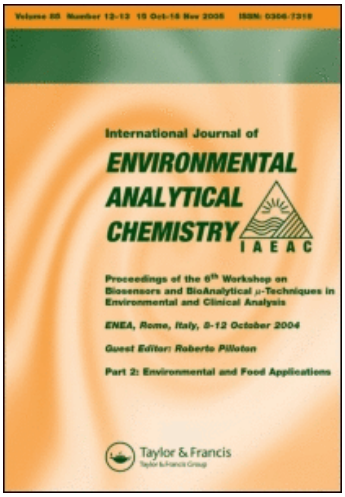

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P. Subra[a]; M. -C. Hennion[a]; R. Rosset[a]; R. W. Frei[b]
[a] Laboratoire de Chimie Analytique de l'Ecole Supérieure de Physique et Chimie de Paris, Paris, France
[b] Department of Analytical Chemistry, Free University, Amsterdam, The Netherlands

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APPLICATIONS OF ON-LINE PRECOLUMN TECHNOLOGY TO WATER QUALITY CONTROL

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

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

and

R. W. FREI

Department of Analytical Chemistry, Free University, De Boelalaan, 1081 HV, Amsterdam, The Netherlands

On-line precolumn technology is applied to the analysis of organics in water samples with relatively low organic contamination (e.g. drinking water or certain surface waters). Two precolumns in series, one packed with a bonded C_{18} silica and the other with the polymer-based PRP-1 are used for the organic concentration and it is shown that a range of organics of medium to low polarity can thus be determined from sample volumes up to 500 ml. With such a volume and depending on the breakthrough volume values measured with the two adsorbents, very apolar compounds are extracted by the C_{18} precolumn alone whereas the moderately and relatively polar compounds are recovered from both C_{18} and PRP-1 precolumns. Hence, the ratio of amounts preconcentrated on C_{18} and on PRP-1 precolumns and the variations of this ratio with the sample volume are useful information for the identification of solutes. In complex mixtures, simple identification of a solute by its retention time during the analytical gradient is not sufficient and needs confirmation. In addition, three detection modes (UV absorbance, fluorescence and electrochemistry) are carried out after the C_{18} analytical column and comparisons of the chromatograms from each detector can also confirm a possible identification. Applications to the research of moderately polar pollutants at the ppb level in drinking water and relatively polar herbicides in river water are presented.

KEY WORDS: Drinking water, surface water, water quality control, on-line precolumn technology organics, breakthrough volumes.

INTRODUCTION

The low concentrations of organics in relatively pure water (e.g. natural compounds or pollutants in drinking water) necessitate the development of analytical techniques sensitive at the sub-ppb level. At this level a concentration step is necessary before the analysis proper and sample concentration based on liquid-

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solid sorption techniques has been shown to be a good alternative to liquid-liquid extractions.

Off-line concentration techniques are widely used for the research of pollutants in rivers, industrial or waste waters. Trace components are concentrated on a convenient sorbent packed in a small column or cartridge and then eluted by a small volume of suitable solvent. Non selective reversed phase materials such as the n-alkyl silicas are widely used and many examples dealing with the research of relatively apolar compounds (e.g. hydrocarbons, phthalates, pentachlorophenol, apolar herbicides...) are reported in the literature. In these off-line concentration-analyses, there are manual handling steps of the concentrated samples as evaporation and transfer so that loss and contamination risks can occur. Many of these drawbacks can be avoided using on-line enrichment-analysis on precolumns.[1-10] Trace components are trapped with a convenient sorbent packed in a precolumn coupled to an analytical column via switching valves and the compounds adsorbed are then directly eluted from the precolumn to the analytical column by a suitable mobile phase. One can then expect more accurate results in trace analysis because there is no sample manipulation between preconcentration and analysis and because also the totality of the organics concentrated is transferred and analysed. Selectivity towards specific compounds can be provided by using more selective adsorbents than C_{18} silicas such as ion exchangers[2,11-13] or metal loaded phases.[14-17] When the trace compounds are very different in size and polarity, selectivity has to be researched during the sample handling step by coupling several precolumns in series. Nielen *et al.*[12] applied on column technology to the determination of many different pollutants in waste waters; combination of three precolumns gives satisfactory group separation prior to chromatographic analysis: a C_{18} silica sorbent traps the non polar compounds, a styrene divinylbenzene copolymer the moderately polar ones and a cation exchanger the more polar solutes. Each precolumn is separately eluted and analysed. Analysis of organics of different polarity can be performed from a sample volume of waste water from 10 ml to 30 ml.

In this study, this analytical approach is applied to drinking water by increasing the sample volume to 500 ml in order to obtain informative fingerprints. The cation exchanger cannot be used because it is not possible to percolate through it a sample volume higher than 30 ml owing to the impossibility of a sufficient elimation of the inorganic cations by precipitation and complexation reactions.[12] When two precolumns are used, it is possible to know which solutes are extracted by the precolumns by determining their breakthrough volumes; a previous study[18] has shown that some solutes are extracted by both precolumns depending on sample volume and on breakthrough values. For each sample volume the ratio between the amount preconcentrated on C_{18} and on PRP-1 precolumn is known and this ratio varies with the sample volume and we show here that it is a useful information for identification of solutes. Solutes are very often identified by their retention times over the analytical gradient and this is the weakest point of many publications dealing with pollutant research in such complex mixtures as environmental samples. In a 30 minute long gradient many compounds may have close retention times and confirmations are necessary. In addition to the ratio of

amounts preconcentrated on both precolumns, the variations of this ratio with the sample volume, the comparison between the responses of three detectors coupled to the analytical columns (UV absorbance, fluorescence and electrochemistry) can also assist a possible identification.

Applications to the research of moderately and relatively polar pollutants at the ppb level in drinking water and surface water are presented.

EXPERIMENTAL

Apparatus

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, a Polychrom 9060 diode arrray detector (Varian), a fluorimetric detector from Kratos (Ramsey, NJ, USA) or a LS-4 from Perkin Elmer (Norwalk, CT, USA) and an electrochemical detector, Coulochem model 5100 (ESA, Bedford, MA, USA). Precolumn and analytical column switching was performed with two Rheodyne valves (Berkeley, CA, USA). Quantitative measurements of peak areas were made with a CR3A integrator-computer from Shimadzu (Kyoto, Japan).

