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Journal of Chromatography A, 711 (1995) 257–267

JOURNAL OF CHROMATOGRAPHY A

Comparison of sorbents for the solid-phase extraction of the highly polar degradation products of atrazine (including ammeline, ammelide and cyanuric acid)

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First received 20 December 1994; revised manuscript received 19 April 1995; accepted 1 May 1995

Abstract

Three different types of non-polar sorbents, i.e., C_{18} silica, apolar styrene–divinylbenzene copolymer (PRP-1) and porous graphitic carbon (PGC), were compared for the solid-phase extraction of atrazine, simazine and nine degradation products obtained by dealkylation, dehalogenation, hydroxylation or deamination mechanisms. The C_{18} silica was shown to be effective only for the first degradation products (deethyl-, deisopropyl- and hydroxyatrazine), the others being too polar. Despite a higher retention provided by PRP-1, the retention of the hydroxy-dealkylated derivatives is too low to allow the handling of a sufficiently large volume for determinations below the μg/l level. The more polar derivatives, i.e., ammeline, ammelide and cyanuric acid, are not retained by either C_{18} silica or PRP-1, whereas the capacity factor measured on a PGC column eluted with water was above 100. The conditions of extraction and elution using a cartridge packed with 500 mg of PGC are described for all the series of compounds and recoveries above 90% were obtained from 500-ml samples. The analytical separation was carried out using a C_{18} silica column and confirmation was obtained using a PGC column. Determinations of the degradation products in real samples are presented with detection limits below the 0.1 μg/l level.

1. Introduction

Chlorotriazine herbicides have been extensively used as pre- and post-emergence weed control agents on crops. The potential for contamination of waters and sediments by the widely used herbicides simazine and atrazine is high owing to their relatively high solubility, their weak adsorptivity, as measured by the partition coefficient between soil organic carbon and water, and their relatively long hydrolysis half-life in some soils. Residue levels between 0.01 and 300 μg/l in ground waters have been reported [1]. The degradation of these herbicides after their spreading depends on several factors such as hydrolysis, photolysis and microbial activity.

The main degradation products so far in ground and surface waters and in soils are dealkylated metabolites [1–7] and therefore deethyl- and deisopropylatrazine have been included in the National Pollutants Survey (NPS) list in the USA [8]. According to European Directives for drinking water, the concentration

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0021-9673/95/$09.50
SSDI 0021-9673(95)00527-7

of each pesticide and related components should be lower than 0.1 μg/l. Although it is not clear whether degradation products are included in this regulation, some European countries are now routinely monitoring these two dealkylated metabolites in drinking and ground waters. Another important pathway for atrazine degradation is its conversion to the hydroxy analogue and methods have been reported for the extraction and determination of hydroxyatrazine in soils and waters [2,9–14]. Data on the pollution of ground water with hydroxyatrazine are less numerous because many environmental laboratories employ mostly gas chromatographic (GC) techniques and hydroxyatrazine cannot be determined by GC, but by liquid chromatography (LC). Other degradation products formed by mechanisms involving further dealkylation and hydrolysis have been mentioned in the literature, but their trace-level determination in environmental waters or soils has not been reported [15–20]. One reason is that these further degradation products are more polar so that their extraction from the aqueous media is difficult and/or impossible using conventional extraction techniques.

It is of environmental interest to establish the degradation pathway directly in environmental media, which requires the corresponding analytical techniques. Atrazine is now detected in many surface waters which are used for drinking supply after further purification in treatment plants. Atrazine is oxidazable with difficulty by some classical treatments. It is therefore important that trace-level analytical methods are available for studying the transformation of atrazine during the process under real field conditions and not in laboratory conditions with concentrated pure spiked water samples.

The objectives of the investigation reported in this paper were to provide extraction procedures for the polar degradation products, i.e., for hydroxydeethylatrazine, hydroxydeisopropylatrazine, deethyldeisopropylatrazine (2,4-diamino-6-chloro-1,3,5-triazine) ammeline (2,4-diamino-6-hydroxy-1,3,5-triazine), ammelide (2-amino-4,6-dihydroxy-1,3,5-triazine) and cyanuric acid (2,4,6-trihydroxy-1,3,5-triazine), allowing their determination in environmental waters at the 0.1 μg/l level. No methods are available for extracting these polar metabolites from water. Previous work has shown that the retention of some polar and water-soluble organic compounds in water can be very high using porous graphitic carbon (PGC), available recently as a stationary phase for LC [21,22]. The potential of extraction using C_{18} silica, the apolar styrene–divinylbenzene copolymer PRP-1 and the carbon PGC was investigated with respect to the polarity of the main transformation products, on the basis of LC data, by measuring directly or calculating the capacity factors of each solute. An application to the trace-level determination of the whole series of compounds is presented with detection limits as low as 0.1 μg/l in drinking waters.

