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New method for the rapid determination of triazine herbicides and some of their main metabolites in water by using coupled-column liquid chromatography and large volume injection

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Abstract

Coupled-column liquid chromatography with ultraviolet detection was applied to the trace-level determination of simazine, atrazine, terbuthylazine and terbutryn, as well as the main atrazine metabolites, deisopropylatrazine, deethylatrazine and hydroxyatrazine, in environmental water samples rendering a very sensitive and rapid method which does not require any preconcentration step of the water sample. A sample volume of 2 ml, previously buffered with ammonium acetate for the determination of metabolites, was directly injected in the chromatographic system using two reversed-phase C_{18} coupled columns. Detection limits between 0.1 and 0.5 $\mu g\ l^{-1}$ were directly reached for both the parent pesticides and the polar metabolites. All these compounds were successfully recovered from different environmental waters. Drinking and surface water samples were spiked at different concentration levels (1–20 $\mu g\ l^{-1}$) yielding average recoveries between 86 and 104% ($n=5$) with coefficients of variation between 1 and 7%. If necessary, lower detection limits, between 0.02 and 0.1 $\mu g\ l^{-1}$, were easily reached by preconcentration of 100 ml of water samples using SPE cartridges. Recovery experiments were performed on drinking water samples spiked at 0.1 and 0.5 $\mu g\ l^{-1}$ yielding average recoveries between 84 and 103% with coefficients of variation between 1 and 6%. © 1997 Elsevier Science B.V.

Keywords: Column switching; Water analysis; Large-volume injections; Pesticides; Triazines

1. Introduction

Triazines are pre- and post-emergent herbicides which have been widely applied for crop protection during the last decades. Their residues have been frequently detected in environmental waters [1–5], usually at levels higher than European Community concentration limits for drinking water, which restrict the maximum amount allowed for single pesticides to 0.1 $\mu g\ l^{-1}$ and for the sum of pesticides to 0.5 $\mu g\ l^{-1}$ [6].

Atrazine, one of the most used triazine herbicides, has been banned in recent years in European countries like Italy and Germany [7,8]. Some information about the riskiness of this herbicide as a human carcinogen has been reported by the US Environmental Protection Agency [9]. Atrazine degrades slowly, once applied in soil, over a period of weeks to months [10]. By means of microbiological transformations its dealkylated metabolites, such as deisopropylatrazine (DIA) and deethylatrazine (DEA) are obtained; these two metabolites have also been found in surface and ground water [11,12]. However, chemical hydrolysis is considered to be the predominant degradation pathway of atrazine in the environment [4], hydroxyatrazine (HA) being the major abiotic degradation product in water and soil [13].

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Due to the large amount of these herbicides applied worldwide, numerous analytical methods have been reported until now. Most of the conventional methods proposed for the determination of triazine herbicides and/or some of their metabolites have used GC with detection methods like MS, electron-capture detection or nitrogen-phosphorus detection [1,8,10,14–17]. In these methods, a preconcentration step with organic solvents or by solid-phase extraction (SPE) is necessary in order to make the aqueous sample compatible with the chromatographic system, as well as to improve their global sensitivity yielding lower detection limits. However, they do not allow direct determination of the hydroxy metabolites, and a previous derivatization step, i.e., methylation with diazomethane [8], has to be applied. Therefore, HPLC with UV or MS detection has been usually preferred and numerous methods which generally include on- or off-line preconcentration steps have been proposed [2,3,5,8,10,13,18–25]. In recent years some enzyme-linked immunosorbent methods have also been developed [26–28].

Methods which include off-line preconcentration steps usually add one or more evaporation steps which increase considerably the total analysis time resulting in time-consuming methods, generally not suitable in monitoring programmes, where a large number of samples have to be analyzed. With regard to methods which include on-line preconcentration of analytes, they are in general quite sensitive and highly automated but still very time consuming, mainly when large amounts of sample are preconcentrated.

Coupled chromatographic techniques are amongst the most sensitive and selective techniques available for the trace-level determination of pollutants in environmental samples. Particularly, coupled-column reversed-phase (RP) LC (LC–LC) has been used in previous works for the determination of pesticide residues in different samples [29–33]. This technique now seems to be one of the most powerful and adequate approaches for the analysis of polar pesticides, especially their very polar transformation products, such as atrazine metabolites.