Stationary Phases and Columns

Water samples were preconcentrated on 1 cm × 2.1 mm ID stainless-steel precolumns available from Chrompack (Middelburgh, the Nederlands) which were hand-packed with a thick slurry using a microspatula or with a thin slurry using a syringe. Stationary phases were the 10 μm octadecyl silica RP 18 from Merck (Darmstadt, FRG) and the spherical 10 μm column was a 15 cm × 4.6 mm ID stainless-steel column prepacked with the 5 μm octadecyl silica Spherisorb ODS 2 from Prolabo (Paris, France).

Chemicals

HPLC-grade acetonitrile was from Rathburn (Walkerburn, UK) and methanol from Prolabo (Paris, France). Water was deionised and evaporated in a quartz apparatus from Quartex (Paris, France). The various solutes were supplied by 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.

Breakthrough curves of selected analytes were recorded as follows: the standard solution of a solute at ppb level was first directly coupled to the detector to measure the initial absorbance of the studied solute and then coupled to the precolumn (which has been conditioned before) at a flow rate of 2.5 mL min^{-1}.

The experimental set up is described in Ref. 18. Water sample was introduced on 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 HPLC pump. Precolumns in series were cleaned with pure acetonitrile and regenerated with 25 mL of 10^{-3} M perchloric acid.

Water samples were filtered over a 0.4 membrane before preconcentration.

RESULTS AND DISCUSSION

On-column Technology with Two Precolumns

Breakthrough volume of solutes: During the preconcentration step, water samples are percolated through the two precolumns in series, the first one packed with C_{18} bonded silica and the second one with the copolymer-based PRP-1 (these precolumns are now denoted C18 and PRP1 respectively). To know which solutes are extracted by the precolumns, it is useful to determine the breakthrough volumes on each precolumn by recording the breakthrough curve of a solution of L-C grade water spiked with ppb of solute. Two factors are responsible for breakthrough: one is the retention itself because water is the mobile phase in the chromatographic preconcentration process and the other one is the overloading of the precolumn. We have previously measured the capacities of PRP-1 and C18 adsorbents and shown that owing to the low concentration of organics typically encountered in surface water overloading is rather unlikely to occur. Breakthrough volumes are read in the recorded breakthrough curves at 1% of the sample absorbance (see experimental section) and values obtained for a few solutes are reported in Table 1. Light hydrocarbons (as toluene) are not retained by C18 but are extracted by PRP1 whereas the heaviest ones (as pyrene) are well extracted by C18; the polar compounds as nitro- or chlorophenol, nitroaniline are not extracted by C18 but can be concentrated on PRP1. Many moderately polar compounds (as simazine or di- and trichlorophenols) can be studied by this method but they will be extracted by both precolumns depending on sample volumes.

Selectivity on preconcentration: It is clear that with a sample volume of 300–500 ml, C18 is selective only towards very apolar compounds which will be extracted by C18 alone whereas PRP1 is selective for relatively polar compounds which are not retained on C18 and are extracted by PRP1. But all the moderately polar compounds will be extracted by both C18 and PRP1 and it is difficult to use the term selctivity for their preconcentration. Figure 1 represents the analysis of

Table 1 Breakthrough volumes of a few solutes on C18 and on PRP1 precolumns (in ml)

Solute	*C18*	*PRP1*
Toluene	2.5	65
m-Xylene	6	65
Pyrene	>400	–
Dimethylphthalate	7	212
Diethylphthalate	165	>400
Dibutylphthalate	>400	–
Simazine	19	130
Atrazine	47	>250
Linuron	70	>250
Phenol	<1	3
2-Methylphenol	<1	15
2,4-Dimethylphenol	<1	26
2,4,5-Trimethylphenol	5	60
2-Chlorophenol	<1	30
2-Nitrophenol	1.5	70
2-Nitroaniline	<1	40
2-Naphtylamine	<1	30

pure water spiked with six phenylureas. When the sample volume is 50 ml, solutes No. 1 and 3 are concentrated on C18 and PRP1 whereas the others are only on C18; increasing the sample volume to 500 ml, there is another partition and the six herbicides are extrated by PRP1 and C18 with a higher amount on PRP1. It is then possible to determine the ratio between amounts preconcentrated on PRP1 and on C18 for a given sample volume and the variations of this ratio with the sample volume.

For surface waters with a higher organic content, C18 will concentrate all the non polar interferents and we can expect C18 to act as a "filter", rendering therefore more readable the fingerprint obtained from PRP1.

Quantitative analyses: When several compounds are researched in a given sample volume, for some of them this volume is higher than the breakthrough volumes and therefore the recovery of these solutes is not 100%. It was demonstrated[18] that it is recommended for trace analysis to overcome the breakthrough volumes of solutes because the breakthrough curve is often spread over a large volume range and the important point for trace analysis is the amount preconcentrated and available for detection; for instance the breakthrough volume of simazine on PRP1 is 130 ml but the end of the elution front is 280 ml and when the sample volume is 280 ml the preconcentrated amount is about twice that obtained for a sample volume of 130 ml. This is interesting for detection even if the recovery is lower than 100%.

When compounds are recovered from both precolumns quantitative analyses are still possible even if corresponding recoveries are below 100%. We have also shown[18] that recoveries can be calculated by determining the variations of peak areas obtained during the determination of preconcentrated compounds on each

