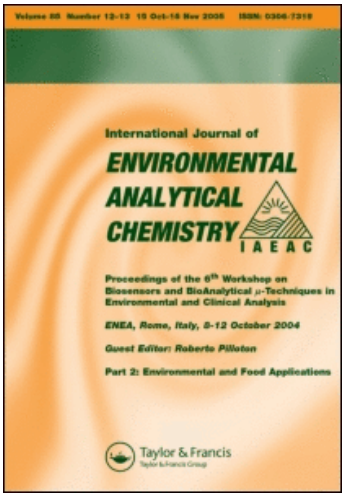

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Trace-Level Determination Of Hydroxyatrazine And Dealkylated Degradation Products Of Atrazine In Waters

V. Coquart[a]; P. Garcia-camacho[a]; M-C Hennion[a]
[a] Laboratoire de Chimie Analytique, Ecole Supérieure de Physique et Chimie de Paris, Paris Cedex 05, France

To cite this Article Coquart, V. , Garcia-camacho, P. and Hennion, M-C(1993) 'Trace-Level Determination Of Hydroxyatrazine And Dealkylated Degradation Products Of Atrazine In Waters', International Journal of Environmental Analytical Chemistry, 52: 1, 99 — 112
To link to this Article: DOI: 10.1080/03067319308042852
URL: http://dx.doi.org/10.1080/03067319308042852

Intern. J. Environ. Anal. Chem., Vol. 52, pp. 99-112
Reprints available directly from the publisher
Photocopying permitted by license only

TRACE-LEVEL DETERMINATION OF HYDROXYATRAZINE AND DEALKYLATED DEGRADATION PRODUCTS OF ATRAZINE IN WATERS

V. COQUART, P. GARCIA-CAMACHO and M-C. HENNION*

Ecole Supérieure de Physique et Chimie de Paris, Laboratoire de Chimie Analytique, 10 rue Vauquelin, 75231 Paris Cedex 05, France

(Received, 9 July 1992; in final form, 9 October 1992)

Dealkylated degradation products of atrazine, dealkyl- and deisopropyl-atrazine have been now detected in environmental waters, but determination of hydroxyatrazine has not been reported just because this product is not amenable to GC–MS. An analytical procedure has been developed for the simultaneous trace-level determination of some widely used chorotriazines and of three main degradation products, deisopropyl-, deethyl- and hydroxy-atrazine, using a selective solid-phase-extraction coupled on-line to liquid chromatography. The preconcentration has been carried out with two precolumns in series. The first one, packed with the PRP-1 sorbent allowed the preconcentration of hydroxyatrazine and other metabolites. Analytes of interest were then desorbed from the PRP-1 precolumn in their ionic form and transferred to a second precolumn packed with a cation exchanger, which was afterwards coupled on-line to an analytical C18 column. The use of the selective cation-exchanger sorbent for the preconcentration and of the on-line HPLC analysis led to detection limits as low as 2–5 ng/l in samples from the river Seine, without any clean-up procedure.

KEY WORDS: Hydroxyatrazine, deethylatrazine, deisopropylatrazine, on-line preconcentration, HPLC.

INTRODUCTION

Chlorotriazine herbicides, especially atrazine, have been extensively used during the past 20 years and are now present in soils and also in surface and ground waters[1–7]. Atrazine can be degraded by mechanisms involving dealkylation, deamination, dehalogenation and hydroxylation. The main degradation products detected in waters up to now are deethyl- and deisopropyl-atrazine at concentration generally below 100–200 ng/l[4,5]. Recently, a gas chromatographic method was described for the determination of residue levels (below 0.1 μg/l) of deethyl- and deisopropylatrazine in drinking and ground water[8]. An important pathway for triazine degradation is also their conversion to hydroxy analogues[2,5,9,10] and

* Presented at the 22nd International Roland W. Frei Memorial Symposium on Environmental Analytical Chemistry, Dortmund, 9–12 June, 1992)

hydroxyatrazine has been detected in soils[2,11]. However, its determination in real waters has not been reported. This analyte is more difficult to be determined at a trace level than other dealkylated metabolites in waters for the following reasons: (i) its concentration by usual methods is not quantitative[12], (ii) its analysis by gas chromatography (GC) is difficult owing to its polarity and thermal unstability, (iii) in liquid chromatography (LC), its detection is not sensitive owing to a much lower UV absorption than atrazine at 220 nm. Analytical methods have been described for determination of hydroxyatrazine in soils with detection limits in the ppb range[13].

Analytical procedures with detection limits in the ng/l range (ppt) in waters are required for a better knowledge of the transport and fate of atrazine down to ground waters and for studying its transformation in treatment plants for drinking water supply. Detection at low levels in surface waters can be obtained either with a selective preconcentration step or by carrying out a drastic removal of interferents (clean-up) with a non-selective preconcentration[14].

In a previous study[15], we have described an analytical on-line procedure allowing the determination of chlorotriazines in environmental waters at the ng/l level using a selective preconcentration with a cation-exchanger, coupled on-line with the liquid chromatographic analysis. As the direct percolation of large water volumes through a cation-exchanger precolumn is impossible owing to the high concentration of inorganic cations in natural waters, a two-step preconcentration was carried out, using a first trapping on a copolymer-based apolar PRP-1 sorbent and a transfer to the cation-exchanger at low pH values (ionisation constants of chlorotriazines between 1.6 and 2).

In this work, a similar strategy was optimised for the trace-level determination of the more polar degradation products of chlorotriazines.