Fig. 1 shows a schematic representation of an LC–LC system. This technique involves two or more chromatographic separations and several steps: after the injection of a relatively large volume of sample

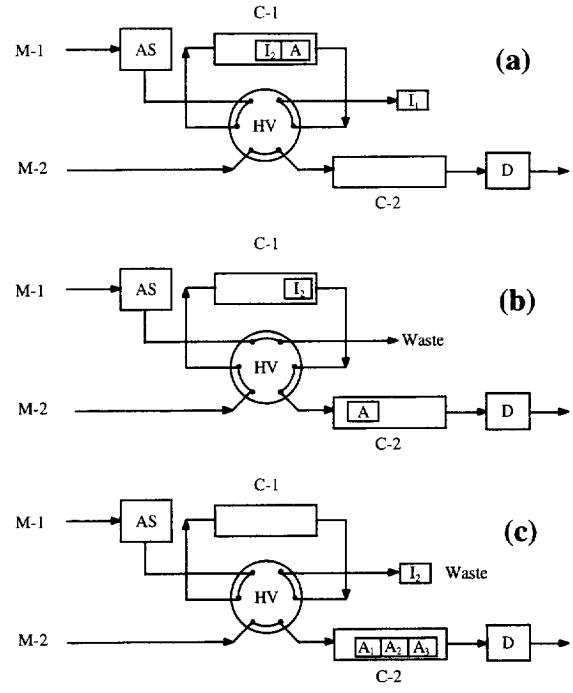


Fig. 1. Schematic representation of a coupled chromatographic system. M-1 and M-2 are mobile phase supplies; AS is the autosampler or injection device; C-1 and C-2 are the first and the second separation columns, respectively; HV is the six-port high-pressure valve; I_1 and I_2 are sample interferences, A (A_1, A_2, A_3) represents the analytes of interest and D is the UV detector. (a) Clean-up; (b) transfer; (c) analysis.

on the first column (C-1) an automated clean-up is performed with a certain volume of the first mobile phase (M-1), in this way the more polar interferences (I_1) are removed (Fig. 1a). Before the first analyte starts to elute from C-1 the switching valve is activated and the fraction containing the analytes (A) is transferred to the second column (C-2) by means of the second mobile phase (M-2) (Fig. 1b). Finally, the analytes are separated on C-2, while the first column is washed with M-1 or any other stronger mobile phase to eliminate the less polar interferences (I_2) (Fig. 1c).

The main characteristics of column-switching optimization for the determination of moderate polar pesticides have been reviewed [34,35]. The introduction of a large volume of an aqueous sample is crucial for the enhancement of sensitivity, however the amount injected depends on the retention of the analytes on C-1 which can be estimated by means of

the capacity factors (k') using 100% aqueous mobile phase. Furthermore, the application of a small transfer volume from C-1 to C-2 enhances the selectivity of the method. For both injected volume and transfer time, the polarity of analytes is the main parameter to be taken into account.

The main objective of this work is the development of a new method based on the use of two coupled LC columns which allows the rapid, sensitive and selective determination in environmental water samples of four triazine herbicides frequently detected in Castellón surface waters [1] as well as the most important atrazine metabolites. In a previous work [33] we have proposed an LC–LC method for the analysis of trace levels of the four parent herbicides (simazine, atrazine, terbuthylazine and terbutryn). In the present paper we have enlarged the scope of the method in order to be able to analyze the main atrazine metabolites as well. The determination of the most polar metabolites (mainly DIA and DEA) is of great interest from an environmental point of view, due to their higher leaching potential which increases the risk of groundwater contamination.

Due to polarity differences between triazine herbicides and metabolites, two different approaches have been developed in order to achieve both the maximum selectivity and sensitivity. The first approach was applied to the parent compounds (simazine, atrazine, terbuthylazine and terbutryn), while the second one was applied to atrazine and its main metabolites (DIA, DEA and HA).