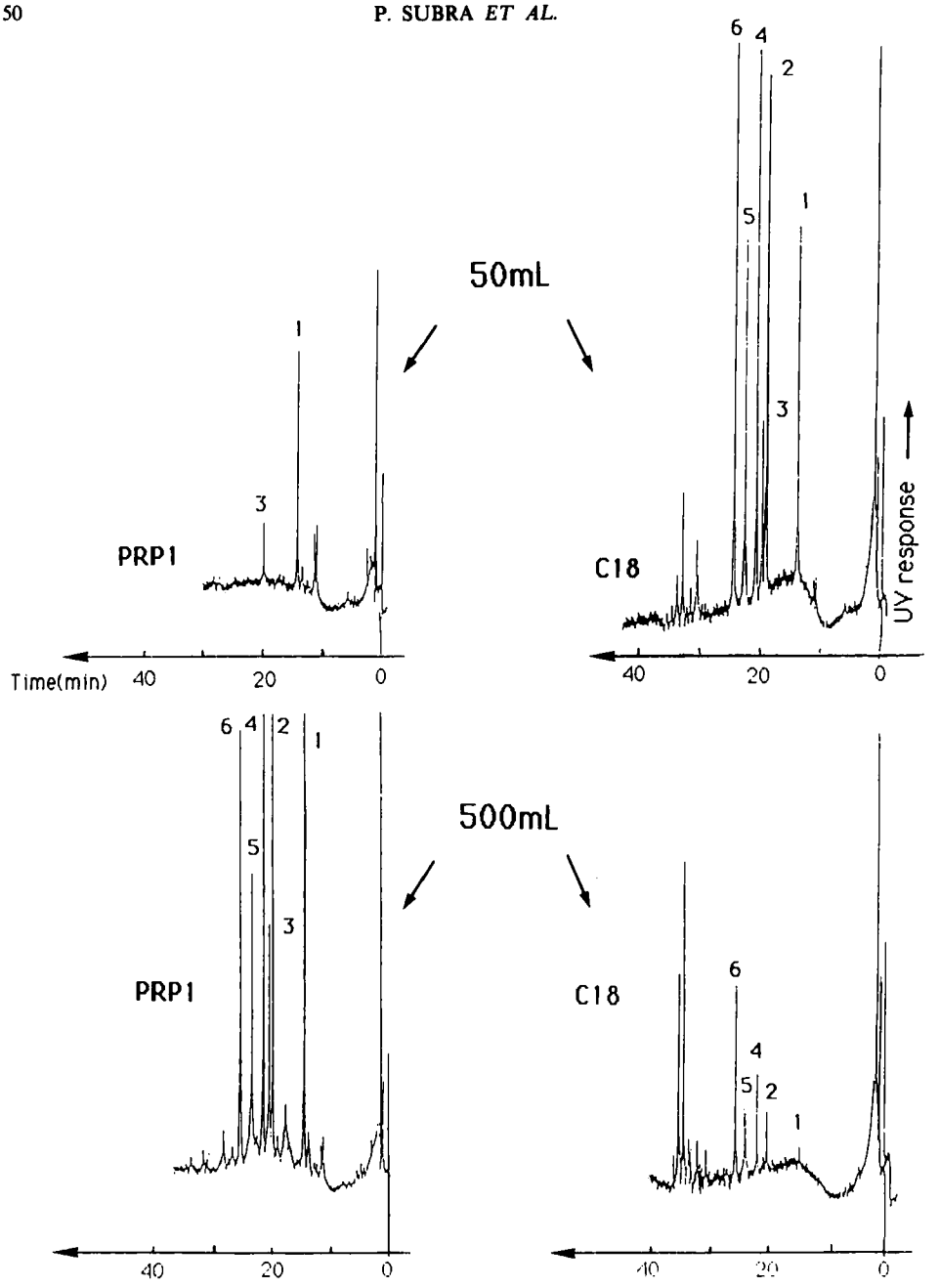

Figure 1 On-line preconcentration of two samples of different volumes (50 and 500 ml) of a standard solution of phenylureas. The amount of compounds is the same in the two samples (different concentrations). Solutes: 1 = metoxuron (0.83 μg), 2 = monolinuron (0.51 μg), 3 = buturon (0.83 μg), 4 = chlortoluron (0.89 μg), 5 = diuron (1.09 μg), 6 = linuron (1.18 μg). Preconcentration through two pre-columns (10 × 2.1 mm ID) in series packed with RP18 silica, 10 μm and with PRP1 copolymer, 10 μm at a flow rate of 3 ml/min; elution to the analytical column (150 × 4.6 mm ID) packed with ODS 2 silica, 5 μm 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 and acetonitrile; gradient: 15% of acetonitrile from time 0 to 5 min, 20% at 8 min, 50% at 25 min and 80% at 35 min; UV detection at 278 nm, sensitivity = 0.01 a.u. (f.s.).

Table 2 Retention time (in min) of some solutes obtained with the analytical water-acetonitrile gradient represented in Figures 2 and 3

Resorcinol	2.2	Atrazine	29.8
Phenol	5.5	Monolinuron	30.1
2-Toluidine	0.2	Buturon	30.2
2-,Ethylphenol	12.2	Chlortoluron	34
2-Chlorophenol	14.6	Diuron	35.9
2-Nitrophenol	15	Diethylphthalate	36.2
4-Chloroaniline	16.2	Linuron	37.2
Metoxuron	17.1	Dibutylphthalate	41.2
Simazine	18.2	Butylbenzylphthale	41.6
Dimethylphthalate	22.3		
2-Naphtylamine	28		

precolumn in increasing volumes of water samples; one condition is that in each sample the concentration is adjusted in order to have a constant amount of solute. In addition to recovery calculations, this method gives the ratio of amounts preconcentrated on each precolumn for a given sample volume and an estimation of the breakthrough volumes.

Analytical gradient for the separation of preconcentrated species: After the percolation of the water sample through the two precolumns in series, the C18 precolumn is coupled to an analytical column packed with n-octadecylsilica and the compounds preconcentrated are desorbed and directly transferred to this analytical column by a water-acetonitrile gradient. This operation is repeated for the PRP1 precolumn with a similar gradient. With a linar gradient from 0 to 100% of acetonitrile, first investigations have indicated the presence of numerous moderately polar compounds in drinking water. This is not surprising because during the treatment for drinking supply, water is oxidized with ozone or chlorine thus generating polar compounds. This is why the analytical gradient is optimised for the separation of these compounds with 15% of acetonitrile at the beginning and a slow slope during thirty minutes (see Figure 3). This gradient does not provide a good separation of very apolar compounds; this is possible but it would be longer than fifty minutes. Table 2 reports the retention time of a few solutes over this gradient and we note that polar compounds are in the first twenty minutes, moderately ones up to thirty-five minutes and the apolar ones in the last part. We report here the retention times of only about twenty solutes; many others have been tested and we note that several solutes have very close retention times. Taking account of many other compounds which may be present in environmental samples, it is obvious that simple identification of a solute by its retention time via the gradient is not sufficient and needs confirmation by other tools. The most powerful one is of course coupling mass spectrometry to the liquid chromatograph but few laboratories have such a set up at their disposition.

