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Interference removal in the organic trace-level analysis of aqueous environmental samples by on-line liquid chromatographic preconcentration techniques with two precolumns[a]

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ABSTRACT

On-line sample handling is used to enrich trace organic compounds in order to isolate and preconcentrate them prior to their liquid chromatographic separation. The main difficulty is that aqueous samples are complex matrices and therefore many interferences are also preconcentrated, giving rise to a high background. It is shown that matrix interferences are not a problem for determination at the ppb (μg/l) level in natural waters, but have to be removed to reach the 0.1 ppb level in drinking water (EEC requirement for many pesticides). Preconcentration is then optimized in terms of interference removal: two precolumns are coupled in series for the preconcentration step, the first acting as an interferent filter and the second trapping the analytes of interest. The methodology is different whether a specific sorbent for the analytes exists or not. Applications to the determination of moderately and rather polar herbicides (chlorotriazines and phenylureas) are presented. When no selective sorbent can be found, it is possible to optimize the fractionation between many rather apolar interferences and analytes by coupling two non-selective materials. Determination of polar herbicides is solved by coupling two precolumns, one packed with an alkylsilica (C_{18} or C_8) and the other with a styrene–divinylbenzene copolymer (PRP-1). The choice of the *n*-alkylsilica (carbon loading and chain length) is then important and is directly related to the solute polarity because the solutes must be slightly retained to have recoveries as high as possible on the PRP-1 precolumn. When a selective sorbent such as an ion exchanger can be selected, inorganic and organic interferences are efficiently removed by a two-step preconcentration and a first PRP-1 precolumn. Detection limits are therefore below 0.1 μg/l.

INTRODUCTION

In recent years, for the determination of trace amounts of organic pollutants in environmental aqueous samples, preconcentration techniques based on liquid–solid sorption extraction have grown in interest as an alternative to laborious and time-consuming liquid–liquid extraction [1–3]. Solid-phase extraction (SPE) is often described as an off-line sample preparation technique, involving the use of disposable

[a] In memory of R. W. Frei.

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prepacked cartridges with a subsequent gas chromatographic (GC), GC–mass spectrometric (MS) or liquid chromatographic (LC) analysis of the extract. Although the off-line procedure usually shortens the time of sample handling, a certain amount of tedious labour remains. On-line trace enrichment and analysis is obviously advantageous from the point of view of sensitivity, rapidity and possible automation. As there is no manual handling of the concentrated sample, the entire sample can be analysed quantitatively and no contamination risk occurs [4]. Although a few examples of on-line SPE preconcentration and GC analyses have been described [5–8], when looking for trace organics in environmental aqueous samples reversed-phase chromatography is the easiest method to be coupled on-line with SPE preconcentration: the residual water does not have to be removed before the analysis and LC offers much potential for the trace determination of many thermodegradable and/or non-volatile organics [9,10].

There is now a great need for methods suitable for determining concentrations below 0.1 μg/l (0.1 ppb) of trace constituents, which is the EEC maximum allowed concentration of a single pesticide in drinking water. Quantitative and accurate determinations at this level require detection limits of the analytical method at a lower level, *i.e.*, 10–50 ppt. When using a precolumn packed with a non-selective reversed-phase sorbent, many other components of the sample matrix will usually be co-extracted and co-eluted together with the analytes. This problem is not important if the concentration of analytes is much higher than that of the matrix components, but it has to be solved when analytes are to be determined at low ppb concentrations, as they are then masked by the complex pattern of interfering substances. Therefore, the detection limits can be strongly influenced by the number and concentration of co-eluting impurities in the sample matrix and an analytical method carried out with spiked LC-grade water samples at the 10–100 ppt level cannot be applied at this level with natural water samples owing to the high interference background. It is then necessary to minimize interferences to lower the detection limits.

On-line sample handling using precolumn technology is a powerful approach to obtaining selective preconcentrations, as several precolumns can be coupled in series to fractionate a complex mixture [11–13]. The sample volume can be increased to 500 ml and more, so that high enrichment factors can be obtained [14], making it possible to use simple UV detection. When concentrating organics from water samples, most of the widely used sorbents are non-selective reversed-phase materials such as *n*-alkylsilicas and to a lesser extent copolymer-based (PRP-1) and carbon-based sorbents [1,11–15]. More selective sorbents have been used, such as metal-loaded phases and ion exchangers [16–24].

The advantage of a selective sorbent is that part of the matrix components does not interfere. Nevertheless, for some relatively polar organic pollutants, no selective sorbent is available and interference removal is still a problem. The aim of this work was to optimize the use of precolumn technology in terms of interference removal: two precolumns are coupled in series for the preconcentration step, the first acting as an interference filter and the second trapping the analytes of interest with high recoveries. We discuss the sorbents to be packed in the two precolumns depending on the solute polarity and on the sample volume to be handled for the required UV or electrochemical detection. The methodology and results are different and depend on whether a selective sorbent for analytes can be found or not. Determination of chlo-

rotriazine and phenylurea herbicides is considered as an example of the two methods. When no selective packing can be used, two reversed-phase materials are coupled [*n*-alkylsilica and a styrene–divinylbenzene copolymer (PRP-1)]. In that case, there is an optimization of the complex mixture fractionation; the choice of the *n*-alkylsilica (carbon loading and chain length) is then important and is directly related to both the nature of the matrix components and the polarity of the solutes, because the solutes must be slightly retained to have high recoveries on the PRP-1 precolumn. Information about the polarity of matrix interferences in river and drinking water samples is also presented. A comparison of the coupling of a non-selective sorbent to remove interferences with a selective sorbent is made for chlorotriazine determinations.

EXPERIMENTAL

Apparatus

On-line percolation of water was performed using a Milton Roy pump (LDC, Riviera Beach, FL, U.S.A.). Precolumn elutions and analyses were carried out with a Varian (Palo Alto, CA, U.S.A.) Model 5500 liquid chromatograph equipped with a Model 200 variable-wavelength spectrophotometer and a Coulochem Model 5100 electrochemical detector (ESA, Bedford, MA, U.S.A.). Precolumn and analytical column switching was connected via two Rheodyne (Berkeley, CA, U.S.A.) valves. Quantitative measurements of peak areas were provided by a CR3A integrator–computer from Shimadzu (Kyoto, Japan).