EXPERIMENTAL

Apparatus

Percolation of water samples were performed with a Chromatem pump (Touzart et Matignon, Paris, France). Precolumn elution and analyses were carried out with a Varian 5060 liquid chromatograph (Palo Alto, CA, U.S.A.) equipped with a variable-wavelength UV 200 spectrophotometer. Precolumn and analytical column switching was connected with Rheodyne valves (Berkeley, CA, U.S.A.). Quantitative measurements of peak areas were provided by a CR3A integrator-computer from Shimadzu (Kyoto, Japan).

Stationary phases and columns

The analytical columns were a 25 cm × 4.6 mm I.D stainless-steel column prepacked with the spherical 5-μm octylsilica Zorbax (Interchim, Paris, France) and a 15 cm × 0.46 cm I.D. stainless-steel column prepacked with the 5-μm octadecylsilica Intersphere ODS-2 (Interchim, Paris, France). Samples were preconcentrated on a 15 mm × 3.2 mm I.D. precolumn prepacked with the 7-μm PRP polystyrene-divinylbenzene polymer (Brownlee Columns,

Applied Biosystem, Inc, San Jose, CA, USA) or with laboratory-made precolumns packed with the 10-μm PRP-1 sorbent (Hamilton, Reno, Nevada, USA). The cation-exchanger precolumn was a 10 mm × 2 mm I.D. stainless-steel precolumn available from Chrompack (Middelburgh, the Netherlands) which was hand-packed with the sulphonic acid-type resin-based cation-exchanger BC-X8, 15–20μm (Benson Co, Reno, Nevada, U.S.A.) using a thick slurry and a microspatula.

Chemicals

HPLC-grade acetonitrile was 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. Final standard solutions did not contain more than 0.5% methanol.

Procedure

The experimental set up with the possibility of using two precolumns in series is described in ref. 16. The following procedure was adopted:

(1) Percolation of a natural water sample adjusted at pH 7–8 through the PRP-1 precolumn;
(2) Flushing the PRP-1 precolumn with 2 ml of LC grade water;
(3) Transfer of analytes to the exchanger precolumn: the PRP-1 precolumn is coupled with the 10 mm-long cation-exchanger precolumn and a mixture of acetonitrile and water acidified at pH 1 with perchloric acid is percolated through the two precolumns in series;
(4) Flushing of the two precolumns with 2 ml of LC grade water;
(5) Backflush desorption from the cation exchanger to the analytical column by a methanol gradient with a potassium phosphate buffer 0.05 M at pH 7;
(6) Regeneration of the exchanger precolumn with 25 ml of 10^{-3} M perchloric acid for a second transfer if necessary (with steps 3 to 5);
(7) Regeneration of the PRP-1 precolumn with 10 ml of pure acetonitrile and then with 20 ml of LC-grade water;

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

RESULTS AND DISCUSSIONS

Investigated analytes are deethylatrazine, deisopropylatrazine (as a result of dealkylation of

Table 1 Characteristics of 2-chloro- or 2-hydroxy-1,3,5 triazines. pKa values are determined from Fig. 1 or taken (pKa*) from ref. 17.

N°	Compound	Substituents in position 4-	6-	pKa
1	Deisopropylatrazine	$-NHC_2H_5$	$-NH_2$	1.3 + 0.2
2	Deethylatrazine	$-NH_2$	$-NHCH(CH_3)_2$	1.3 + 0.2
3	Hydroxyatrazine	$-NHC_2H_5$	$-NHCH(CH_3)_2$	5.2*; 4.9 + 0.2
4	Simazine	$-NHC_2H_5$	$-NHC_2H_5$	1.65*
5	Atrazine	$-NHC_2H_5$	$-NHCH(CH_3)_2$	1.7*
6	Propazine	$-NHCH(CH_3)_2$	$-NHCH(CH_3)_2$	1.85*
7	Terbutylazine	$-NHC_2H_5$	$-NHC(CH_3)_3$	1.95*

atrazine or simazine) and hydroxyatrazine, as hydroxylated degradation product of atrazine. Four widely used chlorotriazines have also been included in this study. Their chemical structures and ionisation constants are reported in Table 1.

Determination of analyte ionisation constants

The analytical strategy described above can be applied to degradation products only if these analytes can be ionised at low pH values. Only hydroxyatrazine pKa was found in the literature[17]. Other pKa constants were not measured directly but were estimated using chomatography by the variation of their retention times with pH values. The analytical column selected was packed with the PRP-1 sorbent which can be used over the pH range 1–13. In reversed-phase chromatography, the retention time of a ionisable analyte depends on its ionisation state. When the pH of the mobile phase is lower than pKa-2, the analyte is in its ionic form and is generally slightly retained by π-π interactions between the polymeric matrix and the organic cation. For pH values higher than pKa+2, the solute is in its neutral form and its retention is higher. The retention time increases between these two values and the inflexion point corresponds to a pH value around pKa. These variations are at the basis of the two step preconcentration strategy, the analytes being adsorbed in their molecular form by the first precolumn packed with PRP-1 and being desorbed in their ionic form. Results have been reported in Figure 1.

The variation of the capacity factor of hydroxyatrazine shows that it is ionisable in the range studied, but dealkylated products are ionised for pH values below 1.5. The estimated ionisation constants are in Table 1. These values are certainly not exact because the mobile phase was not pure water but contained acetonitrile. As expected, the substitution of an hydroxy group instead of a chloro leads to a much higher ionisation constant for hydroxyatrazine, about 5 instead of 1.7 for atrazine. Ionisation constants of deethyl- and deisopropylatrazine are slightly lower than those of simazine or atrazine, between 1.3 and 1.5.

