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Tandem solid-phase extraction of atrazine ozonation products in water

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Abstract

The preconcentration of aqueous solutions containing atrazine degradation products was investigated using solid-phase extraction on octadecyl and cation-exchanger silica phases. The retention and elution steps were studied and evaluated separately in order to define and optimize the critical experimental parameters involved. A strategy which combines sequentially both phases is proposed to fractionate compounds into two groups of increasing polarities: firstly, the native pesticide, hydroxyatrazine and most chlorotriazines on octadecyl support, and secondly monodealkylated hydroxytriazines, ammeline and ammelide on cation-exchanger. This tandem procedure was successfully applied for analysing and quantifying atrazine ozonation products and its efficiency demonstrated using [U-ring ^{14}C]-labelled atrazine experiments.

Keywords: Ozonation; Water-analysis; Atrazine; Pesticides

1. Introduction

The concentration of atrazine (ATZ), known as a major herbicide, has often been reported at the μg/l level in surface water [1]. Two of its degradation products, deethylatrazine (DEA) and deisopropylatrazine (DIA), are also frequently detected [2,3]. The EU directive for drinking water which presently allows 0.1 μg/l for a single pesticide and 0.5 μg/l for the sum of the pesticides as maximum amounts can be guaranteed through the use of an oxidation step, i.e., combining ozone and hydrogen peroxide for an optimal treatment [4]. In this context, the main ozonation products of ATZ (AOPs) are generated by dealkylation of the amino groups and hydroxylation (via dechloration and/or deamination) [4–6] of the parent pesticide. For better knowledge of such processes and the corresponding degradation pathways, enrichment techniques applicable to aqueous solutions are necessary which exclude conventional liquid–liquid extraction and favour the solid-phase extraction (SPE) strategy. In the case of triazines, C_8 and C_{18} bounded silica reversed-phases based on hydrophobic interactions can be utilised [7,8], but the use of these supports is generally limited to moderately polar compounds. Then other supports such as polymers (styrene–divinylbenzene copolymer) [9,10] and graphitised carbon [11–13] using other interactions, i.e., π–π or charge–transfer respectively may

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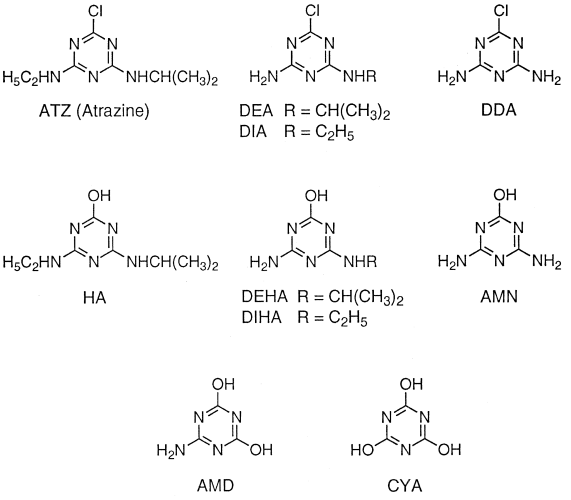
be more suited for extracting polar compounds although some of these supports may have limitations at the elution stage. Cation-exchange supports have also been proposed in the case of hydroxy-triazines [14,15] since their pK_a values are most appropriate. Immunosorbents represent another alternative [16,17] but antibodies may not react with some of the degradation products.

The aim of this work was thus to design a SPE procedure appropriate for the native pesticide and AOPs of various polarities including the highest ones to enable further exhaustive characterisation and/or quantitation. Thorough and independent examination of the retention and elution steps leads us to propose a tandem procedure using sequentially two phases of complementary performances in order to facilitate ozonation studies. This procedure is clearly distinct in its principle from previous ones using mixed-mode phases [18,19] or procedures [9,10,20].