2. Experimental

2.1. Apparatus

A Model 5060 liquid chromatograph equipped with a UV 200 variable-wavelength or a Model 9065 Polychrom diode-array detector (Varian, Palo Alto, CA, USA) was used for direct injection of standard solutions and extracts obtained with off-line preconcentration procedures. On-line preconcentration was performed using a Varian 2010 Model pump for percolation of samples. Precolumn and analytical columns were connected with two Rheodyne (Berkeley, CA, USA) valves. Quantitative measurements were provided by a CR3A integrator computer from Shimadzu or by using the software of the Polychrom detector.

2.2. Stationary phases, columns and precolumns

A commercial column packed with Hypercarb porous graphitic carbon (100 mm × 4.6 mm I.D., 7 μm particle size) from Shandon HPLC (Runcorn, UK), a column laboratory packed with PRP-1 copolymer (150 mm × 4.6 mm-I.D., 10 μm particle size) from Hamilton (Reno, NV, USA) and a commercial column packed with

Sepralyte C_{18} silica (250 mm × 4.6 mm I.D., 5 μm particle size) from Analytichem International (Harbor City, CA, USA) were used for retention measurements. The void volumes of the columns were measured by injecting a 2 *M* solution of sodium nitrate for each buffered mobile phase. The analytical separations were performed on a commercial column packed with Spherisorb ODS-2 C_{18} silica (250 mm × 4.6 mm I.D., 5 μm particle size) from Whatman (Macherey–Nagel, Düren, Germany). A Hypercarb analytical column (100 mm × 4.6 mm I.D., 7 μm) was also used for confirmation.

On-line preconcentrations were made through stainless-steel precolumns (10 mm × 4.6 mm) prepacked with 10–15-μm Hypercarb PGC, provided by Shandon HPLC. These precolumns were coupled on-line to the Hypercarb analytical column. Off-line preconcentrations were performed by packing disposable cartridges with 300–1000 mg of 40–60-μm Hypercarb PGC also provided by Shandon HPLC.

2.3. HPLC conditions

The separation of the three more polar products, ammeline, ammelide and cyanuric acid, was performed using the Spherisorb ODS-2 column, eluted with water, adjusted to pH 3 with perchloric acid, at a flow-rate of 1 ml min^{-1} and with UV detection at 205 nm. The separation of the six other degradation products plus simazine and atrazine was performed on the same analytical column at the same flow-rate with a $5 \cdot 10^{-3}$ *M* aqueous phosphate buffer (pH 7)–acetonitrile gradient. The gradient was 5% of acetonitrile from 0 to 2 min, 30% at 6 min and 80% at 25 min. Detection was carried out at 210 nm.

2.4. Chemicals

HPLC-grade acetonitrile was kindly provided by Baker France (Noisy-le-Grand, France) and methanol was purchased from Prolabo (Paris, France). LC-grade water was obtained from Baker or was prepared by purifying demineralized water in a Milli-Q filtration system (Millipore, Bedford, MA, USA). Pesticides and degradation products were supplied by Riedel-de Haën (Seelze, Germany) or by Cluzeau (Sainte-Foy-la-Grande, France), except ammelide and ammeline, which were prepared by synthesis. Their purities were higher than 98% and traces of ammeline were identified in ammelide and vice versa. Other chemicals were purchased from Prolabo, Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland).

Stock standard solutions of degradation products were prepared by weighing and dissolving them in methanol, except ammeline, ammelide and cyanuric acid, which were prepared in water owing to their higher solubility in water than in methanol. The standard solutions were stored at 4°C and used for the preparation of working standard solutions and for spiking the water samples. Their stability was controlled by LC. The final spiked water samples did not contain more than 0.5% of methanol.

2.5. Sorption and desorption procedures

Because of their differences in terms of polarity and water solubility, the degradation products were divided into two groups, one containing ammeline, ammelide and cyanuric acid and the second, all the other compounds. Before any use, the PGC cartridge was washed with 10 ml of methanol and conditioned with 10 ml of LC-grade water. For the first group, the water samples were adjusted to pH 3 and 250–500 ml were percolated through the cartridge containing 500 mg of PGC at a flow-rate of 5–10 ml/min using vacuum aspiration. The residual water was removed by air aspiration and elution was performed with 20 ml of methanol, the eluate subsequently being evaporated to dryness at 50°C under nitrogen. The residue was dissolved in 500 μl of the mobile phase used for the separation (water adjusted to pH 3 with perchloric acid) and a 100-μl aliquot was injected.