2. Experimental

2.1. Chemicals

Simazine, atrazine, terbuthylazine, terbutryn, deethylatrazine, deisopropylatrazine and hydroxyatrazine were obtained from Dr. Ehrenstorfer (Augsburg, Germany). HPLC-grade methanol and acetonitrile, as well as acetone for pesticide residue analysis, were purchased from Scharlau Science (Barcelona, Spain). HPLC-grade water was obtained by purifying demineralized water in a Nanopure II system (Barnstead, Newton, MA, USA). Analytical-reagent grade ammonium acetate and hydrochloric acid (37%) were bought from Panreac (Barcelona, Spain). Potassium hydroxide of analytical-reagent grade was purchased from Merck (Darmstadt, Germany).

Stock standard solutions of atrazine, terbuthylazine, terbutryn, deisopropylatrazine and deethylatrazine (200 mg l^{-1}) were prepared in acetonitrile, stock standard solution of simazine (200 mg l^{-1}) was prepared in methanol, and stock standard solution of hydroxyatrazine (100 mg l^{-1}) was prepared in HPLC-grade water by dropwise addition of reagent grade hydrochloric acid. These solutions were stored at −20°C. Diluted standard mixtures were prepared in HPLC water (triazine herbicides) and in 1 *M* NH_4Ac (atrazine and metabolites). These mixtures were stored at 4°C.

Disposable 3-ml C_{18} and cation-exchange (propylbenzene sulfonic acid, SCX) SPE cartridges containing 500 mg of sorbent were obtained from Varian (Harbor City, USA).

2.2. Equipment

The modular LC system consisted of a Model 1050 sampler (Hewlett-Packard, Waldbronn, Germany), a manual injector of which, equipped with a 2.0-ml loop, was used to perform large-volume injections (LVI), a Model 1050 gradient LC pump (Hewlett-Packard), a Model C6W six-port switching valve driven by a WE-II actuator from Valco (VIGI, Schenkon, Switzerland) and time-controlled by the sampler, a Model 2150 isocratic LC pump from LKB (Bromma, Sweden) and a Model 1050 ultraviolet detector (Hewlett-Packard). For the LC columns, a 30×4.6-mm I.D. with 5-μm Spherisorb ODS-2 (Scharlau Science) was chosen as first separation column (C-1) and a 125×4.6-mm I.D. column packed with 5-μm Spherisorb ODS-2 (Scharlau Science) as second separation column (C-2). Alternatively, a 100×4.6 mm I.D. column packed with 3-μm Microsphere C_{18} from Crompack (Middelburg, The Netherlands) was also used as C-2.

Recording of chromatograms and quantitative measurements of peak areas were performed with a Hewlett-Packard HPLC ChemStation (software version G1034A). Pipetmans (200, 1000 and 5000 μl) were obtained from Gilson.

Recordings of spectra were performed with a UV-

visible spectrophotometer UV-240 from Shimadzu (Kyoto, Japan).

A Vac-Elut system from Varian was used to perform SPE.

2.3. Chromatographic conditions

Mobile phases M-1 and M-2 used for the determination of triazine herbicides consisted of acetonitrile–water (40:60, v/v) and acetonitrile–water (70:30, v/v) respectively, set at a flow-rate of 1 ml min^{-1}. A wavelength of 223 nm was chosen to monitor the analytes.

For atrazine and metabolites, acetonitrile–water (20:80, v/v) was used as M-1, while M-2 consisted of an acetonitrile–water gradient (see Table 1). Mobile phases were also set at 1 ml min^{-1} and analytes were monitored at 220 nm.

2.4. Procedure

2.4.1. LC–LC analysis

Two ml of water samples containing triazine herbicides were directly injected into the chromatographic system. As stated previously [33], after a short clean-up on C-1 with 2.9 ml of M-1 (injection volume included), C-1 was switched on-line with C-2 for 0.7 min to transfer the fraction containing the analytes to C-2. After transferring, C-1 was rinsed and conditioned with M-1 and the analytes were separated on C-2 with M-2.

For atrazine and its metabolites, the injected sample volume (2 ml) was previously buffered at 1 *M* with ammonium acetate, then a clean-up volume of 2.6 ml and a transfer time of 4.2 min were required as coupling conditions for the LC–LC determination.