Retention on PRP-1 sorbent

Previous studies have shown that the PRP-1 copolymer retained chlorotriazines in water

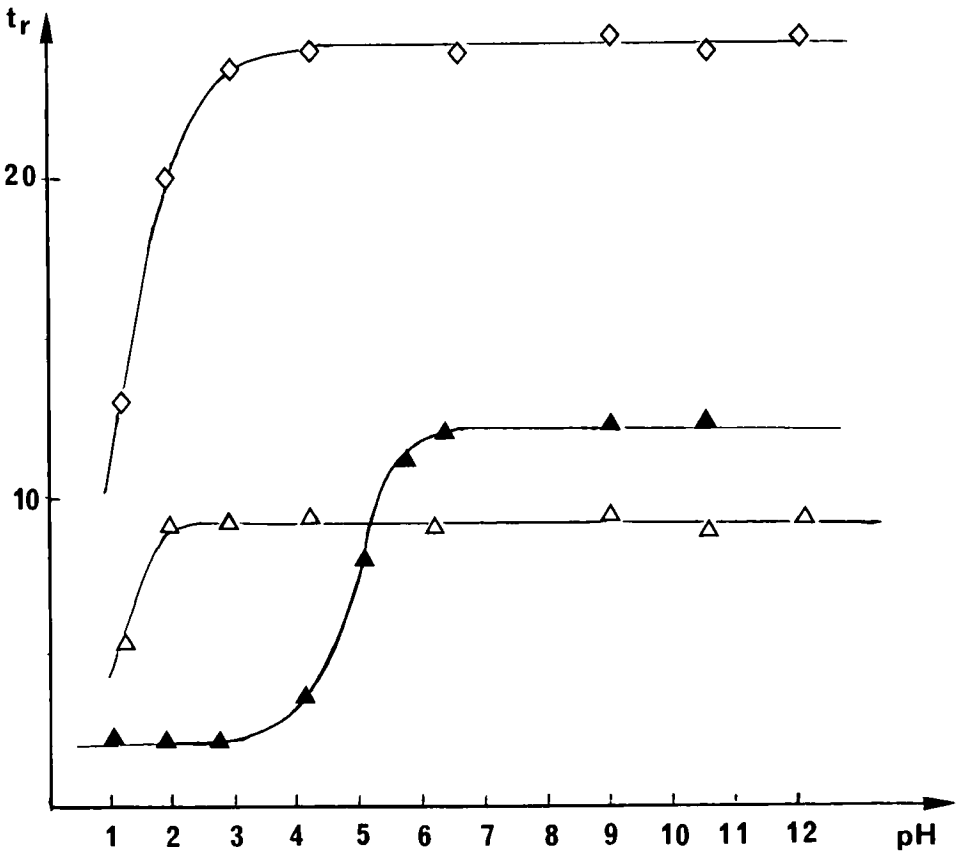

Figure 1 Variation of retention times (min) with pH of the mobile phase. Compounds: ▲ = Hydroxyatrazine; △ = deisopropylatrazine; ◊ = deethylatrazine; Column: 10 cm × 0.46 cm I.D. packed with 10-µm PRP-1 stationary phase; Mobile phase: 10% of acetonitrile with water adjusted at different pH with perchloric acid or sodium hydroxyde for deethyl- and deisopropylatrazine and 20 % of ACN for hydroxyatrazine; Flow rate: 1 ml/min; Direct injection with a 20-µl loop; UV detection at 220 nm.

much more than C18 silica[15,16,18] and was a suitable sorbent for preconcentration. This is explained by π-π interactions that occur between the aromatic structure of the network of the polymeric sorbent and the double bonds in the structure of chlorotriazines.

Breakthrough volumes were not measured directly but were estimated by comparison of the chromatograms obtained after preconcentration of increasing volumes of water samples spiked with decreasing concentration in order to have always the same quantity of analytes in samples[16]. These experiments were made by using a 2.2 cm × 0.46 cm I.D. precolumn packed with PRP-1 and on line elution of this precolumn. As far as breakthrough does not occur, the amounts preconcentrated are constant and peak heights obtained when eluting the PRP-1 precolumn are also constant. When breakthrough occurs for a solute, the corresponding peak heights decrease and recoveries can be calculated by ratio of peak heights. Estimated breakthrough volumes are reported in Table 2.