For the second group, sample volumes of 500 ml of water were percolated through a cartridge containing 300 mg of PGC. After removal of residual water, elution was achieved with a mixture of 15 ml of methanol and 15 ml of tetrahydrofuran. After evaporation of the eluate

to dryness under the same conditions as used for the first group, the residue was dissolved in 500 μl of methanol and 20 μl were injected on to the analytical column.

Previous work indicated that the breakthrough volume of cyanuric acid was ca. 50 ml using a 10 mm × 4.6 mm I.D. precolumn and that the detection limit from 50-ml samples was 3 μg/l. An on-line set-up could not be used here for direct determination at low-μg/l levels. However, on-line preconcentration was used for confirmation of cyanuric acid, in order to inject the whole extract. The precolumn was placed at the loop position of a six-port switching valve. In the load position, the PGC precolumn was washed with 10 ml of methanol and conditioned with 10 ml of LC-grade water. The raw water sample was percolated, then the precolumn was placed in front of the Hypercarb analytical column by switching the valve in the inject position and elution was effected with an aqueous mobile phase containing 30% of methanol. In order to analyse the whole extracts obtained by off-line concentration from the cartridge, the dry extracts were dissolved in 30 ml of LC-grade water and 25 ml were percolated through the precolumn and analysed on-line.

3. Results and discussion

3.1. Degradation products of atrazine

The degradation products studied in this work are listed in Table 1. The water–octanol partition coefficients, P_{oct}, which have been shown to be useful for the prediction of the extraction parameters [23], decrease with the number of dealkylation and hydroxylation, showing that the degradation products can be much more polar than the parent molecule. The last five have negative values, indicating that these compounds are more soluble in water than in octanol and cannot be extracted from water using liquid–liquid extraction techniques. In the literature, there is a great variation in log P_{oct} values depending on the authors and on the methods [24]. An average value of 2.7 was obtained for atrazine using the shake-flask method whereas values measured by HPLC were between 2.2 and 2.8. For simazine, only values calculated or obtained via HPLC have been reported and are between 1.5 and 2.3. The values in Table 1 were calculated according to the method described by Rekker [25] and from the mean value of 2.7 for atrazine. In Ref. [24], values of 1.53 and 1.51

Table 1
Substituents on the 1,3,5-triazine ring, water–octanol partition coefficients and ionization constants of atrazine, simazine and degradation products

Compound	Abbreviation	Substituents in position			Log P_{oct}	pK_a
		2-	4-	6-		
Atrazine	A	$NHCH(CH_3)_2$	NHC_2H_5	Cl	2.7[a]	1.7
Simazine	S	NHC_2H_5	NHC_2H_5	Cl	2.3	1.65
Deethylatrazine	DEA	$NHCH(CH_3)_2$	NH_2	Cl	1.6	1.3
Hydroxyatrazine	OHA	$NHCH(CH_3)_2$	NHC_2H_5	OH	1.4	4.9
Deisopropylatrazine	DIA	NH_2	NHC_2H_5	Cl	1.2	1.3
Hydroxydeethylatrazine	OHDEA	$NHCH(CH_3)_2$	NH_2	OH	0.2	4.5
Deethyldeisopropylatrazine	DAA	NH_2	NH_2	Cl	0	1.5
Hydroxydeisopropylatrazine	OHDIA	NH_2	NHC_2H_5	OH	−0.1	4.6
Cyanuric acid	ACY	OH	OH	OH	−0.2	6.9
Ammelide	ADE	NH_2	OH	OH	−0.7	1.8; 6.9; 13.5
Ammeline	ANE	NH_2	NH_2	OH	−1.2	4.5; 9.4

[a] Value from Ref. [24]; ionization constants from Ref. [16] or measured according to Ref. [13].

were calculated and measured by HPLC, respectively for deethylatrazine (1.12 and 1.15, respectively, for deisopropylatrazine), so that the agreement with the values in Table 1 is good. Another important parameter for the environmental analytical chemist is the ionization constant, because when using a non-polar sorbent for extraction, it is of prime importance to adjust the pH so that the compounds should be in their neutral form.