2. Experimental

2.1. Chemicals

ATZ (>98%, 2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine), DEA (99.9%, 6-amino-2-chloro-4-(isopropylamino)-*s*-triazine), DIA (99.8%, 6-amino-2-chloro-4-(ethylamino)-*s*-triazine), deethyldeisopropylatrazine (DDA; 96.9%, 2-chloro-4,6-diamino-*s*-triazine, hydroxyatrazine (HA; 99.9%, 2-hydroxy-4-(isopropylamino)-6-(ethylamino)-*s*-triazine), hydroxydeethylatrazine (DEHA; 99.9%, 2-hydroxy-4-(isopropylamino)-6-amino-*s*-triazine), hydroxydeisopropylatrazine (DIHA; 99.9%, 2-hydroxy-6-amino-4-(ethylamino)-*s*-triazine) and ammeline (AMN; 99.6%, 2-hydroxy-4,6-diamino-*s*-triazine) were obtained from Promochem (Strasbourg, France). Ammelide (AMD; 2,4-dihydroxy-6-amino-*s*-triazine) was a gift from Ciba-Geigy (Basle, Switzerland). Cyanuric acid (CYA; 98%, 2,4,6-trihydroxy-*s*-triazine) was obtained from Janssen (Geel, Belgium). [U-ring ^{14}C] ATZ (specific activity 925 MBq/mmol, purity >98%) was purchased from International Isotope (Munich, Germany).



Acronyms and chemical properties of these chemicals are given in Table 1.

Acetonitrile (SDS, Peypin, France) was spectrosol grade. LC-grade water was prepared by purification of osmosed water in an Elgastat UHP system (Elga, High Wycombe, UK). Water, ammonium acetate (Sigma, St. Louis, MO, USA) solutions and sodium phosphate (Rectapur, Prolabo, Paris, France) pH 8.6 buffer (25 m*M*, 25% NaH_2PO_4 and 75% Na_2HPO_4, v/v) were filtered through a 0.45 μm filter (Millipore, Milford, MA, USA). The pH was adjusted with hydrochloric acid (HCl) or ammonia (Normapur, Prolabo).

Water from the Seine River taken at Le Pecq, downstream of Paris, contained 90 mg/l of calcium (II) (conductivity 0.34 mS/cm). After being spiked with ATZ and/or AOPs, calcium was eliminated

Table 1
Ionization constants and partition coefficients of atrazine and AOPs taken from Refs. [21,26,27] and [21,28] respectively

Acronym	Compound	pK_a	log P_{oct}
ATZ	Atrazine	1.68	2.7
DEA	Deethylatrazine	1.65	1.6
DIA	Deisopropylatrazine	1.58	1.2
DDA	Deethyldeisopropylatrazine	1.5	0
HA	Hydroxyatrazine	5.2	1.4
DEHA	Hydroxydeethylatrazine	4.75	0.2
DIHA	Hydroxydeisopropylatrazine	4.65	−0.1
AMN	Ammeline	4.5; 9.4	−1.2
AMD	Ammelide	1.8; 6.9; 13.5	−0.7
CYA	Cyanuric acid	6.9; 10.6	−0.2

from this water by precipitation using ca. 2 mmol of oxalic acid (Normapur, Prolabo) per litre and monitoring conductivity until a minimum was reached. The resulting solutions were filtered through glass wool and a 0.45 μm filter. Amounts of ATZ (0.05 μg/l) and DEA (0.06 μg/l) present before spiking were considered as negligible.

2.2. SPE

SPE was performed with an Autotrace SPE workstation (Tekmar, Cincinnati, OH, USA) using 500 mg/2.8 ml prepacked Bond-Elut octadecyl (C_{18}) and propylbenzenesulfonic acid (SCX) bonded-silica cartridges (Varian, Harbor City, CA, USA). The SPE supports were preconditioned with 5 ml of methanol and, then, 5 ml of water (adjusted to pH 2 with 0.2 *M* HCl for the SCX). Typically, 250 ml of the triazines were percolated at 5 ml/min. After rinsing with 1 ml water (SCX), the phase was dried for 10 min under a nitrogen flow. The sequential use of the C_{18} and SCX supports is described in Section 3.2. and the solvents used for elution are mentioned in Section 3.1.