Identification of solutes: When a possible solute has been identified by the

presence of a peak at a suitable retention time, one has to verify if this peak does really correspond to the possible solute. First it is possible to spike the sample with the solute and observe the shape of the peak but this method is not a real confirmation. Using preconcentration with two precolumns gives powerful information. The ratio of amounts preconcentrated on each precolumn is easily calculated and compared with that obtained with pure water spiked with the solute for the same sample volume. Another sample volume can be studied and the variations of the ratio have to be similar.

Other confirmations are given by the use of several detectors. The solutes studies are not specific compounds but comprise a wide range of possible pollutants and three detection modes are chosen (UV absorbance or diode-array, fluorescence, electrochemistry). The comparison of the responses between the three detectors for the peak and for the solute are also a complementary information. Moderately polar compounds as derivatives of phenol or aniline can be selectively detected by the electrochemical detector. We use a coulometric detector with an electrochemical cell containing two analysis electrodes in series through which the liquid chromatograph effluent flows. The first electrode reacts with 100% of electroactive compounds and this reaction may completely eliminate potentially interfering compounds or one part of the compounds from subsequent dectection at the second analysis electrode. Figure 2 shows the UV chromatogram (a) and the electrochemical chromatogram (b) corresponding to the separation of a few derivatives of phenol and aniline at the ppb concentration range; we can observe that some solutes are oxidized at the first electrode (No. 4) the potential of which is 0.78 V (vs Ag/AgCl) and not at the second one, the potential of which is 0.90 V (vs Ag/AgCl); the area of the small peak observed at the second electrode is less than 2% in comparison with the peak area obtained at the first electrode. Other solutes are not oxidized at the first one but at the second one (No. 6) whereas others are oxidized at both (No. 3). The behavior of the solutes can be studied by determining the half-wave oxidation potential or by measuring the intensity of the signal for different potentials in order to choose better selective potentials at the two electrodes, depending on the potentials of beginning and end of the oxidation wave. Comparison between signals at the two electrodes for one peak and for the solute supposed to be present in the sample is then another argument for identification of solutes.

In conclusion working with on-line preconcentration with two precolumns and using three detection modes gives at least two or three confirmations for identification of peaks.

APPLICATIONS TO DIFFERENT WATERS

Drinking Water

We firstly applied the above method to drinking water in order to determine if selectivity was given by the two precolumns and to choose the sample volume. The chromatograms obtained from a 500 ml sample of drinking water are represented for each precolumn in Figure 3 for the UV detector at 244 nm (a), the

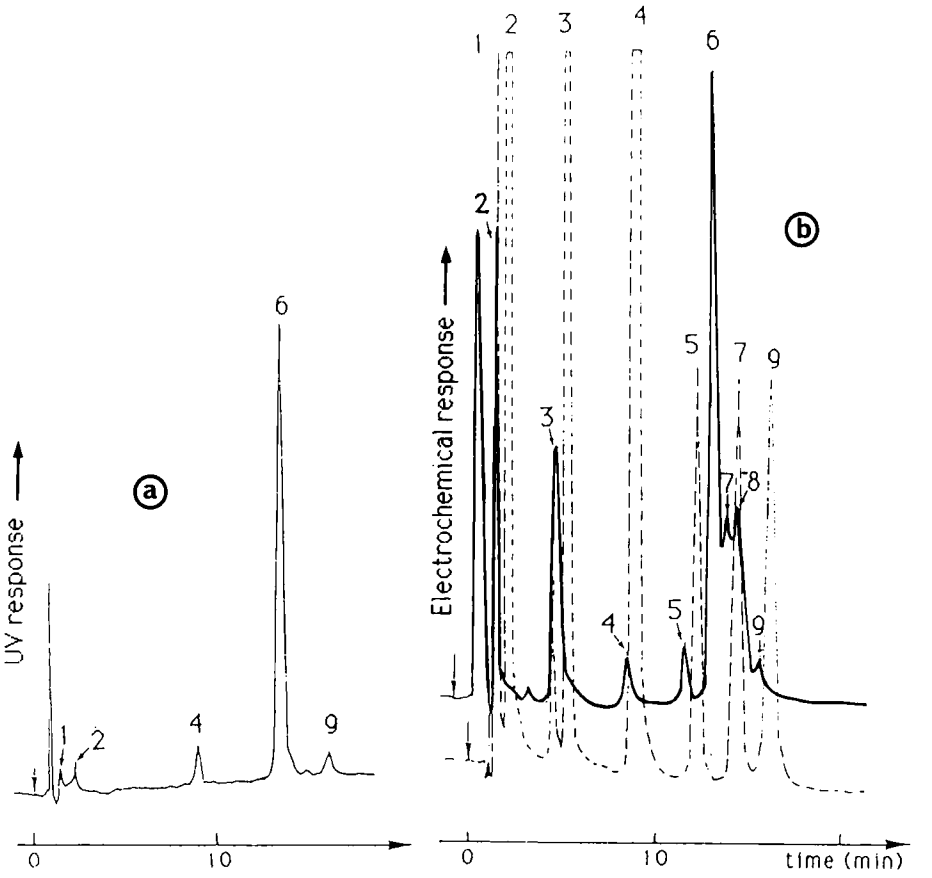

Figure 2 UV detecton (a) and electrochemical detection (b) of some phenol and aniline derivatives at ppb level. Solutes: 1 = hydroquinone, 2 = resorcinol, 3 = phenol, 4 = o-toluidine, 5 = 2-methylphenol, 6 = 2-nitroaniline, 7 = 2-chlorophenol, 8 = 2-nitrophenol, 9 = 4-chloroaniline. Analytical column (150 × 4.6 mm ID) packed with ODS 2 silica, 5 μm 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 and acetonitrile; gradient: 15% of acetonitrile from time 0 to 5 min, 20% at 20 min, 30% at 30 min and 100% at 45 min. a = Detection by UV at 244 nm, sensitivity: 0.01 a.u. (f.s.) b = detection by electrochemistry at 0.78 v (vs Ag/AgCl) for the first electrode (dotted line), sensitivity: 1.5 μA (f.s.) and at 0.90 V (vs Ag/AgCl) for the second electrode (solid line), sensitivity: 1.5 μA (f.s.).