These compounds were selected because they represent the most probable transformation products. Studies of drinking water treatment with ozone and addition of hydrogen peroxide under laboratory conditions indicated that the ultimate identified transformation products are ammeline and cyanuric acid; most of the compounds in Table 1 have been identified as intermediate compounds [26–28].

3.2. Comparison of retention factors in water

To a first approximation, solid-phase extraction is a simple chromatographic process, the sorbent being the stationary phase and the water of the sample the mobile phase, so that data generated by LC measurements can be used for predicting the SPE parameters [23,29]. Solutes are trapped provided that they are not eluted by water. In practice, the most important parameter is the volume that can be percolated with 100% recovery, known as the breakthrough volume, V_b, which can be estimated from the retention volume V_r measured with water as mobile phase. As V_r can be easily calculated from the capacity factor of solutes in water, k'_w, by the equation $V_r = V_0 (1 + k'_w)$, V_0 being the void volume, one can rapidly obtain the order of magnitude of the breakthrough volume. For example, a log k'_w value higher than 2.2 is required for a V_r value higher than 100 ml using a cartridge packed with 500 mg of sorbent.

The values of k'_w can be measured in water or can be extrapolated from more rapid measurements in water–methanol. For the three reversed-phase sorbents, the capacity factors were measured for each solute in Table 1 with various methanol–water mobile phases and the results are reported in Fig. 1. As expected, only DEA, OHA and DIA can be preconcentrated using C_{18} silica. The others are not retained enough and ADE, ANE and ACY were not reported as they have log k' values below −0.5 even in pure water. These results could have been predicted, without any calculation, from the relationship between log k'_w and log P_{oct}, which has been intensively studied in reversed-phase chromatography with C_{18} silicas [30].

The retention of compounds on the apolar copolymer PRP-1 was shown to be between 20 and 40 times higher than that measured on C_{18} silicas [22]. Fig. 1b effectively shows that atrazine, simazine, DEA, OHA and DIA are more retained. However, the log k'_w values of the more polar OHDEA, DAA, OHDIA, ADE, ANE and ACY are very similar to those obtained on C_{18} silica. The limitation of the extraction potential of both C_{18} and the apolar copolymer is clearly shown for highly polar compounds.

The retention mechanism was shown to be different on PGC, so that log k'_w cannot be predicted from the hydrophobicity (Fig. 1c). First, simazine and atrazine are more retained than they are on PRP-1 and the retention order is different. The same inversion is found for DEA and DIA and for OHDEA and OHDIA. In comparison with simazine, atrazine contains a more hydrophobic substituent, isopropyl instead of ethyl, on the nitrogen atom in position 2, and the retention order on C_{18} silica and on PRP-1 is easily explained by this difference in hydrophobicity. On PGC, the retention mechanism depends on both the hydrophobicity and the local dipoles in the molecule, so that the inversion between simazine and atrazine can be explained. However, the most important point is that the very polar ACY, ANE and ADE are very well retained by the PGC in water with log k'_w values higher than 2.5. All other compounds have log k'_w values above 3. These results are in agreement with previous work where we have shown that the log k'_w values of 1,3,5-trihydroxybenzene

