupling). In most papers, this problem is avoided, the application generally consisting of a study of a sample spiked with the sought compounds which are of course identified by their retention times. In our example

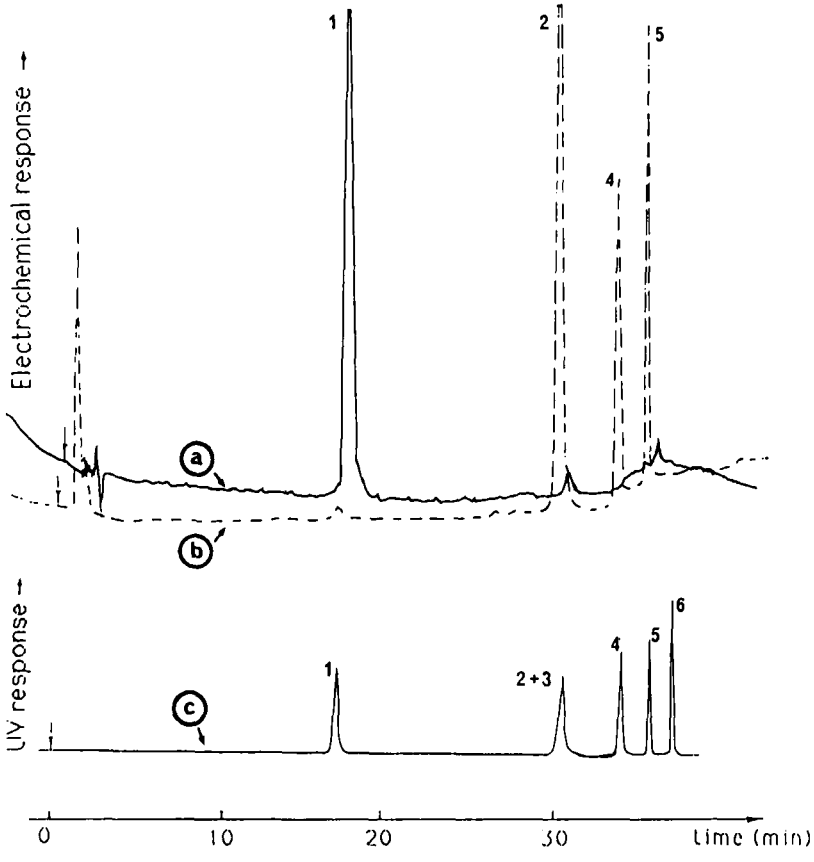

Figure 6 Comparison between electrochemical detection and UV detection: (a) electrochemical detection at the first electrode at 0.78 V (vs. Ag/AgCl), sensitivity 3 μA (f.s.); (b) electrochemical detection at the second electrode at 0.90 V (vs. Ag/AgCl), sensitivity 1.5 μA (f.s.); (c) UV detection at 244 nm, sensitivity: 0.01 u.a. f.s. Solutes numbered as in Figure 1; other conditions as in Figure 5.

of a non-spiked sample, the supplementary information, i.e. the ratio of the amounts preconcentrated on each precolumn, shows that identification by retention times is not sufficient in case of such a complex sample as river water. This is why another detection mode has to be carried out. For phenylureas, electrochemical detection can be a third criterion for identification as shown in Figure 6, where the UV signal at 244 nm and the electrochemical response at two different oxidation potentials are shown. The electrochemical cell contains two analysis electrodes in series; the first electrode reacts with almost all electroactive compounds which are therefore absent at the second electrode working in the amperometric mode. Figure 6 shows that at the first electrode (0.78 V vs. Ag/AgCl), metoxuron is the only phenylurea detected, whereas at the second electrode (0.90 V vs. Ag/AgCl), monolinuron, chlortoluron and diuron are detected. Buturon and linuron have oxidation potentials above 0.90 V and are only detectable by