fluorimetric detector (b) and the electrochemical detector at two oxidation potentials (c). UV detection shows a lot of non resolved compounds preconcentrated on C18 all along the gradient whereas on PRP1 we can observe a few peaks in the area of moderately polar compounds before 30 minutes. Selectivity towards nonpolar and more polar compounds does not appear clearly. The chromatogram represented here has been obtained at 244 nm with a sensitive classical detector at 0.02 a.u. full scale, indicating a small amount of organic compounds having UV properties. Whatever wavelength we choose, we obtain similar chromatograms with a lot of interfering background compounds. A diode-array UV detector was

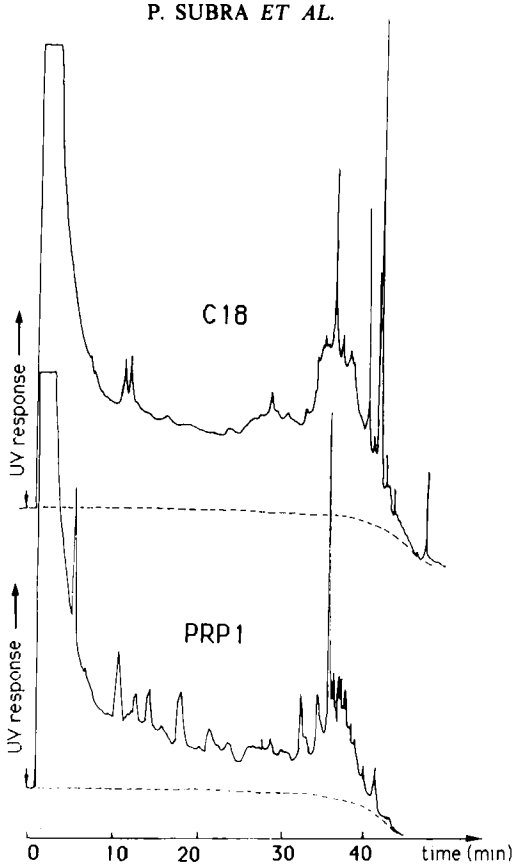

Figure 3 On-line preconcentration and analysis of 500 ml of drinking water from Paris area. Chromatograms obtained for the analysis of each precolumn with the three detection modes. Preconcentration through two precolumns (10 × 2.1 mm ID) in series packed with RP18 silica, 10 μm and with PRP1 copolymer, 10 μm at a flow rate of 3 ml/min; elution to analytical column (150 × 4.6 mm ID) packed with ODS 2 silica, 5 μm at a flow rate of 1.5 ml/min; mobile phase: acetonitrile gradient with a solution of potassium acetate/acetic acid 0.1 M and pH 6 and acetonitrile; same gradient as in Figure 2. (**a**) = Detection by UV at 244 nm, sensitivity: 0.02 a.u. (f.s); the dotted line represents the blank gradient.

tried but did not give any information from UV spectra of the peaks recorded in Figure 3a; these detectors can be used only in case of major pollution when the concentration of the analytes is much higher than the other compounds. Fluorescence gives more interesting information and better selectivity for fluorescing compounds preconcentrated. On C18 (Figure 3b) we just observe non polar compounds and specially a high amount of solutes at the end of the gradient after 40 minutes; these compounds are not recovered from PRP1, where several polar and moderately compounds are found before 35 minutes. Similar observations can be drawn from the electrochemical detection (Figure 3c) where several oxidizable compounds are found on PRP1. The use of these three detectors gives complementary information and we observe that UV absorbance is less selective than fluorescence or electrochemistry for drinking water analysis.

Sample volume: Figure 4 shows the chromatograms obtained at the detector after

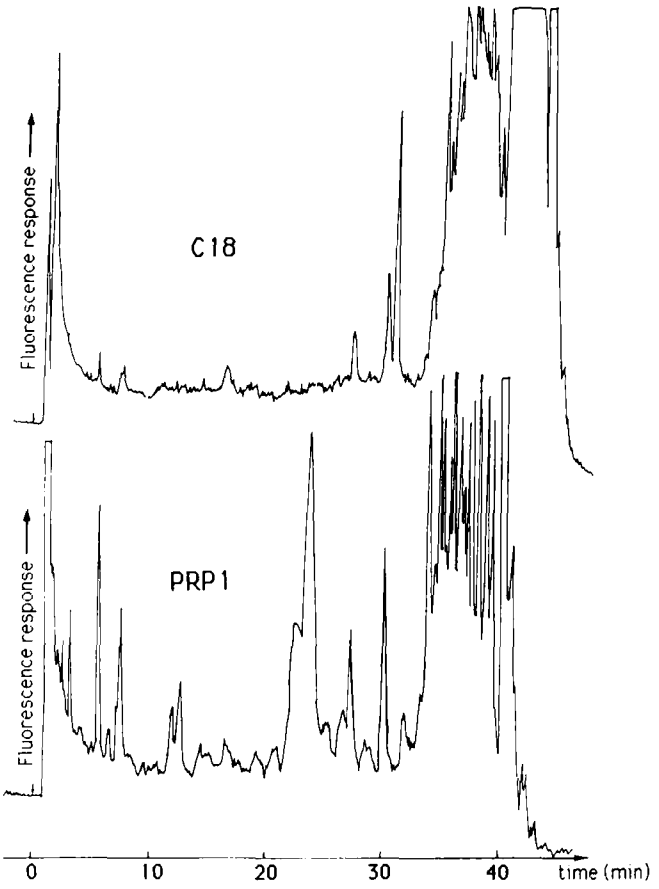

Figure 3 (b) Detection by fluorescence at 285 nm excitation and 320 nm emission wavelength.

preconcentration of two different volumes of the same drinking water. It can be seen that with 500 ml we can detect solutes which cannot be detected from 100 ml.

Identification of solutes: A few solutes were identified by their retention times and by comparison between UV response and electrochemical oxidation at two different potentials as shown in Figure 2. In the water sample shown in Figure 3, 2-chlorophenol and 2-nitrophenol are found below the ppb level.