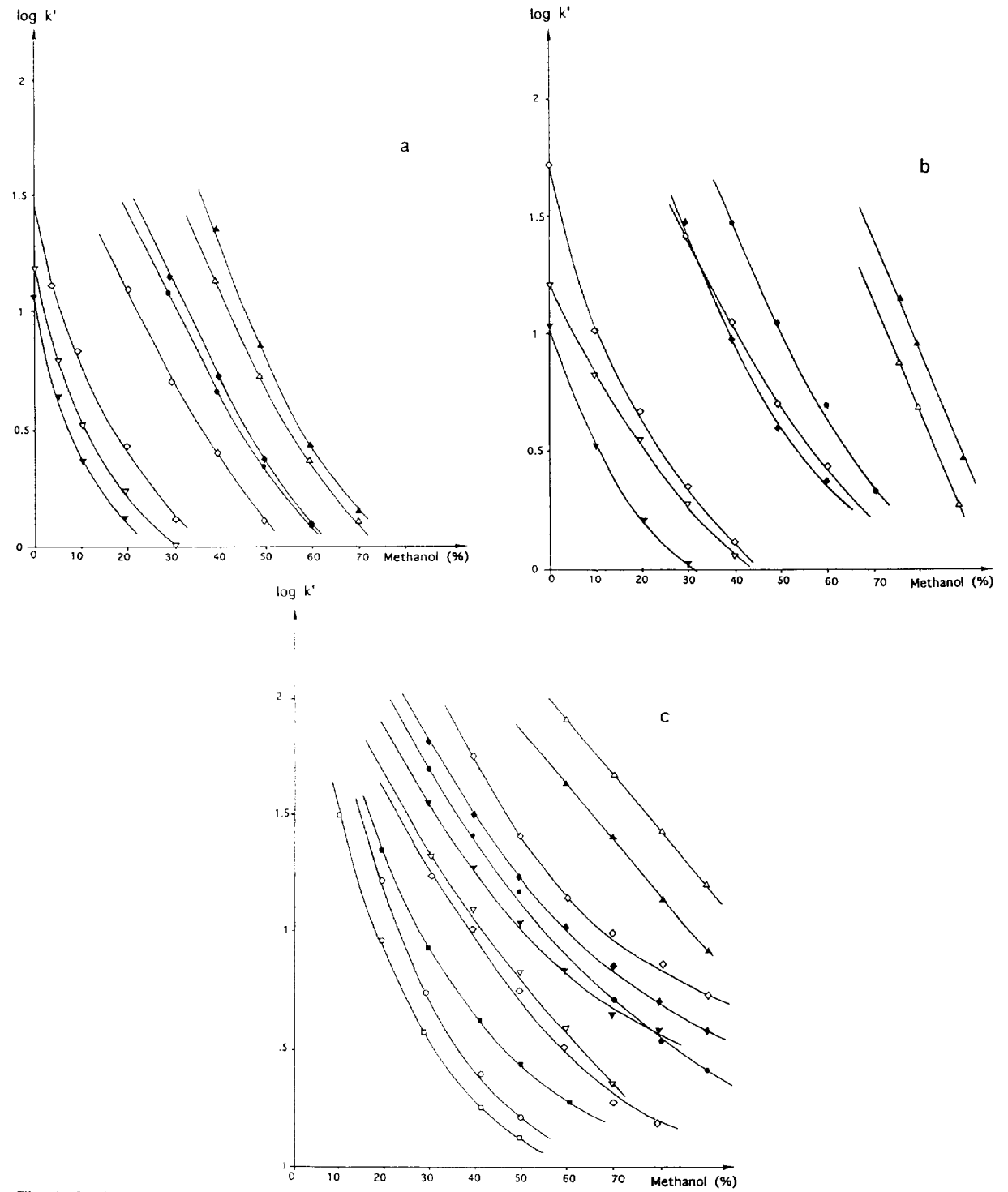

Fig. 1. Variation of capacity factors ($\log k'$) with the mobile phase composition obtained on (a) C_{18} silica, (b) PRP-1 copolymer and (c) porous graphitic carbon. Solutes: ▲ = atrazine; △ = simazine; ◆ = OHA; ● = DEA; ◊ = DIA; ◇ = OHDEA; ▽ = DAA; ▼ = OHDIA; ■ = ACY; ○ = ADE; □ = ANE. Mobile phase, methanol–0.05 *M* sodium phosphate adjusted to pH 7, except for ADE and ACY on PGC (pH 3); flow-rate, 1 ml/min; unretained compound, 2 *M* sodium nitrate.

were around 3 whereas this compound was not retained at all on C_{18} silica [21].

3.3. Analytical separation

The analytes were divided into two groups because of their different solubility properties and also because of the different pH values that should be used. The separation of ADE, ANE and ACY was performed on a C_{18} column eluted with pure water adjusted to pH 3, showing that these compounds are just slightly retained with C_{18} silica (Fig. 2). Bad peak shapes were obtained on dissolving the injection mixture in aqueous solutions containing methanol or acetonitrile. The solubility in other solvents was very poor and this practical problem prevented us from separating these compounds in the normal-phase mode. The other compounds were separated with an acetonitrile gradient at pH 7. A similar separation was not possible using the only available 10-cm long analytical column of PGC because of the lack of efficiency in comparison with a 25-cm C_{18} column [31]. Nevertheless, the PGC column was used as a confirmation column, the retention volume of ACY being the same as that with C_{18} silica, but using an aqueous mobile phase containing 30% of methanol.