Stationary phases and columns

The analytical columns were 15 cm × 4.6 mm I.D. stainless-steel columns prepacked with 5-μm octadecylsilica Nucleosil C_{18} (Macherey, Nagel & Co., Düren, Germany) or with 5-μm octadecylsilica Spherisorb ODS-2 (Whatman, Clifton, NJ, U.S.A.). Water samples were preconcentrated on 10 mm × 2.1 mm I.D. stainless-steel precolumns available from Chrompack (Middelburgh, The Netherlands), which were packed manually with a thick slurry using a microspatula or with a thin slurry using a syringe. The stationary phases packed in precolumns were 10-μm octylsilica RP-8, 10-μm octadecylsilica RP-18 (Merck, Darmstadt, Germany), 10-μm octadecylsilica Partisil-10 ODS, carbon loading 5% and Partisil-10 ODS-2, carbon loading 15%, from Whatman, the spherical 10-μm styrene–divinylbenzene copolymer PRP-1 (Hamilton, Reno, NV, U.S.A.) and the sulphonic acid-type resin-based cation exchanger BC-X8, 15–20 μm (Benson, Reno, NV, U.S.A.). A 15 mm × 3.2 mm I.D. precolumn prepacked with a 7-μm PRP polystyrene–divinylbenzene polymer (Brownlee Columns, Applied Biosystems, San Jose, CA, U.S.A.) was also used.

Chemicals

High-performance liquid chromatographic (HPLC)-grade acetonitrile was obtained from Rathburn (Walkerburn, U.K.) and methanol from Prolabo (Paris, France). LC-grade water was prepared by purifying demineralized water in a Milli-Q filtration system (Millipore, Bedford, MA, U.S.A.). Other chemicals were from Prolabo, Merck or Fluka (Buchs, Switzerland).

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

ppb or ppt level. The final standard solutions did not contain more than 0.5% of methanol.

Procedure

The experimental set up is described in ref. 14. When using two non-selective precolumns, the water sample was introduced on the two precolumns in series; then the precolumns were flushed with 4 ml of 10^{-3} *M* perchloric acid. Each precolumn was separately coupled to the analytical column by switching a valve and back-flush 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.

When using a selective cation-exchange precolumn, the following procedure was adopted. A natural water sample adjusted to pH between 6 and 8 (if necessary) was percolated through the PRP-1 precolumn alone. After flushing with 2 ml of LC-grade water, the PRP-1 precolumn was coupled to the 10-mm long cation-exchange precolumn and 3 ml of a mixture containing 25% of acetonitrile and water acidified at pH 1 with perchloric acid were percolated through the two precolumns in series. After flushing the two precolumns with 2 ml of LC-grade water, the cation-exchange precolumn was coupled alone to the C_{18} analytical column and back-flush eluted by an acetonitrile gradient with lithium perchlorate-perchloric acid (0.05 *M*) at pH 4 via the HPLC pump. The PRP-1 precolumn was cleaned with 10 ml of pure acetonitrile and regenerated with 20 ml of LC-grade water. The cation-exchange precolumn was regenerated with 25 ml of 10^{-3} *M* perchloric acid.

Drinking water samples were analysed without any filtration. River water samples were filtered over a glass-fibre filter (Whatman GF/F).

RESULTS AND DISCUSSION

The selected herbicides for this study are listed in Table I and are representative of a range of moderately to relatively polar compounds, as shown by their water–octanol partition coefficients [25]. As an indication of polarity, the hydrophobic constants of simazine and atrazine are comparable to those of phenol (log P = 1.48) and 2-chlorophenol (log P = 2.16), respectively. For phenylurea herbicides, no selective sorbent has been reported; for some of them, the detection limit can be slightly improved by the use of electrochemical detection or by a derivatization reaction [26].

TABLE I

WATER–OCTANOL PARTITION COEFFICIENTS (LOG P_{oct}) AND IONIZATION CONSTANTS (pK_a) FOR SELECTED HERBICIDES

Phenylureas		Log P_{oct}	Triazines		Log P_{oct}	pK_a
Abbreviation	Name		Abbreviation	Name		
M	Metoxuron	1.98	S	Simazine	1.51	1.65
C	Chlortoluron	2.55	A	Atrazine	2.05	1.68
I	Isoproturon	2.65	P	Propazine	2.59	1.85
			T	Terbutylazine	2.65	1.95

Chlorotriazines can be considered as ionizable compounds (with low ionization constants) and can be selectively concentrated by a cation-exchanger [27].

A simple calculation indicates the sample volume to be handled in order to reach the required detectable amount: the average UV or electrochemical detection limit of analytes being 1–5 ng [28], a 100–500-ml sample volume is necessary to reach the 10 ppt level for spiked LC-grade water samples and provide easy determinations at the low ppb level in river water samples. Therefore, the analyte retention in water with the selected sorbent must be high, as the precolumn dimensions are small in order to avoid band broadening of analytes during their transfer from the precolumn to the analytical column (for a classical 15 cm × 0.46 cm I.D. column, the precolumn dimensions should not exceed 1 cm × 0.46 cm I.D.) [29]. Among the non-selective sorbents, previous studies have shown that the styrene–divinylbenzene copolymer-based PRP-1 sorbent provides efficient retention of relatively polar aromatic compounds in aqueous samples [14].

Interference removal using two non-selective materials

Description of the methodology. When using two non-selective reversed-phase materials for the preconcentration, the fractionation has to be optimized to remove many interferences on the first precolumn and concentrate analytes on the second. Retention of analytes depends on the sample volume, on the sorbent characteristics and on the nature of the analyte. Sorption can be appreciated by determining breakthrough volumes on each precolumn. Breakthrough volumes of apolar solutes on the first alkylsilica precolumn are high and these solutes are recovered only on the first precolumn; polar solutes, not retained on the alkylsilica, are recovered only on the second precolumn, but many moderately polar compound are revovered on both precolumns and the respectively preconcentrated amounts depend on the sample volume and on the analyte breakthrough volumes on each precolumn. Quantitative determinations are still possible and a direct experimental method of recovery measurement has been described [14]. It consists in measuring the peak areas obtained with a 10-ml preconcentration of spiked LC-grade water. The 10-ml volume is chosen so that no breakthrough occurs from the alkylsilica precolumn. Then the sample volume is increased but the solute concentration is decreased to have a constant amount in each sample. For each percolation, the peak areas are measured on the chromatograms corresponding to the elution of each precolumn. Recoveries are calculated by dividing these values by the peak-area values obtained for the first 10-ml percolation. This experimental measurement of recovery has the advantage of taking into account the transfer and the desorption processes from the column to the analytical column. Breakthrough of solute on the alkylsilica precolumn starts when its recovery decreases on this precolumn. If no breakthrough occurs from the PRP-1 precolumn, the sum of recoveries from alkylsilica and PRP-1 is 100%, and each recovery represents the part of the analyte preconcentrated on each precolumn. Breakthrough on the PRP-1 precolumn starts when the sum of the recoveries begins to fall below 100%. For the selected analytes, breakthrough volumes higher than 500 ml have been measured with a 15 mm × 3 mm I.D. precolumn packed with the PRP-1 sorbent.