2.3. Breakthrough volume (V_b) and elution profile

V_b values on C_{18} were determined by recording the UV absorbance at 220 nm (chlorotriazines) or 230 nm (hydroxytriazines) of single-compound solutions. The initial concentration was 0.2–0.5 mg/l (0.02 AU initial absorbance). The equipment included a HPLC pump (Waters 590), a UV–visible detector (Varian 9050), a recorder (Sefram Servotrace, Paris, France) and a switching valve (Rheodyne 7010, Cotati, CA, USA) to direct the effluent to the cartridge or to a bypass. As the SCX phase released contaminants during percolation, V_b values were determined indirectly by collecting the output-effluents and subjecting them to HPLC quantitation. The elution profiles were established after percolation of 250 ml solutions of 5 and 0.5 mg/l ATZ and AOPs through either SPE phase and HPLC–UV quantitation of successive 1 or 2 ml fractions obtained by elution with the appropriate solvent (cf. Section 3.1).

2.4. Apparatus and analysis conditions

HPLC–UV was performed with a Waters system (Bedford, MA, USA) including an automatic injector model 717, a 600-MS pump and a 991-MS photodiode array detector interfaced with a NEC 386/25 computer. Most compounds were analysed on a Nucleosil 100-5 C_{18} AB 250×4.6 mm I.D. column (Macherey-Nagel, Düren, Germany). The eluent was a mixture of acetonitrile and 50 m*M* ammonium acetate in water at 0.8 ml/min flow-rate either 25:75 v/v (condition 1) to elute chlorotriazines or 10:90 v/v (condition 2) for the elution of hydroxytriazines. AMN, AMD and CYA were analysed (condition 3) on a quaternary ammonium silica anion-exchanger Nucleosil 100-5 SB 250×4.6 mm I.D. (Macherey-Nagel) with a 25 m*M* phosphate buffer (pH 7.3). For ozonation samples containing polar compounds, a benzenesulfonic silica cation-exchanger Nucleosil 100-5 SA 250×4.6 mm I.D. (Macherey-Nagel) was also used (condition 4), the mobile phase being 5% acetonitrile and 95% 40 m*M* ammonium acetate pH 3.5 adjusted with acetic acid. Quantitations were obtained by integration of the LC–UV traces recorded at 220 nm (5–20 μl injected) and using an external standard method for calibration. For uncommon or new AOPs (cf. ozonation experiments), concentrations were estimated using the response factors of adjacent eluting triazines.

Radioactivity was monitored on a Wallac model 1410 (Turku, Finland) liquid scintillation counter.

2.5. Ozonation procedure

ATZ treatment was performed on a 5 l LC-grade water solution (1 mg/l). This concentration allowed the detection of AOPs including those of low relative abundances with a limit of ca. 0.5% of initial ATZ. In the experiment conducted with [U-ring ^{14}C] ATZ, the radiolabelled material (375 kBq) was dissolved in 0.5 ml methanol which was added to a 5 l aqueous solution of unlabelled ATZ. Ozone in air (2 mg/l) produced by a Degremont ozone generator (Rueil Malmaison, France) was introduced continuously (1 l/min) through a glass frit at the bottom of a 10-l batch reactor. Hydrogen peroxide (Sigma) was introduced in the liquid recirculation loop at a 4 mg/min

(2 ml/min) rate in parallel. The 200 ml aliquots taken during the process were treated with 1 ml 0.2 *M* sodium thiosulfate (Aldrich, St. Quentin-Fallavier, France) to stop the reaction, extracted following the tandem SPE procedure (cf. Section 3.2), measured for radioactivity and HPLC–UV analysed (conditions 1 and 2 for the C_{18} extracts and 2 and 4 for the SCX extracts).

3. Results and discussion

3.1. Preliminary studies for establishing protocol

The SPE protocol was established using standard AOPs of various polarities. As the performance of a SPE procedure is dependent on both retention of analytes on the support and their subsequent elution, these steps were investigated separately.

3.1.1. Evaluating the retention step

3.1.1.1. C_{18} support

V_b values were estimated using 500 mg phase cartridges (Table 2). On the C_{18} support, ATZ itself appeared by far as the most retained compound ($V_b > 1500$ ml). HA came in second ($V_b \sim 400$ ml) followed by the monodealkylated chlorotriazines (DEA and DIA) of moderate V_b values. The other AOPs being poorly retained, a complementary support should be essential to complete their recovery from substantial volumes of solutions. These data are consistent with previous reported determinations on C_{18} [10,21] and log P_{oct} values (Table 1).