Table 1
Mobile phase gradient (M-2) used for the determination of atrazine and its metabolites

Time (min)	Acetonitrile (%)	HPLC water (%)
0	20	80
3.5	20	80
7	35	65
11	90	10
12	20	80

2.4.2. SPE experiences

The enrichment of triazine herbicides was performed on C_{18}-bonded-phase cartridges preconditioned sequentially with 6 ml of methanol, acetone and HPLC water. A water sample volume of 100 ml was percolated at a flow-rate of 5 ml min^{-1} and air-dried for 10 min. After elution with 2 ml of acetone, the eluate was evaporated to dryness under a gentle stream of nitrogen on a water bath at 45°C and redissolved in 5 ml of HPLC water [33].

For atrazine and its metabolites, two different sorbents, C_{18} and SCX, were assayed. In the case of C_{18} cartridges, 100 ml of water sample containing 0.8 g of NH_4Ac (final buffer concentration 0.1 *M*), were percolated through a preconditioned cartridge with 6 ml of methanol, acetone and 0.1 *M* NH_4Ac. Elution was performed sequentially with 5 ml of 1 *M* NH_4Ac–acetone (80:20 v/v) and 1 ml of acetone. After evaporation of acetone, the final volume was adjusted to 5 ml with 1 *M* NH_4Ac.

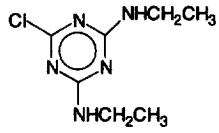
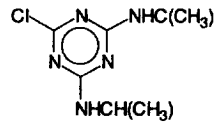
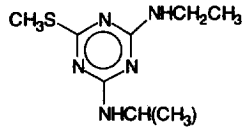
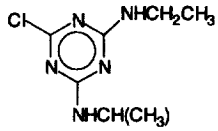
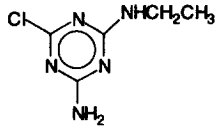
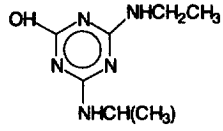
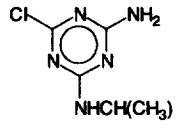
On the other hand, SCX cartridges were conditioned with 6 ml of methanol, acetone and acidified HPLC water (pH 1). The water samples (100 ml) were also acidified at pH 1 and percolated through the cartridge. The analytes were eluted with 5 ml of a mixture of 1 *M* NH_4Ac–acetone (80:20, v/v); after acetone evaporation, the final volume was also adjusted to 5 ml with 1 *M* NH_4Ac.

Finally, 2 ml of concentrated extracts were injected into the LC–LC system.

3. Results and discussion

Sensitivity and selectivity of methods depend largely on the RPLC-UV properties of analytes. Therefore, the UV spectra of the compounds were recorded to evaluate their maximum wavelengths as well as their UV response (Table 2). Then, the retention on C_{18} was studied, since it influences both the maximum injection volume and the potential for separation between analytes and interferences. Capacity factors for different mobile phases with an acetonitrile content ranging from 10 to 70% were obtained. The results are shown in Fig. 2. In general, analytes showed high C_{18} retention in pure water, with capacity factors larger than 50 (except for DIA, $k'=27$). It has been reported that these values are

Table 2
Properties of triazine compounds analysed by LVI–LC–LC with UV detection

Compound	*Formula*	S_{H_2O} *(mg/l)*	λ_{max}*(nm).*	ε *(l0E4·l·mol^{-1}·cm^{-1})*
Simazine		5	223	3.67
Terbuthylazine		8.5	224	3.87
Terbutryn		25	224	4.33
Atrazine		30	223	4.16
DIA		>330	214	2.73
HA		6* 230**	240	2.64
DEA		330	214	3.10

*pH 13; **pH 2.

large enough to allow an acceptable separation between the analytes of interest and the more polar sample interferences on short columns [34].

Large volume injection (LVI) was also possible due to the relatively high retention of analytes on C_{18} columns. Different sample volumes were assayed (from 100 to 4000 μl) injecting standard mixtures of the analytes on C-1 (30 mm long, packed with 5 μm C_{18}). A sample volume of 2 ml was selected as optimum as a compromise between sensitivity and speed of analysis.