Analysis of a Mineral Water

A mineral water stored in a plastic bottle was preconcentrated and analysed. It is interesting to study such a water the total organic content of which is below 0.5 mg/l. Figure 5a shows the UV chromatogram at 282 nm obtained after preconcentration of 100 ml of this water. On PRP1 nearly nothing is observed

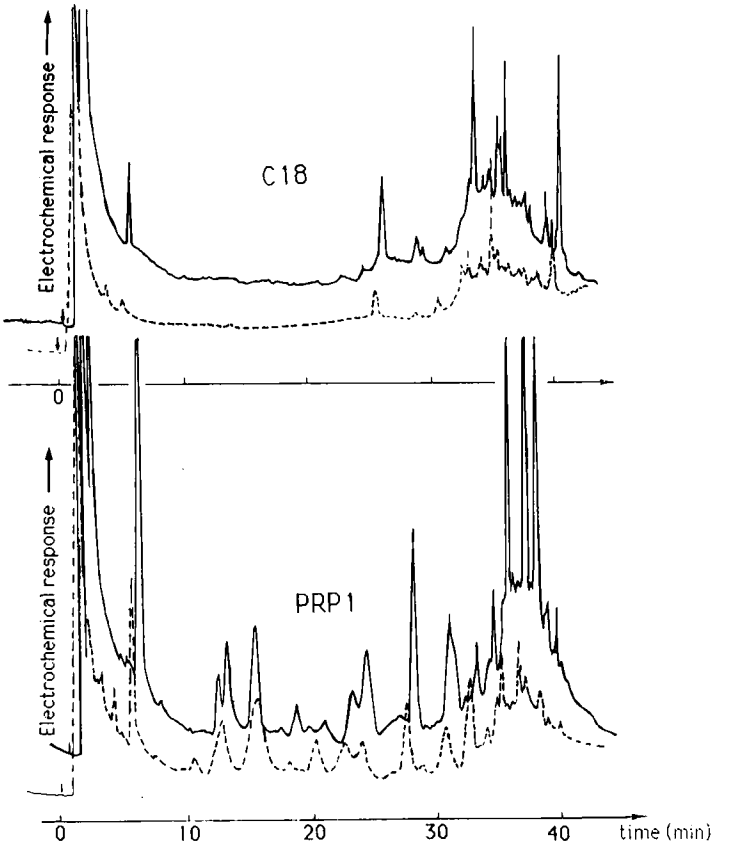

Figure 3 (c) Detection by electrochemistry at 0.78 v (vs Ag/AgCl) for the first electrode (solid line), sensitivity: 3 μA (f.s.) and at 0.90 V (vs Ag/AgCl) for the second electrode (dotted line), sensitivity: 1.5 μA (f.s.).

which is not surprising with this 100 ml volume (the base-line drift is due to the difference in absorbance between the two constituents of the mobile phase) whereas a few peaks are detected on C18. A spiking of this water by 4 phthalates (see Figure 5b) allows identification of diethyl and dibutyl phthalate at a concentration of 3 ppb. These compounds were not found in this same mineral water stored in a glass bottle.

Research of Polar Herbicides in a River Water-Identification Process

The last application is the analysis of a river water. The sample has been taken in March after several days of rain and this river, Yerres river, runnning in an agricultural area may contain some herbicides. Figure 6 shows the UV chromatogram at 244 nm obtained from C18 and PRP1 after preconcentration of 100 ml and 450 ml. From 100 ml five peaks are recovered from C18 and three from PRP1

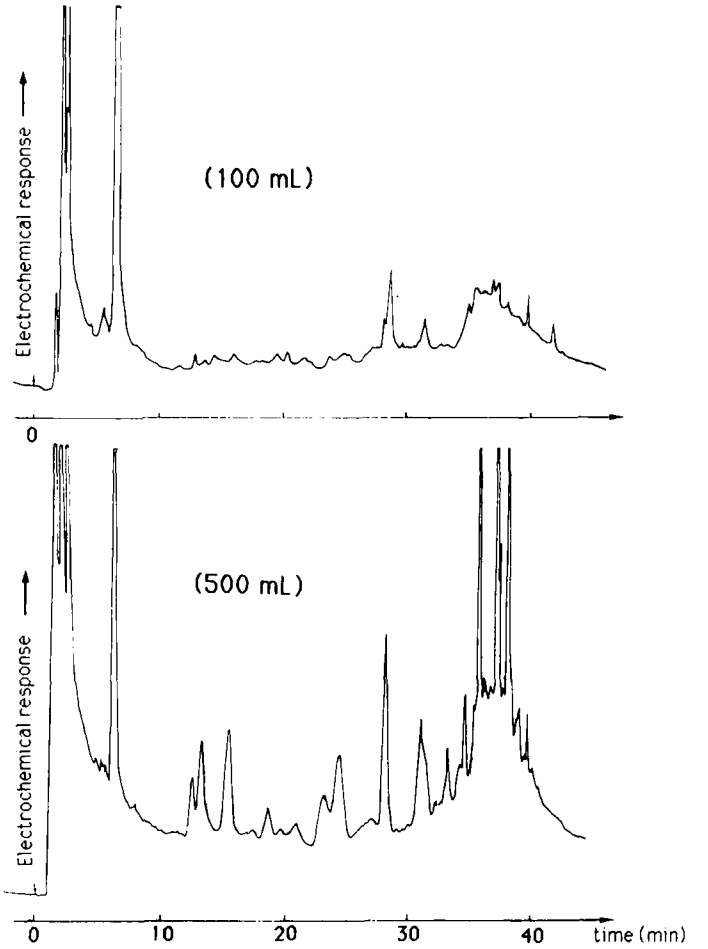

Figure 4 Comparison of chromatograms obtained from the preconcentration of 100 and 500 ml of drinking water; Analysis of the PRP1 content and detection by electrochemistry at 0.78 V (vs Ag/AgCl) sensitivity: 3 μA (f.s.). Other conditions as in Figure 3.