Effect of n-alkylsilica carbon loading. Four *n*-alkylsilica sorbents, one C_8 and three C_{18} having different carbon loadings, were tested to investigate their potential for interference removal with drinking and river water samples.

Large volumes of raw drinking water and river water were spiked with 1 μg/l of each analyte. Four replicate runs were performed with 500-ml samples of each type of spiked water which were passed through the two precolumns in series, the first packed with one of the tested alkylsilicas and changed between two runs and the second packed with the PRP-1 sorbent and unchanged. In each run, the two precolumns were eluted on-line with UV and electrochemical detection. Fig. 1 shows the UV chroma-

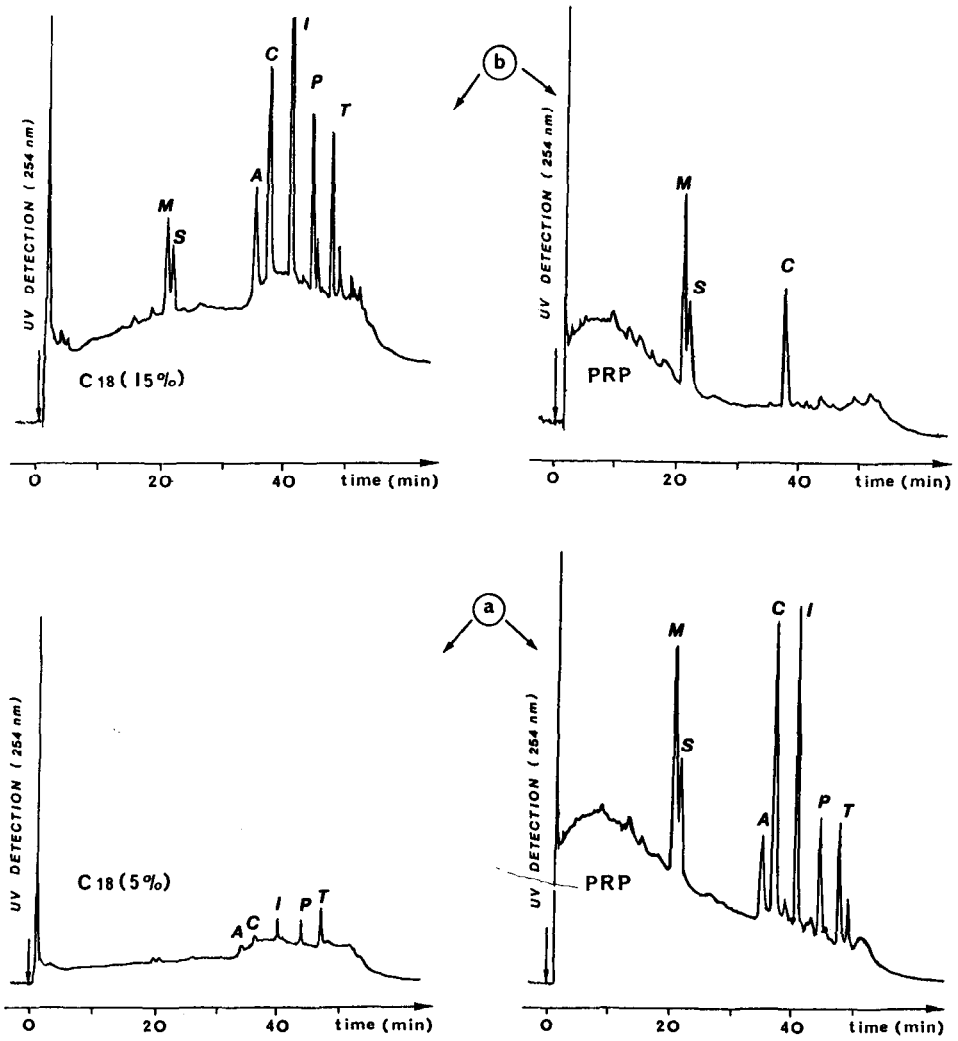

Fig. 1. On-line preconcentration of 500-ml drinking water samples spiked with 1 μg/l of each herbicide. See Table I for peak identification. Preconcentration through two precolumns in series packed with (a) octadecylsilica Partisil-10 ODS with 5% carbon loading and PRP-1 and (b) octadecylsilica Partisil-10 ODS-2 with 15% carbon loading and PRP-1 at a flow-rate of 5 ml/min; elution to the analytical column (15 cm × 4.6 mm I.D.) packed with 5-μm Spherisorb ODS 2 silica 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 4.6; gradient from 14.5% to 23.5% of acetonitrile from time 0 to 40 min, to 37% at 60 min and to 100% at 80 min. UV detection at 254 nm; sensitivity, 0.016 a.u.f.s.

tograms obtained for the elution of both precolumns when concentrating a 500-ml drinking water sample and when using a C_{18} silica with a low carbon content (Fig. 1a) and a high carbon content (Fig. 1b). First, it can be observed that the ratio of the amount preconcentrated by both precolumns depends greatly on the carbon loading of the first precolumn: the 5% carbon silica slightly retains the more apolar analytes and almost everything else is recovered on the PRP-1 precolumn. In contrast, with the 15% carbon silica, analytes are mainly retained on the first precolumn, and only the more polar ones are recovered from the second PRP-1 precolumn. Fig. 1 shows also that when analytes are to be determined at the 1 μg/l level in drinking water samples,