As stated before, two different approaches were applied due to polarity differences between analytes: the first approach allows the rapid determination of the four triazine herbicides [33]. To summarize, it can be emphasized that using two reversed-phase C_{18} columns (C-1 and C-2) and two mobile phases, acetonitrile–water (40:60, v/v; M-1; 70:30, v/v;

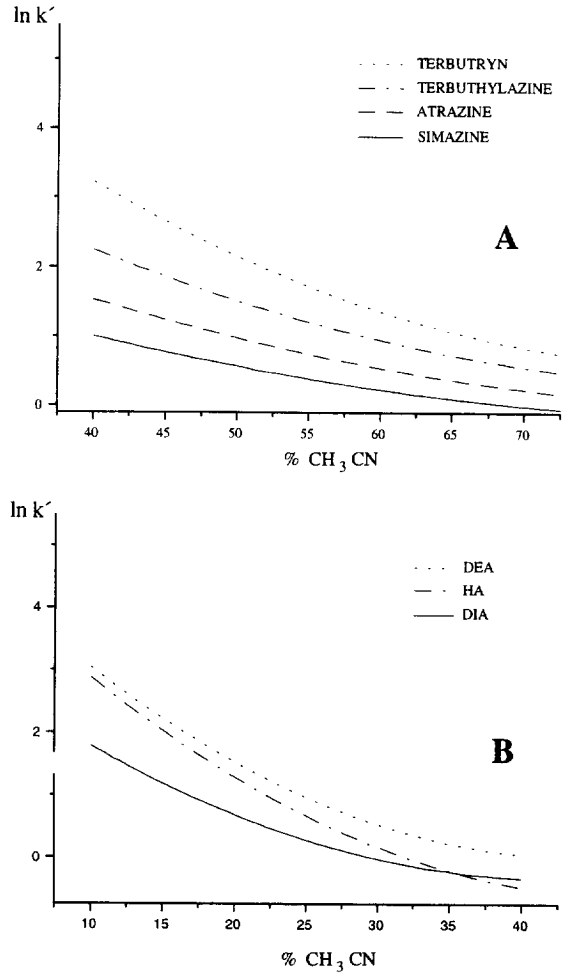


Fig. 2. Retention of triazine herbicides (A) and metabolites (B) on a C_{18} column vs. mobile phase composition plot. The retention is expressed in terms of capacity factor, k'. Where $k'=(t_r-t_0)/t_0$. The values of t_r and t_0 represent the analyte retention time and the void time of the column, respectively.

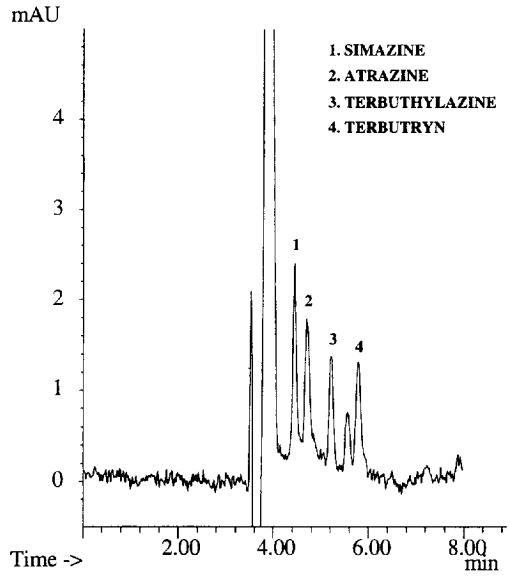


Fig. 3. LC–LC chromatogram of a surface water sample spiked at 0.4 μg l^{-1} with triazine herbicides registered at 223 nm. Volume of sample injected, 2 ml; clean-up time, 2.90 min; transfer time, 0.7 min. Blank subtracted.

M-2), a rapid procedure for the analysis of simazine, atrazine, terbuthylazine and terbutryn is proposed, yielding limits of detection of about 0.1–0.15 μg l^{-1}. Recoveries for drinking and surface water samples, both at 4 and 0.4 μg l^{-1}, ranged between 86 and 104% ($n=5$) with coefficients of variation between 1 and 6%.