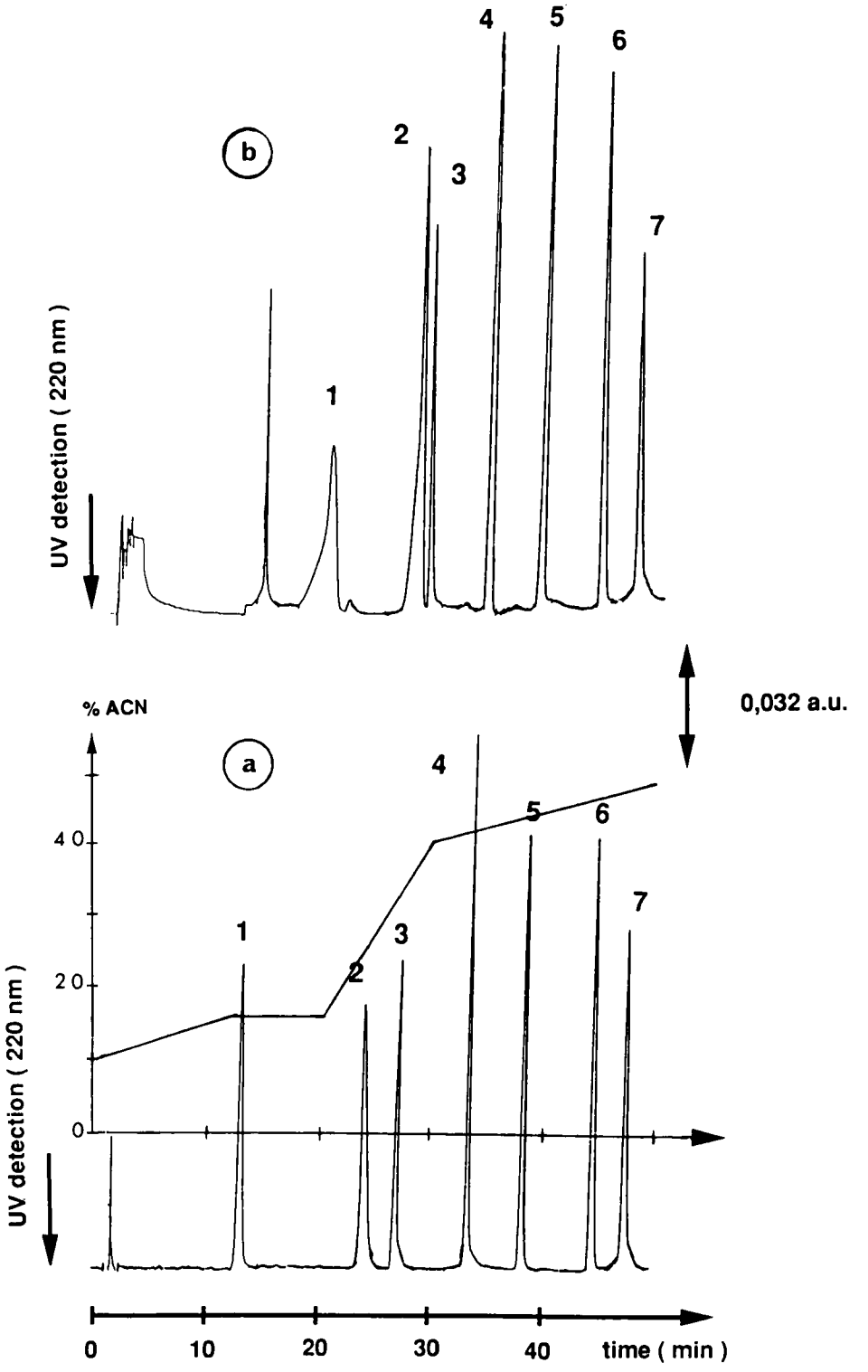

Table 2 Breakthrough volumes (in ml) estimated with a 2.2 cm × 0.46 cm I.D. precolumn packed with PRP-1. See text for determination.

Compound	*Breakthrough volume (ml)*
Deisopropylatrazine	80 ± 10
Deethylatrazine	100 ± 15
Hydroxyatrazine	150 ± 20
Simazine	> 1000
Atrazine	> 1000

In comparison with breakthrough values obtained for simazine and atrazine which are higher than 1 l, degradation products are much less hydrophobic with breakthrough volumes around 100 ml. In a previous study[19], using a 1 cm × 0.21 cm I.D. precolumn packed also with PRP-1, breakthrough volumes of simazine and atrazine were measured to 130 ml and above 250 ml respectively. The precolumn selected here has a volume about ten times higher so that breakthrough volume of simazine is estimated to 1300 ml.

Taking into account that the sample volume can be slightly larger than breakthrough volume with an increase in the amount preconcentrated, this 2.2-cm long precolumn can allow the handling of a sample volume up to 150–200 ml. If detection limits are too high, the sample volume has to be increased and then a larger PRP-1 precolumn is required. A large size precolumn was made (5 cm × 0.6 cm I.D.) for this purpose. One advantage is that water sample can be percolated with high flow rate up to 10 ml/min. One disadvantage is that it cannot be coupled on-line with the HPLC separation, but it is not a important drawback since the content of cation-exchanger precolumn is alone on-line analysed.

Analytical separation

The analytical separation of degradation products and four chlorotriazines has been optimised for an on-line coupling. When carrying out this technique, it is advisable to elute the first peak after 10 min, because of the presence of a large interfering peak at the beginning of the chromatogram. It can be noticed that the band broadening depends on the slope of the applied mobile phase gradient. As the maximum of UV absorbance is obtained at 220 nm for degradation products, it is better to use acetonitrile instead of methanol. Figure 2a represents the optimum separation obtained with a water-acetonitrile gradient. Nevertheless, when the cation-exchanger precolumn is coupled on-line to the analytical column, a large band broadening is observed for the first two dealkylated metabolites, due to the shape of the gradient, as shown in the chromatogram 2b. Accurate determinations of traces of hydroxyatrazine in presence of deethylatrazine are therefore difficult to be obtained.

Figure 2 Effect of the gradient shape in on-line preconcentration. (a) Direct loop-injection of a standard solution of chlorotriazines and degradation products, (b) Preconcentration and on-line elution of 50 ml of LC-grade water spiked with 10 µg/l of each compound. Compounds: numbers corresponding are in Table 1; precolumn: 2.2 cm × 0.46 I.D. packed with PRP-1; Analytical column: 15 cm × 0.46 cm I.D. packed with 5-µm C18 silica, Intersphere ODS-2; Mobile phase: acetonitrile gradient with a potassium phosphate buffer at pH 7 as represented in (a); flow-rate: 1 ml/min; UV detection at 220 nm.