Table 2
Breakthrough volumes (ml±standard deviation) of atrazine and AOPs determined on C_{18} and SCX phases (500 mg cartridges)

	C_{18} (pH 5.7)	SCX (pH 2)
ATZ	>1500	1230±100
DEA	92±2	490±40
DIA	35±1	470±30
DDA	2.4±0.2	130±10
HA	390±10	1660±30
DEHA	16±1	520±40
DIHA	8±0.5	600±120
AMN	1.3±0.2	330±30
AMD		18

3.1.1.2. Cation-exchange (SCX) support

When operating on a SCX phase (at pH 2, see Table 2), large V_b values were found for most hydroxytriazines. Because these AOPs have pK_a in the 4.5–5.2 range (Table 1), e.g. far above the chosen pH, the cation-exchange process was expected to be efficient. However chlorotriazines also appeared to be well retained, although pH was equal to or higher than their pK_a. This would indicate that retention of triazines does not depend exclusively on ion-exchange but most probably also on hydrophobic interactions due to the benzenic groups of the SCX phase [14]. This hypothesis is supported by the fact that the same increasing order of V_b values was observed on SCX and on C_{18} for both groups of triazines (DDA<DIA≤DEA<ATZ and AMN< DIHA≤DEHA<HA respectively for chloro- and hydroxytriazines). Furthermore, such progression corresponds to the decreasing order of polarities. In contrast to the above-mentioned compounds, AMD (pK_a=1.8) [21] was poorly retained on this support and CYA was not retained at all.

3.1.2. Evaluating the elution step

3.1.2.1. C_{18} support

After optimisation, a 10^{-2} *M* HCl methanol–water (96:4, v/v) solution was found to be most efficient for recovering the adsorbed molecules (ca. quantitative yield for HA and chlorotriazines ATZ, DEA and DIA in the first 2 ml). Furthermore, successive extractions could be performed on the same cartridge without exhibiting any memory effect in contrast with experiments done with methanol only as eluent.

3.1.2.2. Cation-exchange (SCX) support

Solvent composition, pH, nature and concentration of ions present are known to influence the elution process of strong cation-exchangers. Their influence on the elution profiles were thus studied using hydroxytriazines HA, DEHA and DIHA as model compounds considering the delay before effective elution, the slope of the elution curve and the final yield. The solvent composition appeared to influence both the initial delay and the elution profile. A water–acetonitrile mixture containing 0.1 *M* ammonium acetate was in general more efficient than the corresponding water–methanol one (although

giving a shorter delay) and the 75:25 ratio was found preferable for recovering hydroxytriazines (for DIHA: 74% vs. 45% with the 50:50 ratio). Changing ammonium concentration to 0.2 *M* gave a shorter delay for elution but the final yields were lower for most compounds. The pH in the 7 to 9.6 interval also appeared to have a significant effect (ca. +1 ml shift) on the delay before elution without however affecting the yields.

The elution profiles were finally established for all standard AOPs using 0.1 *M* ammonium acetate in water–acetonitrile (75:25, v/v) at apparent pH 8.6 as the best compromise. Under these conditions, chlorotriazines were eluted in 5 ml (3 ml delay) and ca. 90% yields. Hydroxytriazines HA, DEHA, DIHA and AMN were eluted later (4–5 ml delay) in ca. 75% yields when using 7 ml, whereas AMD was recovered (~63%) in the first 6 ml. To take into account this diversity of behaviour and satisfy the need for the highest recoveries within the lowest volumes (e.g. highest concentration factors), the following operating sequence was adopted for elution from the SCX phase: (i) 2 ml of the eluent to recover AMD, (ii) 5 ml and (iii) 2 ml of the same eluent respectively to obtain most AOPs and complete collection of hydroxytriazines.