(the two peaks near 10 min are in the blank) and identified by their retention times. With 450 ml preconcentration, the peaks No. 2 and 3 are found in a greater part on PRP1. The peak near 30 min (No. 1) is found only on C18 with 100 ml but is recovered from both C18 and PRP1 with 450 ml whereas for this volume the peak at 41.7 min (No. 5) is still extracted only by C18 and therefore corresponds to an apolar solute because its breakthrough volume on C18 is larger than 450 ml. Comparing between the amounts of solutes in peaks No. 2 and 3 extracted by C18 from 450 ml and 100 ml, one can observe that these peaks have about the same height thus indicating that the breakthrough volumes of the compounds are below 100 ml; this confirms the presence of peaks No. 2 and 3 on PRP1 with 100 ml. Peak No. 4 corresponds to a solute having a small breakthrough on C18. So one can get information about the polarity and breakthrough volumes by the

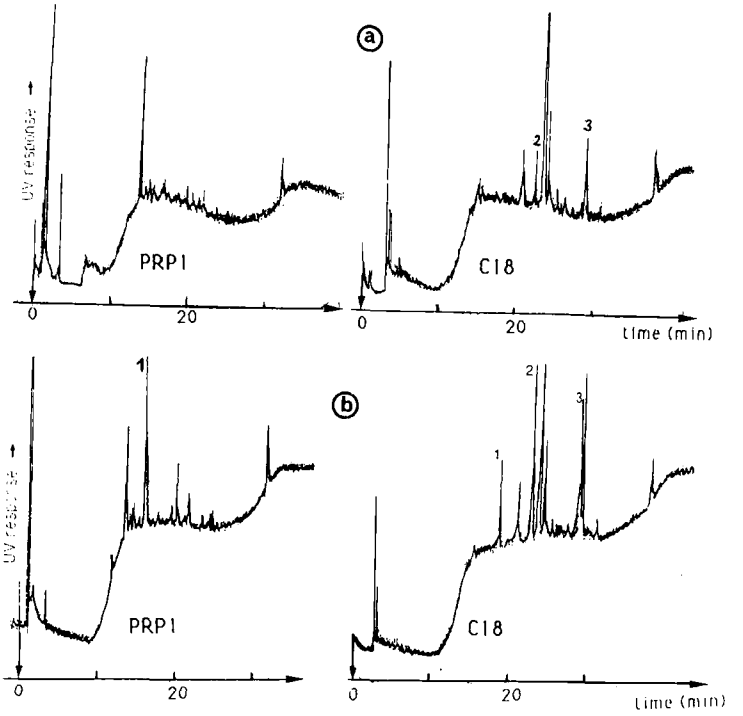

Figure 5 On-line preconcentration and analysis of 100 ml of (a) mineral water stored in a plastic bottle and (b) same water spiked with phthalates at a concentration of 10 ppb for each solute: 1 = dimethyl phthalate, 2 = diethyl phthalate, 3 = dibutyl phthalate, 4 = butylbenzyl phthalate. Preconcentration through two precolumns (10 × 2.1 mm ID) in series packed with RP18 silica, 10 μm and with PRP1 copolymer, 10 μm at a flow rate of 3 ml/min; elution to analytical column (150 × 4.6 mm ID) packed with ODS 2 silica, 5 μm 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 and acetonitrile; gradient: 10% of acetonitrile from time 0 to 6 min and linear increase to 100% at 30 min; UV detection at 282 nm, sensitivity = 0.01 a.u. (f.s.).

comparison of fingerprints obtained with two different volumes. Another important observation can be given by this figure. Looking at the 450 ml preconcentration, a lot of interferents are preconcentrated on C18 as shown by the great amount of non resolved compounds whereas on PRP1 we have a chromatogram of good quality. C18 acts as a filter to many compounds therefore rendering the reading of PRP1 fingerprint more efficient.

Looking at the table of retention times, Table 3 reports the possible solutes that may be present in these waters and six herbicides may correspond to these peaks. For 100 ml preconcentration and for each peak the percent of amount preconcentrated on C18 is calculated (by dividing the peak area determined on C18 by the sum of peak areas determined on the two precolumns) and is compared to that obtained for pure water samples spiked with the possible solutes. These values are also reported in Table 3. For 450 ml the percent of amount preconcentrated on PRP1 for the peaks and spiked solution are also reported in Table 3. An examination of these values indicates that monolinuron buturon and linuron

Table 3 Identification of solutes by their retention times and amounts preconcentrated on each precolumn from 100 ml and 450 ml sample volumes. a = experimental value calculated from peak areas in the chromatograms represented in Figure 6. b = values calculated from peak areas in chromatograms obtained with pure water samples spiked with the corresponding solute

Retention time	*Possible solutes*	*% on C18 with 100 mL*		*% on PRP1 with 450 mL*	
		a	*b*	*a*	*b*
29.9	Monolinuron	100	65	62	93
	Buturon		35		90
	Atrazine		96		64
33.8	Chlortoluron	93	79	78	82
36.1	Diuron	77	97	70	72
37.2	Linuron	0	100	–	–
41.7	Dibutylphthalate butylbenzylphthalate	100	100	0	3