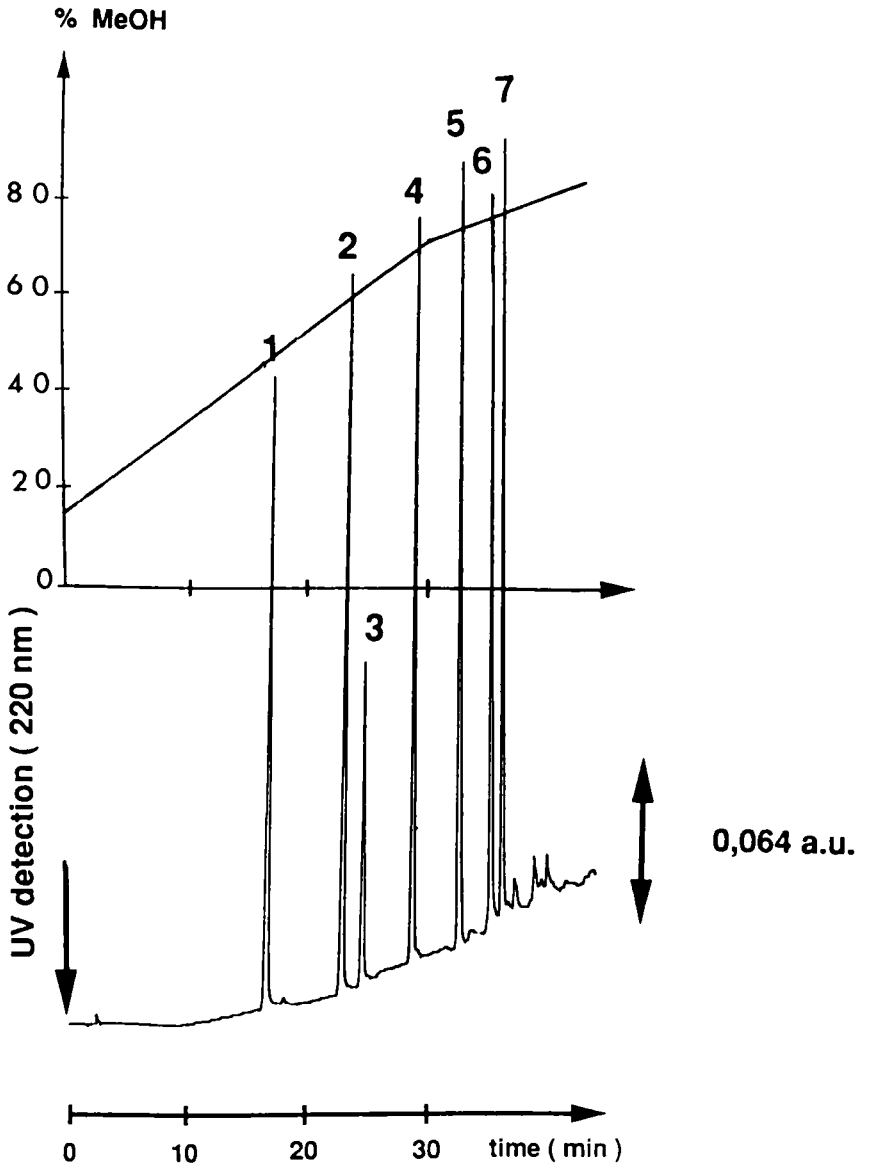

Figure 3 Direct loop-injection of a standard solution of chlorotriazines and degradation products with a methanol gradient. Compounds: numbers corresponding are in Table 1; Analytical column: 25 cm × 0.46 cm I.D. packed with 5-μm C8 silica, C8 Zorbax; Mobile phase: methanol gradient with a potassium phosphate buffer at pH 7 as represented; flow-rate: 1 ml/min; UV detection at 220 nm.

Changing the characteristics of the C18 or C8 column did not improve the separation. A similar separation was obtained with a methanol-water gradient with a difference in the slope of the applied gradient, as shown in Figure 3. The stronger increase in methanol during the gradient helped for the transfer and the band broadening was less important as can be

observed in Figure 4. A major drawback due to methanol is its UV absorption at low wavelengths, causing an increase in the base line signal when the methanol content increases. The base line can be recorded at different attenuation with a blank gradient and can be substracted.

Optimisation of the two-step preconcentration

Desorption from the first PRP-1 precolumn and transfer to the second cation-exchanger precolumn are carried out at the same time by flushing the two precolumns in series with a "transfer solution". Its volume and composition must allow a complete desorption and an efficient fixation on the cation exchanger. Figure 4 shows the difficulty encountered for both a complete desorption from PRP-1 and a complete fixation on the cation-exchanger for each analyte. When using the 2.2 cm × 0.46 cm I.D. PRP-1 precolumn, a first transfer was carried out by washing the two precolumns in series with 2 ml of a solution of perchloric acid 0.1M (pH=1) containing 35% of acetonitrile (Figure 4a).

Degradation products are well recovered from the cation-exchanger precolumn but not