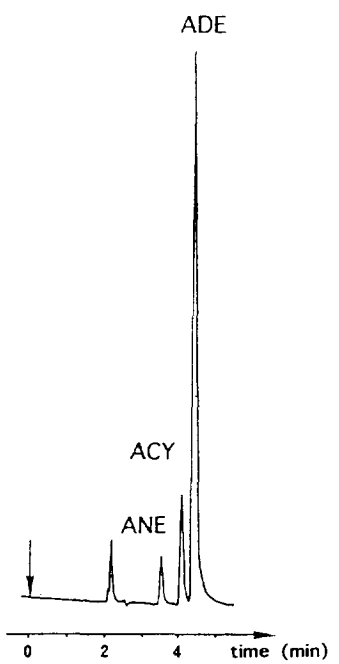

Fig. 2. Analytical separation of simazine, atrazine and the degradation products on a C_{18} column. Mobile phase, 10^{-3} *M* perchloric acid; detection UV, at 205 nm.

3.4. Solid-phase extraction conditions

The extraction also has to be carried out separately for the two groups, owing to the different solvents used for dissolving the corresponding extracts. Only water was effective for dissolving the extract when the three more polar analytes were studied. For the three more polar analytes, a cartridge packed with 500 mg of PGC was selected in order to increase the V_b values. Recoveries were first measured by preconcentrating 250 ml of LC-grade water samples spiked with 5 μg/l of ADE, ANE and ACY. Average recoveries above 95% were obtained on eluting the cartridge with 15 ml of methanol or 15 ml of acetone. The organic solvent was evaporated to dryness at ambient temperature under a stream of nitrogen and the residue was dissolved in 0.5 ml of water adjusted to pH 3. An aliquot of 100 μl was injected and recoveries were calculated by comparison with standard solutions. The sample volume can be increased to 500 ml with an amount of 1 g of PGC sorbent and a desorption volume of 20 ml of methanol. The recovery obtained with 500 ml of water samples spiked with 5 μg/l of ACY was 96 ± 5% (three replicate extractions). ANE was shown to be fairly unstable. This was verified by regularly monitoring the stock solution containing ADE, ANE and ACY and it was observed that the concentration of ADE increased while the concentration of ANE decreased, indicating a slow transformation of ANE into ADE.

For the other group, as the log k'_w values were above 3, a 300-mg PGC cartridge was selected. However, the elution was more difficult owing to the strong retention of the less polar analytes. The curves Fig. 1c indicate that simazine and atrazine are still retained in pure methanol. The recoveries were first measured with an elution volume of 15 ml of pure organic solvent. Metha-

nol, acetonitrile, THF and methylene chloride could not elute each analyte completely. The highest recoveries were obtained with THF, except for the hydroxy analogues, which were better eluted with methanol. The recoveries obtained with an eluent consisting of 15 ml of methanol and 10 ml of THF were above 90% for each analyte with a sample volume of 500 ml and using a cartridge containing 300 mg of PGC.

3.5. Application to drinking waters

Cyanuric acid was first studied. The off-line procedure described previously using a 500-mg PGC cartridge was applied to 250 ml of LC-grade water spiked with 5 μg/l of cyanuric acid, to 250 ml of non-spiked drinking water and to a 250-ml sample of the same drinking water spiked with 5 μg/l of cyanuric acid. The chromatograms of the extracts are presented in Fig. 3. The drinking water shows numerous interfering compounds and peaks identified with asterisks have the same retention times as ammeline, cyanuric acid and ammelide, indicating that PGC is not a selective extraction sorbent and that C_{18} silica is not able to separate the interferents from the analytes in the extract. As the mobile phase is pure water, it is impossible to modify it to delay the analytes. When spiking the drinking water with cyanuric acid alone, it was verified that both the retention time and the shape of the peak were identical (Fig. 3c). The analytical PGC column was therefore used as a confirmation column. As it was impossible to dissolve the whole dry extract in less than 500 μl of water and to inject more than 100 μl on to the 10-cm long Hypercarb column, this procedure could not provide determinations below 3 μg/l. Owing