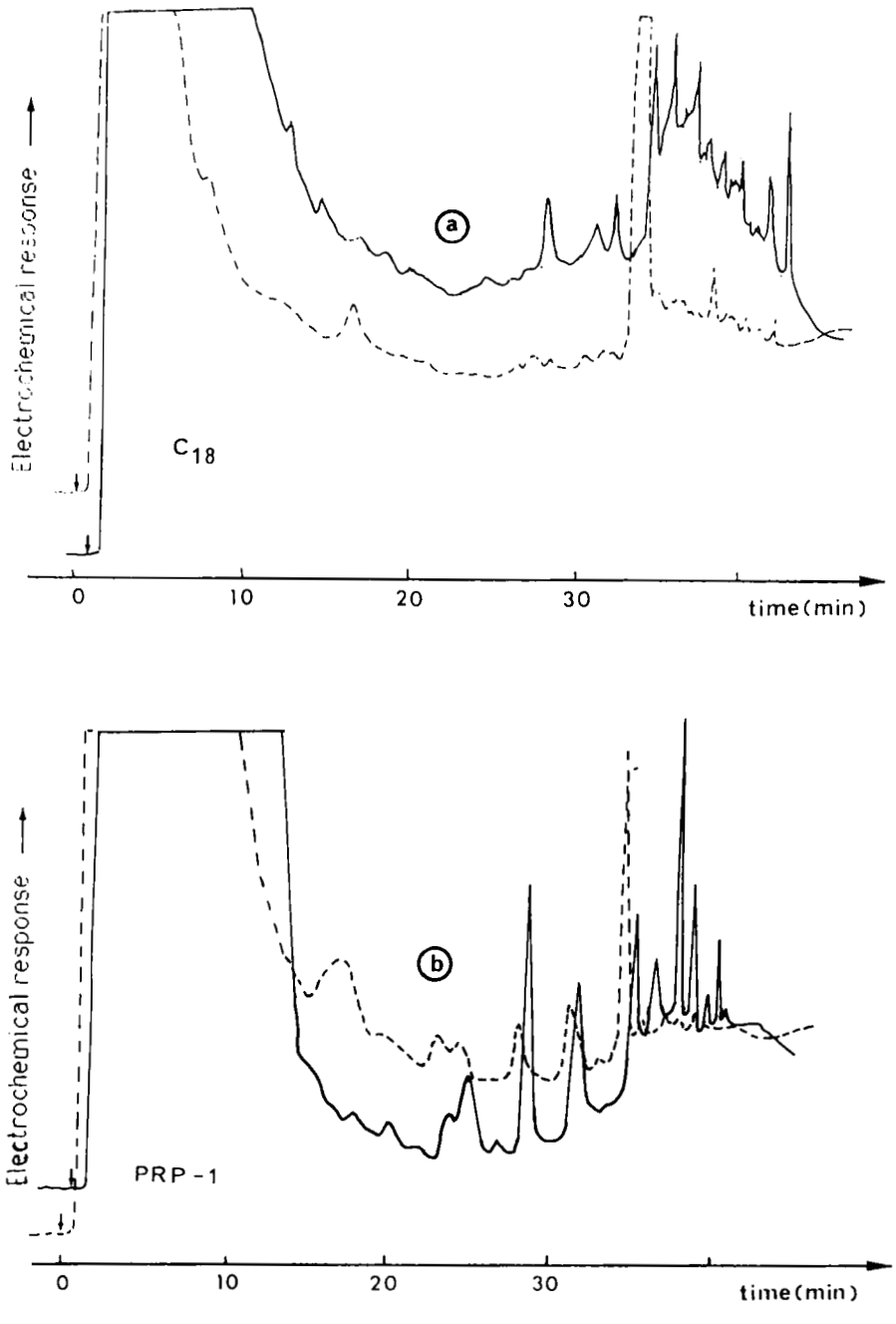

Figure 7 Electrochemical detection of the 100 ml river sample of Figure 5; (a) analysis of the RP-18 precolumn content, (b) analysis of the PRP-1 precolumn content. Solid line: detection at the first electrode at 0.78 V (vs. Ag/AgCl), sensitivity 3 μA (f.s.); Dotted line: detection at the second electrode at 0.90 V (vs. Ag/AgCl). sensitivity 1.5 μA (f.s.).

UV. A ratio between the intensity of the UV signal and the electrochemical response for the same amount of analyte injected can be calculated from these chromatograms as a supplementary identification tool. Figure 7 shows the electrochemical chromatograms for the 100 ml river water sample corresponding to the UV chromatogram in Figure 5a. Obviously, peak C is not due to diuron because no electrochemical response is obtained at the second electrode; peak A can well be due to atrazine which is not at all oxidizable, and peak B to chlortoluron, but certainly with an interfering peak on the PRP-1 precolumn. On the C18 fingerprint, peak B corresponds to chlortoluron because the ratio between the amount oxidized at the two potentials corresponds to the pure chlortoluron ratio, whereas, on the PRP-1 fingerprint, the observed ratio indicates the presence of an interfering compound. Another advantage of electrochemical detection is that it discriminates between phenylureas and their degradation products, the anilines: since the electrochemical response of anilines is much higher than that of parent phenylureas there is a greater difference between the UV and the electrochemical responses. In the present study the interfering peak with chlortoluron cannot be due to the corresponding aniline because these two products have different retention times. The presence of atrazine and butylbenzylphthalate have been confirmed by mass spectrometry using the off-line preconcentration procedure; the effluent from the analysis shown in Figure 3 has been fractionated, each fraction evaporated and then injected in a mass spectrometer. That is, out of the six herbicides identified by their retention times, two of them are identified by closely examining the ratios preconcentrated on both precolumns for two different volumes and with two complementary detection modes. Their concentration is estimated at about 2 μg/l.