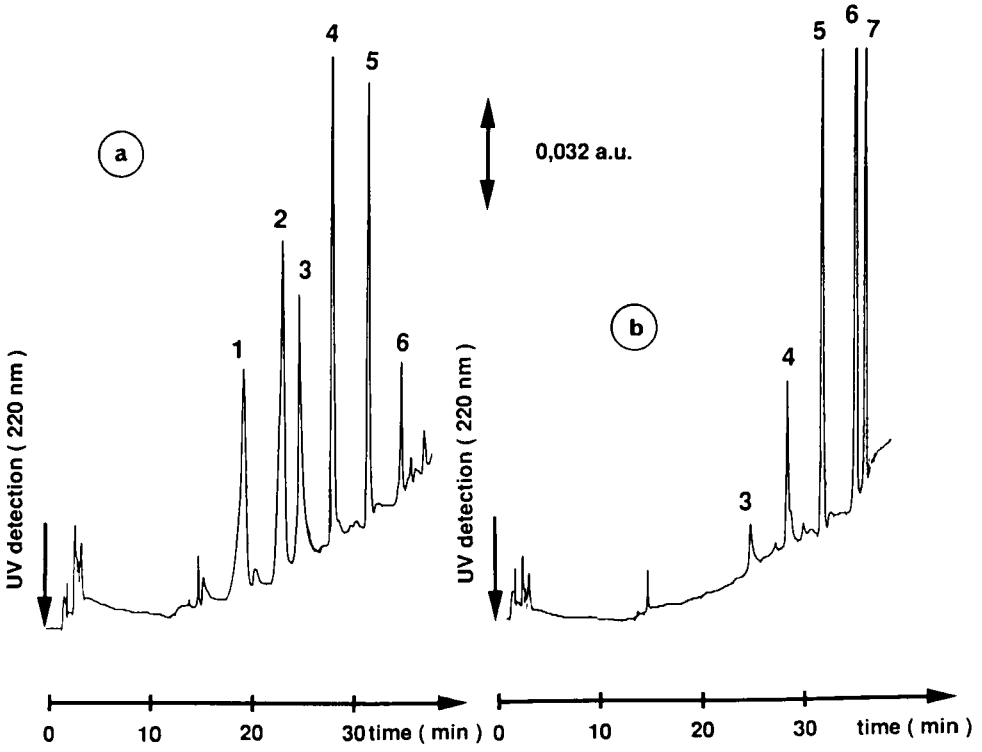

Figure 4 Effect of the composition of the transfer solution. Preconcentration and on-line analysis of 10 ml of LC-grade water spiked with 50 µg/l of each compound. (a) first transfer by washing the two precolumns in series with 2 ml of a perchloric acid solution at pH 1 containing 35 % of ACN. (b) second transfer by washing the two precolumns in series with 2 ml of a perchloric acid solution at pH 1 containing 30 % of ACN. Same other experimental conditions as in Figure 3.

the apolar propazine and terbutylazine, which are left on the PRP-1 precolumn. As triazines are only partially ionised at pH 1, it is necessary to add some acetonitrile (ACN) to help for desorption from PRP-1 for the most apolar ones. If too much ACN is added, apolar solutes are desorbed and transferred, but breakthrough occurs on the cation-exchanger for the polar degradation products and very low recoveries are therefore obtained for these polar products. In our experiment, a solution was found by applying two subsequent transfers. A first transfer was carried out with a solution giving high recoveries for all polar products (Figure 4a). Then, after a rapid regeneration of the cation exchanger precolumn, a second transfer was made in order to desorb the apolar triazines and the corresponding chromatogram is represented in Figure 4b. This illustrates the fact that in trace analysis, it is sometimes difficult to analyse organics over a wide range of polarity.

When changing the size of the PRP-1 precolumn, the composition of the transfer solution was also optimised for high recoveries of degradation products. Table 3 reports the effect of both the volume and the ACN content of the transfer solution. The difference in recoveries obtained with 4 and 5 ml containing 35% of ACN illustrates again the difficulty encountered. A transfer volume of 4 ml is not large enough for efficiently desorbing atrazine from the PRP-1 precolumn and only a small amount is transferred on the cation exchanger, as shown by the 9 % recovery. When the volume is increased to 5 ml a higher amount is desorbed and transferred and the recovery is increased to 25 %. But, at the same time breakthrough occurs for deisopropylatrazine on the cation exchanger as shown by the decreasing recovery from 83 to 31 % when increasing the volume from 4 to 5 ml. It is not necessary to know exactly these recoveries because quantitative measurements are made by preconcentration and on-line analysis of spiked samples through the whole of the procedure. The repeatability of the method is then studied with on-line experimental conditions and is given below.

The final procedure was adopted: (i) with the 2.2 cm × 0.46 cm I.D. precolumn, first transfer with 2 ml of perchloric acid 0.1 M with 25% of ACN and second transfer with 2 ml and 30 % of ACN; (ii) with the 5 cm × 0.6 cm I.D. precolumn, first and second transfers with 4 ml of perchloric acid 0.1 M with 35 % of ACN.

Applications to drinking and river waters

Figure 5 represents the chromatogram corresponding to the analysis of 100 ml of drinking water non-spiked (a) and spiked (b) with 0.1μg/l of each compound. In the blank, there is

Table 3 Effect of the compositon of the transfer solution on the desorption from the PRP-1 precolumn (5cm × 0.46 cm I.D.) and on the fixation on the cation-exchanger precolumn (1 cm × 0.2 I.D.). Recoveries (%) are calculated by comparing peak areas obtained with the on-line analysis of a 25 ml spiked with 20 μg/l of analytes via the whole procedure and peak areas obtained by direct injection of the same amount of analytes (0.5 μg).

Transfer solution		*Compounds*				
ACN (%)	*Volume (ml)*	*Deisopropyl-*	*Deethyl-*	*Hydroxy-*	*Simaz.*	*Atraz.*
35	3	92	85	48	35	2
35	4	83	84	67	64	9
35	5	31	38	22	75	25
40	4	28	22	15	42	20