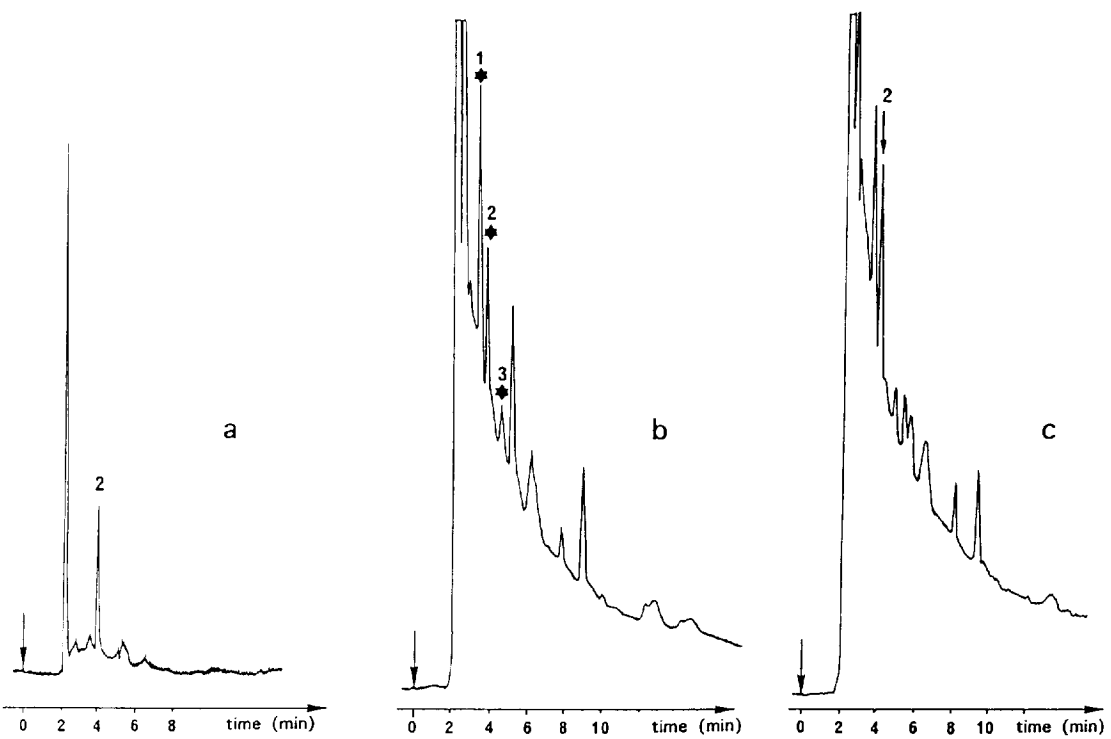

Fig. 3. Analysis of the off-line water extracts on the C_{18} analytical column. (a) 250 ml of LC-grade water spiked with 5 μg/l of cyanuric acid; (b) 250 ml of drinking water, non-spiked, taken in Paris, May 1993; 1 = ANE, 2 = ACY and 3 = ADE; (c) 250 ml of the same drinking water spiked with 5 μg/l of cyanuric acid (peak 2). Experimental conditions as in Fig. 2a. Dissolution of the extract in 0.5 ml of mobile phase and injection of a 100-μl aliquot; UV detection at 205 nm, (a) 0.01 AUFS, (b) and (c) 0.02 AUFS.

to the poor UV property of cyanuric acid, there was interest in injecting nearly all of the dry extract, which was possible by diluting it in a larger volume of water and using an on-line set-up, as described in the Experimental section. The three extracts analysed in Fig. 3 were then analysed on the PGC analytical column and the corresponding chromatograms are presented in Fig. 4. There are considerable differences between the chromatograms in Figs. 3 and 4 and it can be seen that the analytical PGC column is able to separate the interferents from the analytes using an aqueous mobile phase containing 30% of methanol. Therefore, it was possible to confirm that the chromatograms in Fig. 3b were false-positive. The detection limit obtained using this procedure was 0.2 μg/l in drinking water samples.

The other less polar metabolites were also determined using a 300-mg PGC cartridge, according to the experimental conditions described above. Fig. 5 represents the analysis of an extract obtained from the preconcentration of 500 ml of drinking water spiked with 0.5 μg/l of each analyte. Detection limits below the 0.1 μg/l level are easily obtained even for OHDIA, OHDEA and DAA.

4. Conclusion

Many transformation products of pesticides are more polar than the parent molecules and their extraction from aqueous media requires specific sorbents. Although the limitations of C_{18} silica and apolar copolymers can be predicted according to the well known retention behaviour of solutes with the sorbents in LC, little is known about the retention mechanism of polar compounds on PGC and more studies are necessary. The potential of PGC for the extraction of some water-soluble analytes has been demonstrated in this study, since previously no conventional sorbent was able to extract the water-soluble degradation products of atrazine in drinking waters. Moreover, it was also pointed out in this particular example that C_{18} silica columns were not able to analyse the extracts, but that PGC used as an HPLC stationary phase was able to separate interferents from the analytes, thus