3.2. Tandem solid-phase extraction on C_{18} and SCX supports

Since the less polar compounds (including the native pesticide) can be retained on C_{18}, they might be separated from other AOPs using a two-step SPE procedure. Such a strategy would provide two groups of compounds that could be analysed subsequently under specific and optimal HPLC conditions. The following procedure is thus proposed which includes first a C_{18} extraction for ATZ, HA and — to some extent — the monodealkylated chlorotriazines DEA and DIA, and in a second step (after acidification of the percolated solution to pH 2) a SCX extraction for the remaining DEA/DIA and other AOPs (DDA, DEHA, DIHA, AMN, AMD). Elution from either phase should be performed using the conditions specified above. The complete procedure was tested using 50 and 5 μg/l spiked solutions per compound in pure, tap or Seine River water. The volume of the percolated solutions was 250 ml and the evaluation was carried out on two groups of compounds in mixtures, both comprising DIA. Table 3 shows the results obtained with the 5 μg/l solutions.

The recoveries for ATZ and HA were almost total on C_{18} for any type of water. A total of ca. 90% of DEA and ca. 35% of DIA was recovered from the same phase which was more than expected from the V_b data. This improvement was most probably due to the much lower concentrations used in this experiment which would have caused a positive shift of the breakthrough curve. Interestingly, remaining DEA and DIA were further recovered from the SCX phase. A further 4–10% DEA was recovered (considering all types of water) when 50 μg/l solutions were used vs. 0.7–6% for the 5 μg/l solutions. All remaining DIA was recovered on SCX in pure water and even in water from the Seine River (provided the resulting spiked solutions were pretreated with oxalic acid to reduce the Ca^{2+} cation content) [22] but recovery became lower in tap water (ca. 40%). For

Table 3
Percent recoveries of atrazine and some AOPs following the tandem solid-phase extraction procedure for 250 ml pure, tap or Seine River water, 5 μg/l/compound spiked solutions (two groups of compounds, each value is the mean of four replicates); spiked Seine River solutions were pretreated with oxalic acid [22]

		First group				Second group			
		ATZ	DEA	DIA	HA	DIA	DDA	DEHA	AMN
Pure water	C_{18}	97±2	90±4	37±3	93±2	48±5	4.5±1.7	46±1	0
	SCX	0	1.5±1.1	63±3	0	42±8	58±1	51±2	97±1
Tap water	C_{18}	96±4	89±5	40±4	95±2	32±12	4.6±0.7	5.7±1.4	0
	SCX	0	0.7±0.3	25±8	0	42±12	13±10	88±1	12.3±11.5
Seine water	C_{18}	93±2	87±8	29±3	96±2	32±7	0	8.4±2.9	0
	SCX	0	6±1	72±2	0	61±16	46±11	95±5	50±11

DEHA, recovery from the C_{18} phase was moderate (ca. 23%) or even good (ca. 50%) when the concentration was decreased from 50 to 5 μg/l in pure water. This effect was again due to a favourable shift of the breakthrough curve. The low yields obtained with tap and Seine water might be explained by the competition with organic matter during the adsorption process. In any case, the remaining amount of DEHA was totally recovered from the SCX support. Since adsorption of this AOP was not limited on this phase by the presence of mineral cations (tap water, treated or even untreated water from Seine River), hydrophobic interactions certainly prevailed in this case.

In pure water, DDA and AMN (poorly retained on C_{18}) had good extraction yields on SCX as expected from their V_b values on this support. The yields became very low in tap or untreated Seine water but could be partly restored in Seine River solutions pretreated with oxalic acid. This contrasting behaviour vs. that of DEHA indicates that ionic interactions are preeminent for DDA and AMN, making these compounds more susceptible to competition with mineral and organic cation interferents in tap or Seine water (respective measured conductivities of 0.65 and 0.34 mS/cm).

3.3. Application to ozonation studies

The tandem SPE procedure was applied in the framework of an extensive study of ATZ ozonation [23]. The reaction in the presence of labelled ATZ described below was designed for the special evaluation of the method.