As an example, a chromatogram of a surface water sample spiked at 0.4 μg l^{-1} is shown in Fig. 3.

The second approach allows the rapid determination of atrazine and its main metabolites. In this case, compositions ranging between 15 and 25% of acetonitrile for M-1, and different linear gradient elutions for M-2 were assayed. Finally, the following optimum conditions were chosen: acetonitrile–water (20:80, v/v) for M-1; and the acetonitrile–water gradient shown in Table 1 for M-2.

It has been reported that the use of neutral buffered mobile phases improved the HA peak shape [24]. This statement has been proved in our case, but in order to preserve the LC pumps from high concentrations of salts, and also to improve the preseparation on C-1, buffering the water samples before injection was attempted. Two different buffers, KH_2PO_4 and NH_4Ac, with compositions ranging between 0.1 and 1 *M* were assayed. Finally, NH_4Ac was selected in order to avoid the precipitate that phosphate produced in real water samples. The influence of the NH_4Ac concentration is shown in Fig. 4 and demonstrates the effect of buffer concentration on resolution between HA and DEA. In order to achieve maximal resolution and better peak shape, a buffer concentration of 1 *M* was selected.

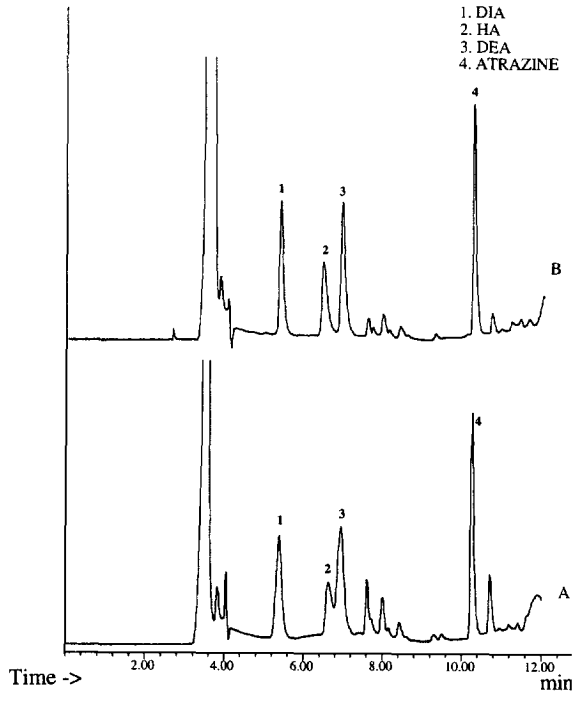


Fig. 4. LC–LC chromatograms of a 40-μg l^{-1} standard mixture solution at 220 nm with different concentration of NH_4Ac. (A) 0.1 *M*; (B) 1 *M*. Volume injected, 2 ml; clean-up time, 2.60 min; transfer time, 4.2 min.

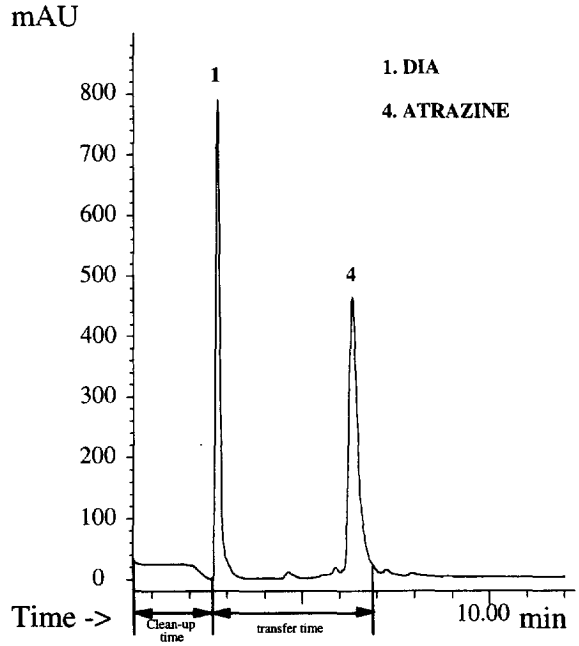


Fig. 5. LC chromatogram of a standard mixture of DIA and atrazine at 400 μg l^{-1} recorded with C-1 (30×4.6 mm I.D., 5-μm Spherisorb ODS-2) connected to the UV detector set at 220 nm. Volume injected, 2 ml; clean-up time, 2.60 min; transfer time, 4.2 min.