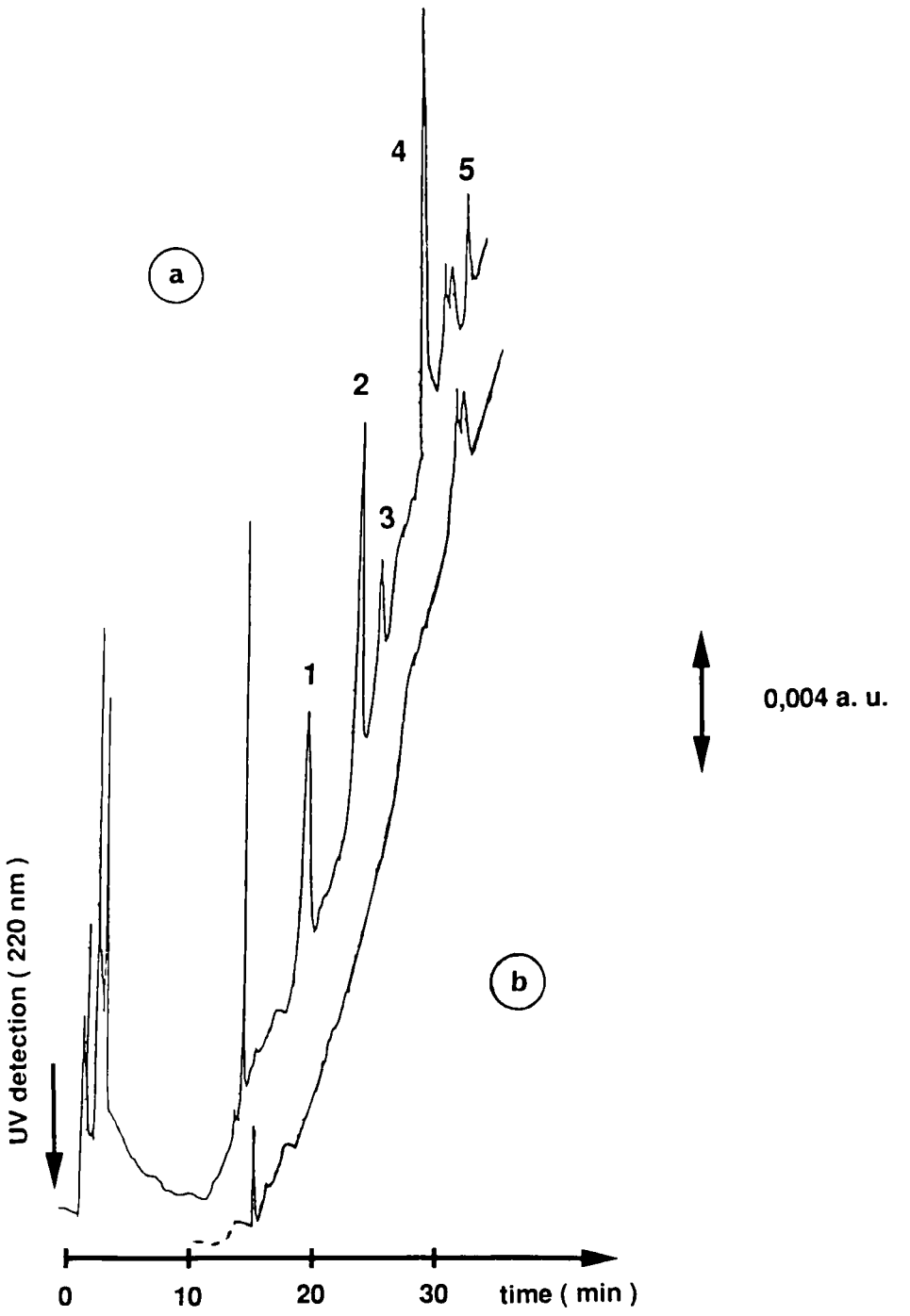

Figure 5 On-line analysis of a 100-ml drinking water sample. (a) non-spiked and (b) spiked with 0.1 μg/l of each compound. (sample taken in Paris, january 1992). Preconcentration using the 2.2 cm × 0.46 cm I.D. PRP-1 precolumn and tranfer to the cation-exchanger precolumn with 2 ml of perchloric acid solution at pH 1 containing 25 % of ACN. Other conditions: see Figure 3.

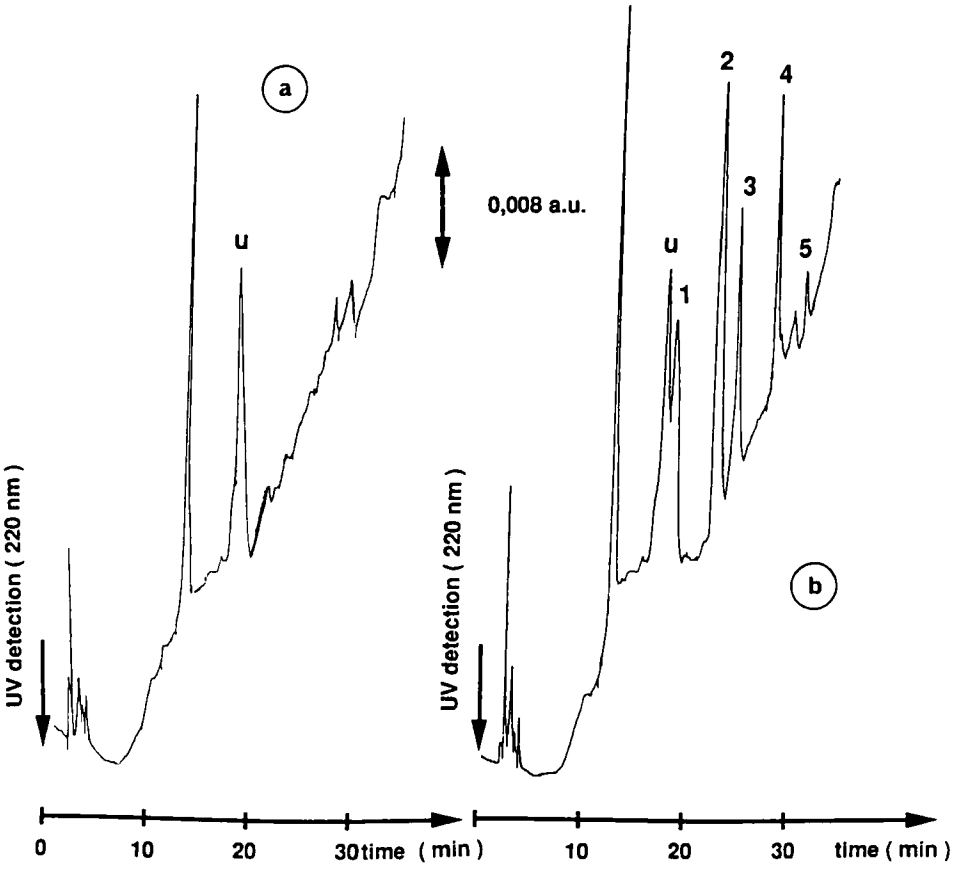

Figure 6 On-line analysis of a 500- ml river Seine water sample. (a) non-spiked and (b) spiked with 0.05μg/l of each compound. (sample taken in Paris, february 1992). Preconcentration using the 5 cm × 0.6 cm I.D. PRP-1 precolumn and tranfer to the cation-exchanger precolumn with 4 ml of perchloric acid solution at pH 1 containing 35 % of ACN. Other conditions: see Figure 3.