ATZ spiked with [U-ring ^{14}C] ATZ was ozonated and each step of the post-reaction treatment was analysed by scintillation counting to determine with precision the SPE tandem procedure efficiency. According to the data (Table 4), ca. 99% of the radioactivity was recovered by C_{18} extraction when starting the reaction and the yield of the compounds extracted on this support decreased to 79% after 120 min. The remaining radioactivity was mostly found by elution of the SCX phase which increased from 1.2% to ca. 17%. Elution from the C_{18} phase was almost total (thus indicating no irreversible adsorption) using a 2-ml methanolic fraction and the unextracted portion (unretained on C_{18}) was entirely or partially retained on the SCX support depending on how advanced the degradation process was. Elution from the latter apparently required a 7 ml volume (combining 2 and 5 ml fractions, see Table 4). These observations confirmed that both supports are complementary for extraction with an increasing proportion of AOPs extracted by SCX, but the unextractable portion (ca. 5% at 120 min in this case) might not be negligible under stronger ozonation conditions. It has to be noted further that $^{14}CO_2$ was never detected at any time indicating that mineralisation did not occur during reaction. It was shown additionally by HPLC–UV analysis (based on the degradation of the unlabelled ATZ also present in the

Table 4
Distribution of the radioactivity (%) of ozonated [U-ring ^{14}C] atrazine aqueous solutions during the tandem solid-phase extraction procedure vs. reaction time (means from two replicates)

Time (min)	0	15	30	60	90	120
Extraction on C_{18}						
Fraction C_{18} 1 (2 ml)	97±2	96.7±0.1	90±3	88±2	79±2	77±3
Fraction C_{18} 2 (2 ml)	2±0.6	1.8±0.1	2.4±1	2.7±1	2±0.6	2.4±0.2
C_{18} extracted	99±2	98.5±0	92±3	86±2	81±1	79±3
C_{18} unextracted	1.8±0.3	4.2±0	7.7±0.2	14.7±1	19±3	23±3
Extraction on SCX						
Fraction SCX 1 (2 ml)	0.4±0	0.3±0.2	2.5±0.5	3.9±0.4	6±2	7±2
Fraction SCX 2 (5 ml)	0.8±0.3	3.4±0.6	4±0.1	7.9±0.8	9.9±0.8	9.4±0.7
Fraction SCX 3 (2 ml)	0.03±0.01	0.06±0.01	0.08±0.02	0.15±0.02	0.19±0.01	0.19±0.02
SCX extracted	1.2±0.3	3.8±0.4	6.6±0.6	11.9±1.2	16±3	17±2
SCX unextracted	0.6±0.2	0.6±0.2	1±0.2	2.1±0	2.8±0.3	4.7±0.4
Total extracted	100±1	102.8±0.2	99±3	98±1	97±2	96±1

starting solution) that the C_{18} extract obtained at 120 min contained 41% ATZ and 29% AOPs (including 9% DEA, 2% DIA, 1% HA and 12% of intermediate amides) whereas the SCX extract accounted for ca. 18% of AOPs (2.5% DEA, 6% DIA, 2% DDA, 1% DEHA and 6% AMN).

Because the above conditions required the use of a small volume of methanol for the initial dissolution of labelled ATZ (see Experimental), the degradation was kinetically reduced in this case (scavenger effect) [24]. However, the same tandem SPE procedure used on solutions of unlabelled ATZ-only oxidised in more drastic conditions (due to the absence of methanol) was also very efficient. After 30 min, the C_{18} extract contained 2% DEA, 1% DIA and 2% of intermediate amides (but no more ATZ) whereas ca. 45% of AOPs (4% DDA, 12% AMN and unknowns) could be retained and analysed [23] with the SCX support.

4. Conclusion

After optimising the critical parameters, it was demonstrated that a C_{18} reverse support and a SCX cation-exchanger could be used sequentially to separate ATZ (parent pesticide) and some of the AOPs from compounds including AMN resulting from more drastic oxidation processes. This strategy makes it possible to fractionate between two groups of polarities and thus facilitates the subsequent HPLC–UV, –MS or –MS–MS [25] analysis under the most specific and optimal chromatographic conditions. Its application in retaining a number of uncommon or even new byproducts of ATZ formed by ozonation was found to be highly efficient [23] shedding new light on degradation pathways involved.