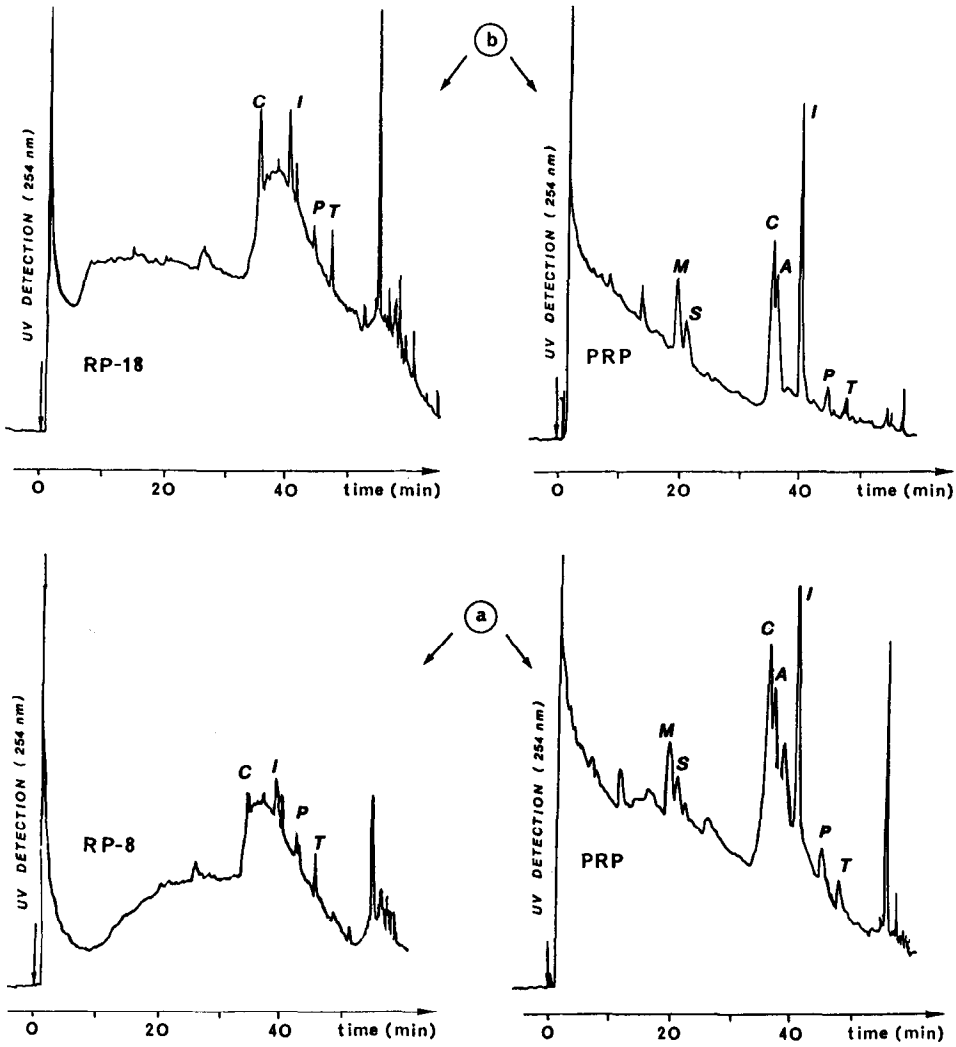

Fig. 2. On-line preconcentration of 500-ml River Yerres samples (March 89) spiked with 1 μg/l of each herbicide. Preconcentration through two precolumns in series packed with (a) octylsilica RP-8 and PRP-1 and (b) octadecylsilica RP-18 and PRP-1 at a flow-rate of 5 ml/min. UV detection at 254 nm; sensitivity, 0.032 a.u.f.s.; other conditions as in Fig. 1.

the problem of matrix interferences is not important and a single precolumn packed with a high carbon content C_{18} silica or a PRP-1 sorbent can be used. If analytes are to be determined at the 0.1 μg/l level, one has to divide each peak height by 10 and it is clear that peaks will not then emerge greatly from the interference background.

Information about the polarity of interferences in this drinking water sample is also obtained. The 5% C_{18} silica can retain very apolar solutes which would be eluted at the end of the gradient (above 50 min), so that the matrix does not contain many very apolar components, having UV absorption properties at 254 nm; the PRP-1 chromatogram in Fig. 1a indicates a larger amount of interferences during the first 30 min, which correspond to rather polar and moderately polar components. These observations are confirmed by the chromatograms in Fig. 1b: the 15% C_{18} silica traps many moderately polar interferences and only the more polar ones are recovered on the PRP-1 precolumn, as shown during the first 20 min of the gradient.

Interferences are more numerous in river water, as can be seen in Fig. 2, which shows the chromatograms obtained with similar experiments to those in Fig. 1 when using RP-8 (Fig. 2a) and RP-18 (Fig. 2b) in the first precolumn for the preconcentration of a 500-ml river water sample spiked with 1 ppb of each analyte. In comparison with Fig. 1, the background is much more important. As expected, the matrix components trapped by RP-18 are more numerous than those trapped by RP-8, but the baseline obtained on the PRP-1 chromatogram is very different, owing to the "interference filter effect" of the first precolumn. For instance, if the analytes of interest are atrazine or chlortoluron, their determination will be more accurate when using RP-18 as the first precolumn because with RP-8 there are too many interferences left in this area of the chromatogram. When using the 15% carbon content C_{18} silica (not shown), the filter effect is higher but the compounds are trapped too much on the first precolumn with the interfering material. Table II reports the recoveries obtained for the four couplings studied above on the PRP-1 precolumn from 500-ml samples. With RP-18 as the first precolumn, the recoveries of moderately polar compounds are between 80 and 85% and those of apolar compounds between 60 and 40%. As the detection limit depends on the baseline quality, there is a compromise between efficiently minimizing interferences and obtaining good recoveries of analytes on the second precolumn. This compromise depends on the polarity of both analytes and matrix components. For many types of drinking water and river water, coupling

TABLE II

RECOVERIES OF HERBICIDES ON THE PRP-1 PRECOLUMN WHEN IT IS COUPLED TO A FIRST PRECOLUMN PACKED WITH DIFFERENT *n*-ALKYL-BONDED SILICAS

Mean values obtained from triplicate measurements from 500-ml samples spiked with 1 μg/l of each analyte. See Table I for herbicide identification.

n-Alkylsilica	Recovery on PRP-1 precolumn (%)						
	M	C	I	S	A	P	T
ODS 5%	98	98	94	97	93	87	78
ODS-2 15%	70	37	13	60	18	12	10
RP-8	97	91	86	98	87	72	59
RP-18	98	85	80	97	80	60	40