CONCLUSION

The most important result of this study is that copolymer-based PRP-1 is an excellent sorbent for liquid–solid extraction of phenylureas and other polar herbicides such as atrazine from water. Thus efficient on-line concentration analyses can be easily performed by using two precolumns in series, the first one acting as a filter for many interferents. The off-line procedure with a C18 silica column cannot be improved even by increasing the concentration column size because of these interfering compounds, but it can be modified according to the on-line procedure by coupling two cartridges, the first one being packed with C18 silica and the second with a highly pure styrene-divinylbenzene copolymer. The PRP-1 used in this study is not commercially available in larger particle size for disposable cartridges.

Acknowledgements

We thank INSU-CNRS, IFREMER, Ministère de l'Environnement, Compagnie Générale des Eaux and Syndicat des Eaux de l'Ile-de-France for financial support.

References

1. A. de Kok, Thesis, GC and LC determination of polyhalogenated aromatics and phenylurea herbicides in environmental samples, Free University of Amsterdam, De Boelelaan, 1983.
2. U. A. Th. Brinkman, A. de Kok and R. B. Geerdink, *J. Chromatogr.* **283,** 113 (1983).
3. A. de Kok, M. van Opstal, T. de Jong, B. Hoogcarspel, R. B. Geerdink, R. W. Frei and U. A. Th. Brinkman, *Int. J. Environ. Anal. Chem.* **18,** 101 (1984).
4. D. Barcelo, *Chromatographia* **25,** 928 (1988).
5. J. F. Lawrence and D. Turton, *J. Chromatogr.* **159,** 207 (1978).
6. J. de Jong, H. J. van Nieuwkerk, A. H. M. Scholten, U. A. Th. Brinkman and R. W. Frei, *J. Chromatogr.* **166,** 233 (1978).
7. A. de Kok, M. Roorda, R. W. Frei and U. A. Th. Brinkman, *Chromatographia* **14,** 579 (1981).
8. A. de Kok, Y. J. Vos, C. van Garderen, J. de Jong, M. van Opstal, R. W. Frei, R. B. Geerdink and U. A. Th. Brinkman, *J. Chromatogr.* **288,** 71 (1984).
9. R. W. Frei, G. J. de Jong and U. A. Th. Brinkman, *Analusis* **15,** 59 (1987).
10. C. E. Goewie and E. A. Hogendoorn, *J. Chromatogr.* **410,** 211 (1987).
11. A. J. Cessna, *J. Liq. Chromatogr.* **11,** 725 (1988).
12. C. E. Goewie and E. A. Hogendoorn, *Food Additives and Contaminants* **2,** 217 (1985).
13. G. Kulshrestha and R. Khazanchi, *J. Chromatogr.* **318,** 144 (1985).
14. C. E. Goewie, P. Kwakman, R. W. Frei, U. A. Th. Brinkman, W. Maasfield, T. Seshadri and A. Kettrup, *J. Chromatogr.* **284,** 73 (1984).
15. P. Jandera and M. Spacek, *J. Chromatogr.* **366,** 107 (1986).
16. P. Jandera, J. Churacek, P. Butzke and M. Smrz, *J. Chromatogr.* **387,** 155 (1987).
17. M. W. F. Nielen, G. Koomen, R. W. Frei and U. A. Th. Brinkman, *J. Liq. Chromatogr.* **8,** 315 (1985).
18. Q. G. von Nehring, J. W. Hightower and J. L. Anderson, *Anal. Chem.* **58,** 2777 (1986).
19. T. A. Bellar and W. L. Budde, *Anal. Chem.* **60,** 2076 (1988).
20. F. A. Maris, R. B. Geerdink, R. W. Frei and U. A. Th. Brinkman, *J. Chromatogr.* **323,** 113 (1985).
21. R. G. Luchtefeld, *J. Chromatogr. Sci.* **23,** 516 (1985).
22. EEC drinking water guideline 80/778/EEC, *EEC N. L.* **229,** 11 (1980).
23. C. E. Goewie, M. W. F. Nielen, R. W. Frei and U. A. Th. Brinkman, *J. Chromatogr.* **301,** 325 (1984).
24. P. Subra, M.-C. Hennion, R. Rosset and R. W. Frei, *J. Chromatogr.* **456,** 121 (1988).
25. P. Subra, M.-C. Hennion, R. Rosset and R. W. Frei, *Int. J. Environ. Anal. Chem.* **37,** 45 (1989).
26. C. E. Werkhoven-Goewie, U. A. Th. Brinkman and R. W. Frei, *Anal. Chem.* **53,** 2072 (1981).
27. M. W. F. Nielen, U. A. Th. Brinkman and R. W. Frei, *Anal. Chem.* **57,** 806 (1985).