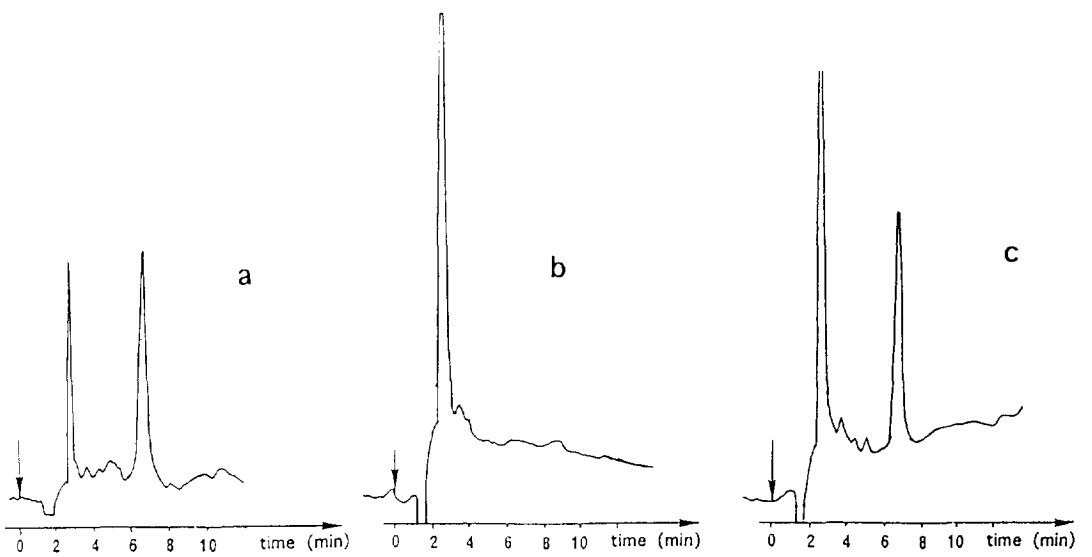

Fig. 4. On-line analysis of water extracts using a PGC precolumn and a PGC analytical column. (a) LC-grade water extract spiked with 5 μg/l of cyanuric acid; (b) non-spiked drinking water extract; (c) spiked drinking water extract with 5 μg/l of cyanuric acid. Dry extracts (obtained by off-line preconcentration) were dissolved in 30 ml of LC-grade water and 25 ml were analysed on-line (see text). Mobile phase, methanol–0.05 *M* sodium phosphate buffer (pH 7) (30:70) detection UV, at 220 nm, 0.05 AUFS.

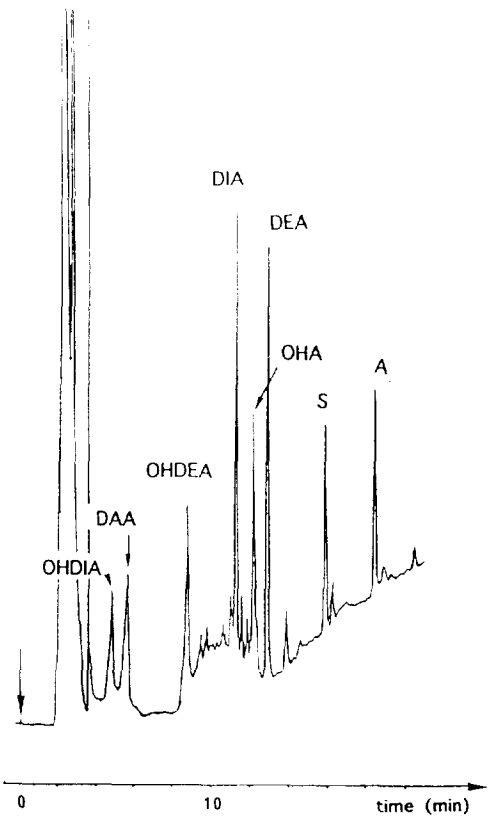

Fig. 5. Off-line analysis of the extract corresponding to 250 ml of drinking water spiked with 0.5 μg/l of each analyte. Experimental conditions: water–acetonitrile gradient at pH 7 (see Experimental section for the gradient shape); dissolution of the extract in 0.5 ml of methanol and injection of a 100-μl aliquot; detection, UV at 210 nm, 0.02 AUFS.

providing a useful confirmation method. Therefore, PGC will contribute to the increase in the number of polar analytes that can be monitored at trace levels in water. The solid-phase extraction of very polar compounds is certainly an area which needs to be developed with the introduction of new sorbents.

Acknowledgements

This work was supported by the National Agronomic Research Institute of France (AIP programme) and by the Environmental R&D programme 1991–94 of the European Communities (contract No. EV5V-CT92-0114). Shandon HPLC (France and UK) are thanked for the supply of carbon materials.

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