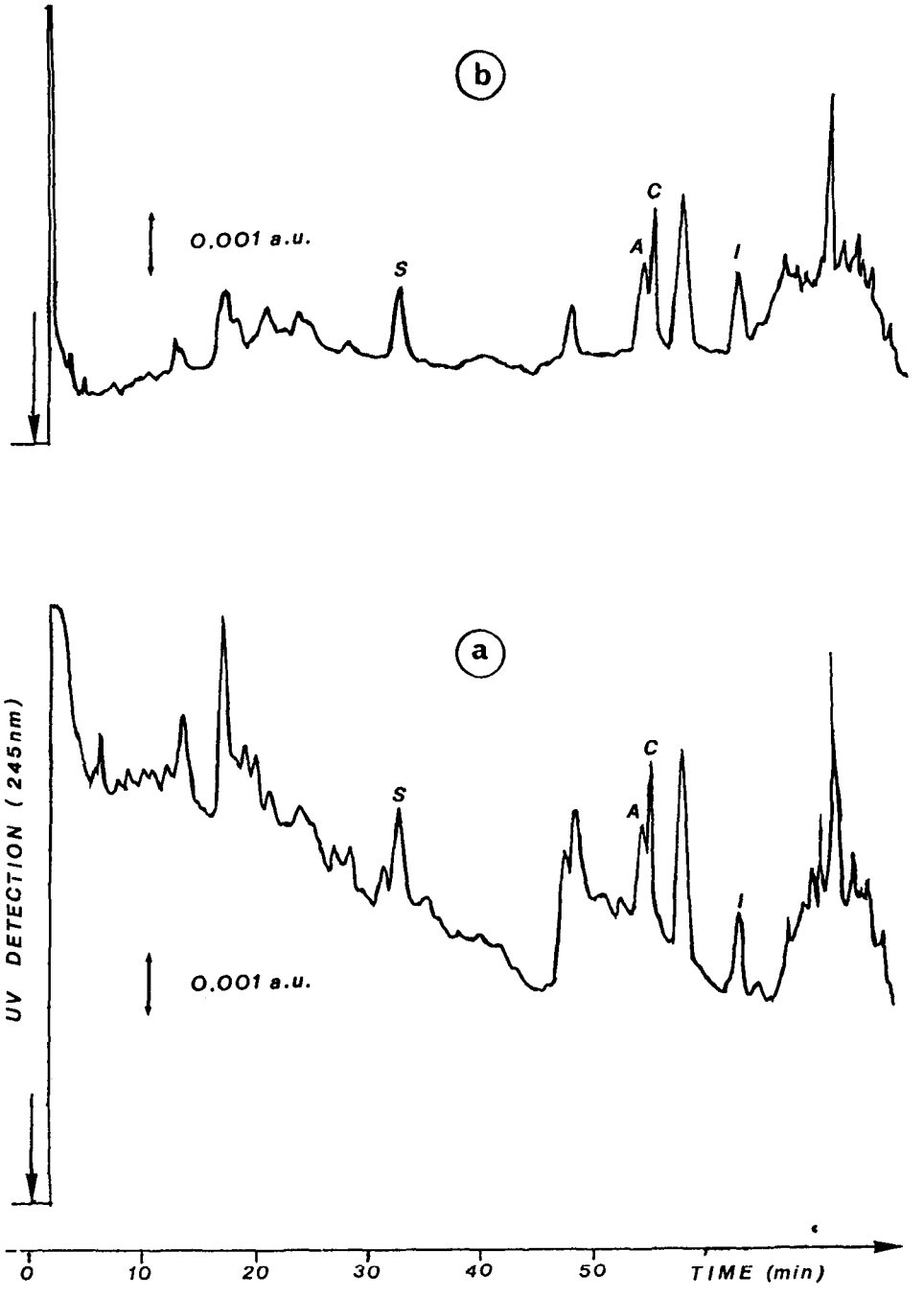

Fig. 3. Clean-up effect. On-line analysis after preconcentration of a non-spiked 500-ml River Seine sample (Paris, April 24th, 1989); elution of the PRP-1 precolumn (a) without clean-up and (b) with flushing with 1 ml of water modified with 10% of acetonitrile. UV detection at 245 nm; other conditions as in Fig. 2 except the analytical column was packed with Nucleosil C_{18}.

RP-18 and PRP-1 has been shown to be a suitable choice for a good fractionation between interferences and moderately polar analytes.

Further clean-up. It is possible to flush the PRP-1 precolumn before its elution by a small volume of water modified with an organic solvent in order to remove some more interferences. This method is widely applied to on-line and off-line preconcentration of apolar analytes which are not eluted from the precolumn by the flushing solution. However, for more polar analytes, elution can occur and tests should be carried out to verify that there is no loss of sorbed analytes during this flushing.

Experiments were carried out with river water samples. Volumes of 500 ml of spiked river water samples were preconcentrated through the two precolumns and the PRP-1 precolumn was flushed before its on-line elution with a few millilitres of water modified with 10–20% of acetonitrile (ACN). With 3 ml of water containing 20% of ACN, some analytes are eluted. Decreasing the ACN content to 10% still does not prevent the loss of the more polar compounds. With 1 ml containing 10% of ACN, the recoveries of metoxuron and simazine are 80% and of other analytes 100%. One can expect this flushing to have a small effect only on the more polar interferences, but Fig. 3 shows that this flushing effect helps to obtain a clearer chromatogram: the background is much higher without flushing (Fig. 3a), especially at the beginning of the chromatogram. In this river water sample, four herbicides have been identified: simazine (*ca.* 0.6 ppb), atrazine (*ca.* 0.6 ppb), chlortoluron (*ca.* 0.2 ppb) and isoproturon (*ca.* 0.2 ppb).