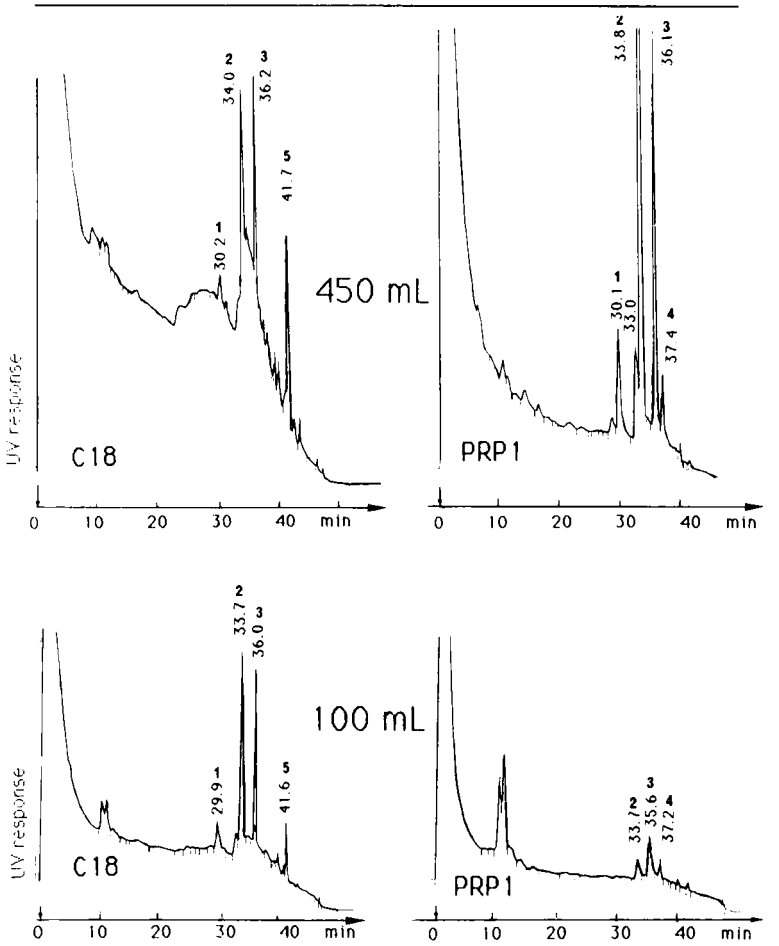

Figure 6 On-line preconcentration and analysis of two different volumes of river water (Yerres). UV detection at 244 nm, sensitivity: 0.1 a.u. (f.s.); other conditions as in Figure 3.

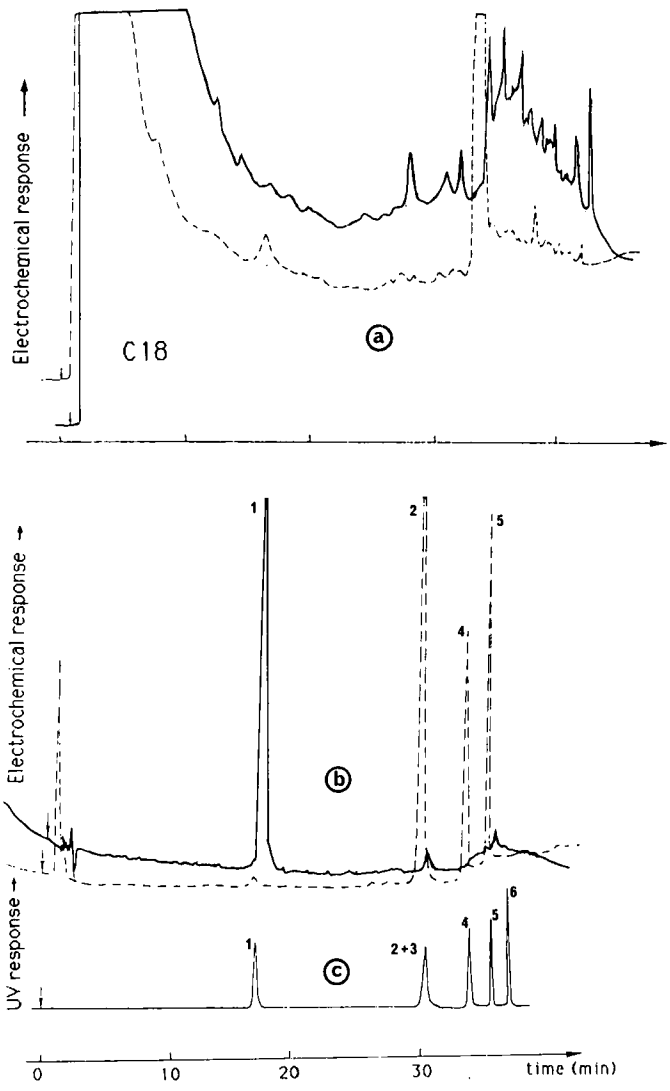

Figure 7 (a) Electrochemical response from C18 precolumn and for 100 ml of preconcentrated river water corresponding to the UV chromatogram represented in Figure 6; solid line: first electrode at a potential of 0.78 V (vs Ag/AgCl), sensitivity: 1.5 μa (f.s.) and dotted line second electrode at a potential of 0.90 V (vs Ag/AgCl), sensitivity: 1.5 μA (f.s.). **(b)** Electrochemical response of a direct injection of a solution of phenylureas; solid line: first electrode at a potential of 0.78 V (vs Ag/AgCl), sensitivity: 3 μA (f.s.) and dotted line second electrode at a potential of 0.90 V (vs Ag/AgCl), sensitivity: 1.5 μA (f.s.). (c) UV detection at 244 nm of the same solution as in (b), sensitivity: 0.1 u.a. (f.s.) solutes: 1 = metoxuron, 2 = monolinuron, 3 = buturon, 4 = chlortoluron, 5 = diuron, 6 = linuron. Other conditions as in Figure 3.

cannot correspond to these peaks. There is a good agreement for atrazine with the two volumes. For chlortoluron and diuron the agreement is good for 450 ml but not satisfactory for 100 ml. This can be explained by an interfering compound. Examination of electrochemical detection can solve this ambiguity. As shown in Figure 7b chlorotoluron and diuron are not oxidized at 0.78 V but at 0.90 V (vs Ag/AgCl). Figure 7a shows the river water chromatogram obtained by electrochemical detection from C18 precolumn after 100 ml preconcentration. The peak at 33.8 min corresponds well to chlortoluron but the peak at 36.1 min does not correspond to linuron as no peak is detected by electrochemistry. On PRP1 (not represented in Figure 7) the peak at 33.8 min is not chlortoluron alone because the ratio between the amounts oxidized at the two potentials does not correspond to the "theoretical" values. So there is an interfering peak with chlortoluron in a small quantity concentrated on C18 and this explains the difference between the experimental ratio higher than that predicted.

In conclusion six herbicides may be identified by their retention times but we are sure that four of them are not present in the sample. This last application illustrates well how important it is to obtain complementary information for identification; on-line preconcentration and selective electrochemical detection are powerful tools for preconcentration and identification of these moderately polar compounds.

CONCLUSION

This study shows that on-line preconcentration with two coupled precolumns, one packed with octadecyl silica and the other with a polymer-based sorbent allows selective preconcentration between nonpolar compounds and relatively polar ones. For the moderately polar ones, it gives a powerful identification process which may be completed by the use of selective detection. Informative fingerprints are obtained from samples of waters with low organic content such as drinking water. This analytical method is rapid and can be automated and could be applied to control the water quality in a treatment plant for drinking water supply.

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