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References

[1] F. Van Hoof, P. Ackermans, J. Celens, Water Supply 10 (1992) 81–88.
[2] E.M. Thurman, D.A. Goolsby, M.T. Meyer, M.S. Mills, M.L. Pomes, D.W. Kolpin, Environ. Sci. Technol. 26 (1992) 2440–2447.
[3] D.W. Kolpin, E.M. Thurman, D.A. Goolsby, Environ. Sci. Technol. 30 (1996) 335–340.
[4] C.D. Adams, S.J. Randtke, Environ. Sci. Technol. 26 (1992) 2218–2227.
[5] P.C. Kearney, M.T. Muldoon, C.J. Somich, J.M. Ruth, D.J. Voaden, J. Agric. Food Chem. 36 (1988) 1301–1316.
[6] C.J. Hapeman-Somich, Z. Gui-Ming, W.R. Lusby, M.T. Muldoon, R. Waters, J. Agric. Food Chem. 40 (1992) 2294–2298.
[7] P.C. Bardalaye, W.B. Wheeler, Int. J. Environ. Anal. Chem. 25 (1986) 105–113.
[8] R.A. McLaughlin, B.S. Johnson, J. Chromatogr. A 790 (1997) 161–167.
[9] M.C. Hennion, V. Coquart, J. Chromatogr. 642 (1993) 211–224.
[10] V. Coquart, P. Garcia-Camacho, M.C. Hennion, Int. J. Environ. Anal. Chem. 52 (1993) 99–112.
[11] A. Di Corcia, C. Crescenzi, E. Guerrierro, R. Samperi, Environ. Sci. Technol. 31 (1997) 1658–1663.
[12] Z. Cai, M.L. Gross, R.F. Spalding, Anal. Chim. Acta 304 (1995) 67–73.
[13] I. Liska, E.R. Brouwer, A.G.L. Ostheimer, H. Lingeman, U.A.Th. Brinkman, R.B. Geerdink, W.H. Mulder, Int. J. Environ. Anal. Chem. 47 (1993) 267–274.
[14] R.N. Lerch, W.W. Donald, J. Agric. Food Chem. 42 (1994) 922–927.
[15] S. Nélieu, M. Stobiecki, F. Sadoun, H. Virelizier, L. Kerhoas, J. Einhorn, Analusis 22 (1994) 70–75.
[16] J.F. Lawrence, C. Ménard, M.C. Hennion, V. Pichon, F. LeGoffic, N. Durand, J. Chromatogr. A 752 (1996) 147–154.
[17] J.G. Rollag, M. Beck-Westermeyer, D.S. Hage, Anal. Chem. 68 (1996) 3631–3637.
[18] M.S. Mills, E.M. Thurman, Anal. Chem. 64 (1992) 1985–1990.
[19] M.S. Mills, E.M. Thurman, M.J. Pedersen, J. Chromatogr. 629 (1993) 11–21.
[20] A. Laganà, A. Marino, G. Fago, Chromatographia 41 (1995) 178–182.
[21] V. Pichon, L. Chen, S. Guenu, M.C. Hennion, J. Chromatogr. A 711 (1995) 257–267.
[22] M.W.F. Nielen, R.W. Frei, U.A.Th. Brinkman, J. Chromatogr. 317 (1984) 557–567.
[23] S. Nélieu, L. Kerhoas, J. Einhorn, Submitted.
[24] S. Nélieu, L. Kerhoas, J. Einhorn, Int. J. Environ. Anal. Chem. 65 (1996) 297–311.
[25] S. Nélieu, M. Stobiecki, L. Kerhoas, J. Einhorn, Rapid Commun. Mass Spectrom. 8 (1994) 945–952.
[26] N.M.J. Vermeulen, Z. Apostolides, D.J.J. Potgieter, P.C. Nel, N.S.H. Smit, J. Chromatogr. 240 (1982) 247–253.
[27] V. Pacáková, K. Stulìk, M. Prìhoda, J. Chromatogr. 442 (1988) 147–155.
[28] S. Guenu, M.C. Hennion, J. Chromatogr. A 665 (1994) 243–251.