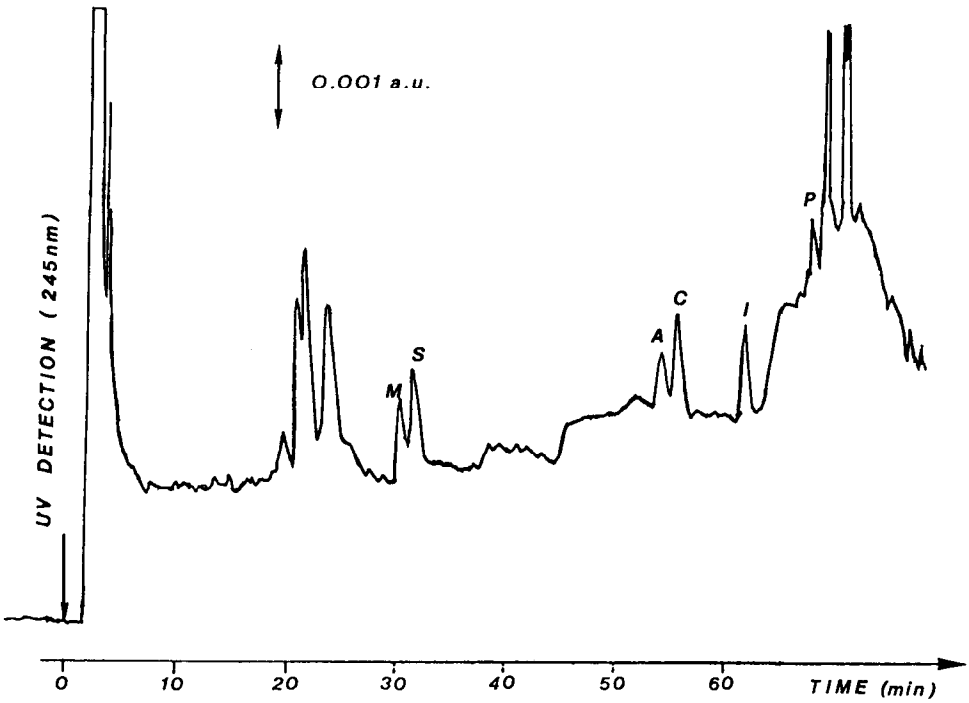

Fig. 4. On-line analysis of the PRP-1 precolumn after preconcentration of a 500-ml drinking water sample (Paris, May 1990) spiked with 0.1 μg/l of each herbicide. The PRP-1 precolumn was flushed with 1 ml of water modified with 10% of acetonitrile. UV detection at 245 nm; other conditions as in Fig. 3.

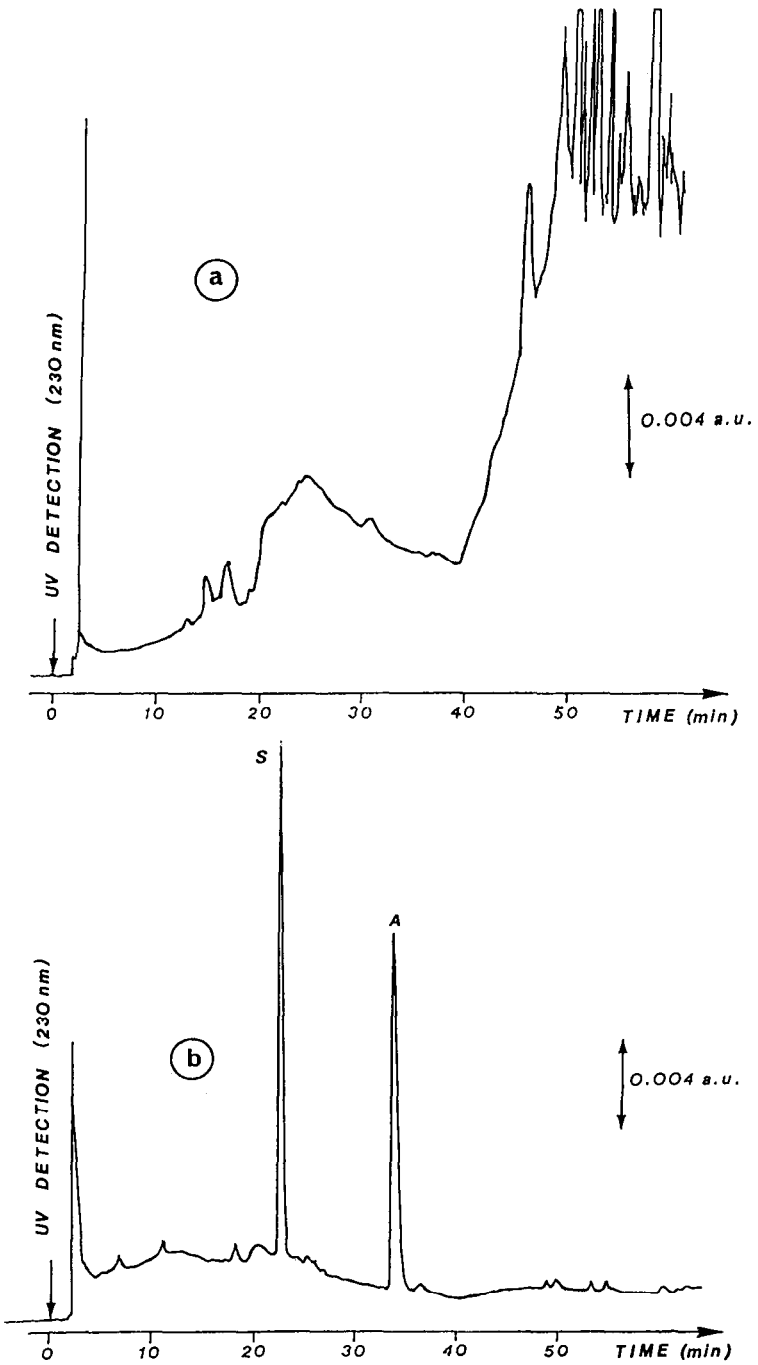

Fig. 5. Filter effect of the PRP-1 precolumn. On-line analysis after preconcentration of a non-spiked 500-ml River Seine sample (Paris, April 24th, 1989; same sample as in Fig. 3). (a) On-line analysis of the PRP-1 precolumn; (b) on-line analysis of the cation-exchange precolumn; preconcentration at pH 6 through a 15 mm × 3.2 mm I.D. precolumn packed with 7-μm copolymer PRP-1, transfer to 10 mm × 2 mm I.D. precolumn packed with 15–20-μm BC-X8 cation exchanger with 3 ml of 0.1 *M* perchloric acid modified with 25% of acetonitrile. Analytical column: 15 cm × 4.6 mm I.D. packed with 5-μm Nucleosil C_{18}; mobile phase, acetonitrile gradient with a 0.05 *M* perchloric acid–lithium perchlorate at pH 4 at a flow-rate of 1.5 ml/min; gradient, 15% acetonitrile from 0 to 20 min, 23.5% from 20 to 35 min and up to 46% at 60 min; UV detection at 230 nm.

Detection limits. In river water samples, under the selected chromatographic conditions, *i.e.*, fractionation for the preconcentration and further clean-up, the detection limits (signal-to-noise ratio ≈ 3) in 500-ml samples are about 0.1 ppb for triazines with UV detection at 254 nm and 0.05–0.1 μl/l for phenylureas with either UV detection at 245 nm or electrochemical detection.

The detection limits obtained in 500-ml drinking water samples by the same method are lower than those obtained in river water, owing to the less numerous interferences. In Fig. 4, the PRP-1 chromatogram of a 500-ml drinking water sample spiked with 0.1 μg/l of each analyte indicates that quantitative analyses can be performed at this level.