an important base-line drift due to the increasing amount of methanol absorbing at 220 nm and of course visible at low sensitivity. The same drift is recorded with a blank gradient obtained without any solute injection and, although it was not done here, it can be substracted easily with any integrator. From this chromatogram, the detection limit can be estimated below 0.1 μg/l. and monitoring these analytes in drinking water according to the EEC ordinance (concentration of any pesticide and degradation product below 0.1 μg/l) can be achieved from a volume of 100 ml. Nevertheless, the detection limit is not far below 0.1 μg/l for hydroxyatrazine (peak 3). If a detection limit below the 0.1 μg/l level is required, it is necessary to increase the sample volume and consequently to increase the size of the PRP-1 precolumn. Using the larger precolumn, it was therefore possible to increase the sample volume to 500 ml.

Detection limits are very low as shown in Figure 6 which corresponds to the analysis of a 500-ml river water sample spiked with 50 ng/l of each analyte. The sample was taken from the river Seine in Paris and even with this water containing a high amount of organic

materials, detection limits are below 5 ng/l for the three main degradation products of atrazine when a 500-ml sample is analysed. The determination of simazine and atrazine with similar detection limits is achieved by the second transfer. These low detection limits are due to the selective preconcentration with the cation exchanger, since many neutral interferents are left on the PRP-1 precolumn. There is just an interfering peak with deisopropylatrazine in the river water sample, which also appeared in the non-spiked sample. Calibration graphs for all the compounds with 500-ml samples and detection at 220 nm were linear over the range 0.05–1 μg/l level. The repeatability ranged between 3 and 10 % (relative standard deviation obtained with n=4) at the 0.1 μg/l level.

CONCLUSION

The low detection limits obtained in this study are due to the combination of a selective preconcentration and the use of on-line technology which has been developed for a few years especially in liquid chromatography. This also demonstrates the advantage of multiresidue methods using liquid-chromatography for thermodegradable analytes and other polar analytes which can thus be handled without any derivatization. The difference in polarity between the parent and degradation products is high, rendering difficult a multiresidue method for all the compounds. Nevertheless, two on-line analyses from the same preconcentration, one optimised for the polar compounds and the second for the other ones, can allow the determination of all the compounds. Monitoring drinking water at the 0.1 μg/l level according to the EEC ordinance can be achieved with the handling of 100 ml and detection limits below the 10 ng/l level can be obtained in surface waters from a 500-ml volume.

Acknowledgement

J-P. Ghestem is thanked for his hepful contribution to this work.

References

1. M. Battista, A. Di Corcia and M. Marchetti, *Anal. Chem.*, **61**, 935–939 (1989)
2. J. M. Schaeppli, W. Föry and K. Ramsteiner, *J. Agric. Food Chem.*, **37**, 1532–1538 (1989)
3. M-C. Hennion, P. Subra, R. Rosset, J. Lamacq, P. Scribe and A. Saliot, *Intern. J. Environ. Anal. Chem.*, **42**, 15–33 (1990)
4. W. E. Pereira and C. E. Rostad, *Environ. Sci. Technol.*, **24**, 1400–1406 (1990)
5. E. M. Thurman, D. A. Goollsby, M. T. Meyer and D. W. Kolpin, *Environ. Sci. Technol.*, **25**, 1794–1796 (1991)
6. M. F. Legrand, E. Costentin and A. Bruchet, *Environ. Technol.*, **12**, 985–996 (1991)
7. R. J. Schneider, L. Weil and R. Niessner, *Intern. J. Environ. Anal. Chem.*, **46**, 129–140 (1992)
8. A. Pachinger, E. Eisner, C. Tertsch, H. Begutter and H. Klus, *J. High Resolution Chromatogr.*, **15**, 302–304 (1992)
9. G. Durand, N. De Bertrand and D. Barcelo, *J. Chromatogr.*, **554**, 233–250 (1991)
10. G. Durand and D. Barcelo, *Analytica Chimica Acta*, **243**, 259–271 (1991)
11. Q. Wenheng, N. A. Schultz, J. D. Stuart, J. C. Hogan and A. S. Mason, *J. Liquid Chromatography*, **14**, 1367–1392 (1991)

12. G. Durand and D. Barcelo, *Toxicologogical of Environ. Chemistry*, **25,** 1–11 (1989)
13. G. Durand, R. Forteza and D. Barcelo, *Chromatographia*, **28,** 597–604 (1989)
14. V. Coquart and M-C. Hennion, *J. Chromatogr.*, **553,** 329–343. (1991)
15. V. Coquart and M-C. Hennion, *J. Chromatogr.*, **585,** 67–73 (1991)
16. P. Subra, M-C. Hennion, R. Rosset and R. W. Frei, *J. Chromatogr.*, **465,** 121–141 (1988)
17. V. Pacakova, K. Stulik and M. Prihoda, *J. Chromatogr.*, **442,** 147–155 (1988)
18. S. Coppi and A. Betti, *J. Chromatogr.*, **472,** 406–410 (1989)
19. P. Subra, M-C. Hennion, R. Rosset and R. W. Frei, *Intern. J. Environ. Anal. Chem.*, **37,** 45–62 (1989)