Interference removal using a non-selective and a selective sorbent (chlorotriazines)

Description of the methodology. Chlorotriazines can be selectively preconcentrated by a cation exchanger if the pH of the aqueous sample is adjusted below 1, which involves the use of a polymer-based cation exchanger. Nevertheless, the sample cannot be directly percolated through a precolumn packed with this specific sorbent because of the large amount of inorganic cations which would quickly overload the precolumn. A sample clean-up can remove these inorganic cations (precipitation with sodium oxalate and complexation with EDTA), but traces of inorganics are still present and the sample volume of raw water which can be passed through the cation-exchange precolumn is limited to 30 ml [24]. To avoid the direct percolation through the cation exchanger and to remove both organic and inorganic interferences, a two-step preconcentration is carried out, as described in detail previously [27]. It is based on the difference in retention observed on a PRP-1 sorbent for triazines, depending on whether they are in their neutral or cationic form. The first step consists in percolation of the 500-ml sample adjusted to pH 7 through a PRP-1 precolumn. Then a small volume of well demineralized water at pH 1 and modified with 20% of ACN allows the organic cations to be desorbed alone from this PRP-1 precolumn and to be transferred and preconcentrated by a second precolumn packed with a cation exchanger which is analysed on-line. Fig. 5 shows the analysis of the same 500-ml river water sample as in Fig. 3. Only simazine and atrazine are detected of the four herbicides present, but, in comparison with Fig. 3, the peaks are much more intense and the baseline is free from interferences (Fig. 5b). This is due to the efficient removal of many neutral interferences which are left on the PRP-1 precolumn, as visible in the eluate of the PRP-1 content in Fig. 5a. Consequently, it was possible to detect triazines at 230 nm, close to their maximum UV absorbance (220 nm). Detection at 230 nm was impossible in Fig. 3 owing to a more important background, indicating a higher UV absorbance of interferences at 230 nm. The inverse was observed in the eluate of the cation exchanger. Fig. 6 shows the UV chromatograms, at two different wavelengths, corresponding to the same cation exchange eluate from a 500-ml river water sample; interferences showed a higher UV absorbance at 254 nm than that obtained at 230 nm, thus indicating the presence of protonated aromatic compounds. The corresponding electrochemical detection was free from interferences, so that these aromatic interferences were not oxidizable.

Detection limits. With this methodology coupling a powerful interference removal and a selective trapping of chlorotriazines, one can expect lower detection limits. In fact, the detection limits obtained with natural water samples are of the

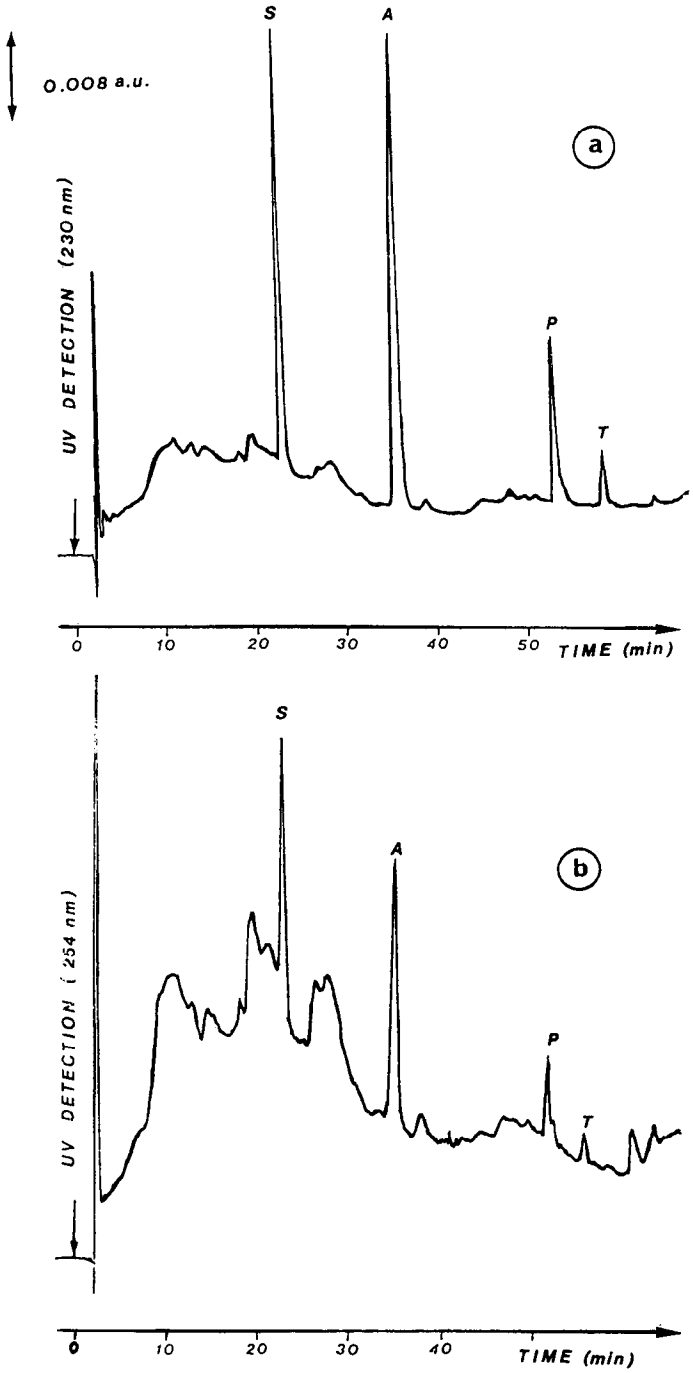

Fig. 6. Influence of the UV detection wavelength. On-line analysis of the cation-exchange precolumn after preconcentration of a 500-ml River Yerres sample spiked with 1 μg/l of each chlorotriazine. UV detection at (a) 230 nm and (b) 254 nm; experimental conditions as in Fig. 5.

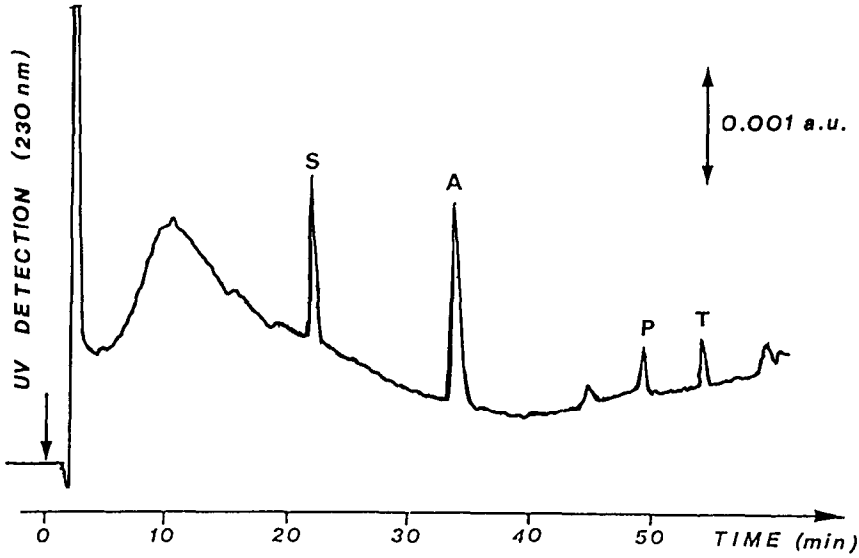

Fig. 7. Preconcentration and on-line analysis of a 500-ml drinking water sample from Paris, April 1990, containing simazine (30 ng/l), atrazine (35 ng/l) and propazine (20 ng/l), terbutylazine (20 ng/l). Experimental conditions as in Fig. 5.

same order as those obtained when injecting analytes directly into the analytical column. Fig. 7 shows the analysis of a drinking water sample containing 30 ng/l of simazine, 35 ng/l of atrazine and 20 ng/l each of propazine and terbutylazine. The detection limits are very low and have been calculated as 2–5 ppt in 500-ml samples (signal-to-noise ratio = 3). Baselines obtained with river water have the same quality as those obtained with drinking water samples, so that detection limits in river water samples are as low as those for drinking water samples. This clearly demonstrates that to lower detection limits, one has to search for selective preconcentrations. However, depending on the selective sorbent, it may be necessary also to remove interferences.

CONCLUSION

The results clearly show that there is an advantage in combining two precolumns for trace organic preconcentration from aqueous environmental samples with an efficient removal of many matrix interferences by the first precolumn and a selective trapping of analytes by the second. This permits analytes to be determined quantitatively and accurately below the 0.1 ppb level. When no selective sorbent can be found, an efficient fractionation of interferences from analytes can help to achieve low detection limits, which are higher than those obtained with the use of a selective sorbent.

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REFERENCES

1 P. Subra, M.-C. Hennion and R. Rosset, *Analusis*, 17 (1989) 163.
2 I. Liska, J. Krupcik and P. A. Leclercq, *J. High. Resolut. Chromatogr.*, 12 (1989) 577.
3 F. I. Onuska, *J. High. Resolut. Chromatogr.*, 12 (1989) 4.
4 M.W. F. Nielen, R. W. Frei and U. A. Th. Brinkman, in R. W. Frei and K. Zech (Editors), *Selective Sample Handling and Detection in HPLC*, Elsevier, Amsterdam, 1988, pp. 5–78.
5 E. Noroozian, F. A. Maris, M. W. F. Nielen, R. W. Frei, G. J. de Jong and U. A. T. Brinkman, *J. High. Resolut. Chromatogr.*, 10 (1987) 17.
6 K. Grob, Jr. and Z. Li, *J. Chromatogr.*, 473 (1989) 423.
7 J. J. Vreuls, W. J. G. M. Cuppen, G. J. de Jong and U. A. T. Brinkman, *J. High. Resolut. Chromatogr.*, 13 (1990) 157.
8 F. Munari and K. Grob, *J. Chromatogr.*, 26 (1990) 61.
9 D. Barcelo, *Chromatographia*, 25 (1988) 928.
10 J. F. Lawrence, *Chromatographia*, 24 (1987) 45.
11 M. W. F. Nielen, U. A. Th. Brinkman and R. W. Frei, *Anal. Chem.*, 57 (1985) 806.
12 R. W. Frei, G. J. De Jong, U. A. Th. Brinkman, *Analusis*, 15 (1987) 59.
13 P. Subra, M.-C. Hennion, R. Rosset and R. W. Frei, *Int. J. Environ. Anal. Chem.*, 37 (1989) 45.
14 P. Subra, M.-C. Hennion, R. Rosset and R. W. Frei, *J. Chromatogr.*, 456 (1988) 121.
15 C. E. Werkhoven-Goewie, U. A. Th. Brinkman and R. W. Frei, *Anal. Chem.*, 53 (1981) 2072.
16 W. Golkiewicz, C. E. Werkhoven-Goewie, U. A. Th. Brinkman, R. W. Frei, H. Colin and G. Guiochon, *J. Chromatogr. Sci.*, 21 (1983) 2.
17 M. W. F. Nielen, H. E. Van Ingen, A. J. Valk, R. W. Frei and U. A. Th. Brinkman, *J. Liq. Chromatogr.*, 10 (1987) 617.
18 M. W. F. Nielen, R. Bleeker, R. W. Frei and U. A. Th. Brinkman, *J. Chromatogr.*, 358 (1986) 393.
19 R. B. Geerdink, *J. Chromatogr.*, 445 (1988) 273.
20 J.-L. Veuthey, M.-A. Bagnoud and W. Haerdi, *J. Chromatogr.*, 393 (1987) 51.
21 J.-L. Veuthey, M.-A. Bagnoud and W. Haerdi, *Int. J. Environ. Anal. Chem.*, 26 (1986) 157.
22 M. W. F. Nielen, G. J. De Jong, R. W. Frei and U. A. Th. Brinkman, *Int. J. Environ. Anal. Chem.*, 25 (1986) 37.
23 M. W. F. Nielen, U. A. Th. Brinkman and R. W. Frei, *J. Chromatogr.*, 317 (1984) 55.
24 M.-C. Hennion, P. Subra, V. Coquart and R. Rosset, *Fresenius' Z. Anal. Chem.*, 339 (1991) 448.
25 T. Braumann, G. Weber and L. H. Grimme, *J. Chromatogr.*, 261 (1983) 329.
26 R. G. Luchtefeld, *J. Chromatogr. Sci.*, 23 (1985) 516.
27 V. Coquart and M.-C. Hennion, *J. Chromatogr.*, (1991) in press.
28 M.-C. Hennion, P. Subra, R. Rosset, J. Lamacq, P. Scribe and A. Saliot, *Int. J. Environ. Anal. Chem.*, 42 (1990) 15.
29 C. E. Goewie, M. W. F. Nielen, R. W. Frei and U. A. Th. Brinkmann, *J. Chromatogr.*, 301 (1984) 325.