Using the proposed mobile phases and the selected buffer, a clean-up volume of 2.60 ml (sample injection included) and a transfer volume of 4.2 ml were estimated by simply connecting the first column (C-1) to the UV detector and injecting the most and least polar analytes, DIA and atrazine (Fig. 5).

Although the wide polarity range between atrazine and its metabolites involves a large transfer volume leading to an expected decrease in selectivity, this does not imply serious problems in the analysis of environmental water samples by RPLC-LC, in which the major sources of interference are usually the more polar compounds [35]. Besides, the separation power of C-1 offers the possibility of removing the large excess of early-eluting polar interferences contributing to the enhancement of selectivity in the analysis of polar analytes like DIA, in contrast to the results shown in a few recently reported methods based on LC with UV detection, which do not allow selective determination of this compound at low concentration levels since it appears in the wide peak of preconcentrated early-eluting interferences [2,18].

The performance of the method is illustrated in Fig. 6, which shows a standard mixture of atrazine and its metabolites at 4 μg l^{-1}. The response linearity was studied for standard solutions with concentrations between 1 and 200 μg l^{-1} (Table 3).

The method was validated by means of recovery experiments with different aqueous matrices. Drinking and surface water samples spiked at several levels were analysed using the developed procedure. Recoveries as well as coefficients of variation are given in Table 4, where it can be seen that both were satisfactory, with values ranging from 86 to 103%, and from 1 to 7%, respectively. A chromatogram of a surface water sample spiked at 2 μg l^{-1} is shown in Fig. 7. Experimental detection limits ($S/N=3$) between 0.2 (atrazine) and 0.5 μg l^{-1} (HA) were obtained for these compounds.

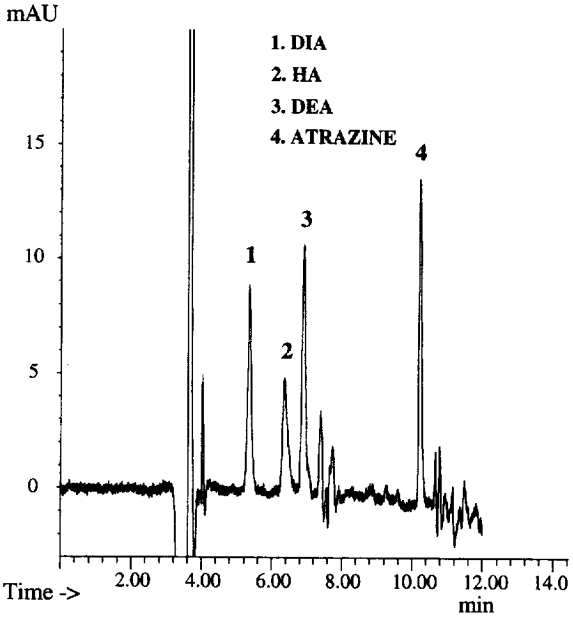


Fig. 6. LC–LC chromatogram of a 4-μg l^{-1} standard mixture solution at 220 nm. Volume injected, 2 ml; clean-up time, 2.60 min; transfer time, 4.2 min. Blank subtracted.

Table 3
Calibration curves (1–200 μg l^{-1}) for atrazine, DIA, HA and DEA in HPLC water samples

	Atrazine	DIA	HA	DEA
S.E.	5.291	7.566	4.500	6.350
R	0.9998	0.9993	0.9992	0.9992
Intercept	−0.716	7.470	−0.312	7.101
(S.D.) intercept	2.949	4.217	2.508	3.540
Slope	2.870	2.365	1.295	1.843
(S.D.) slope	0.030	0.044	0.026	0.037

S.E., standard error; S.D., standard deviation.

The developed coupled-column procedures were significantly rapid, with sample throughputs higher than 60 (for triazine herbicides) and 30 (for atrazine

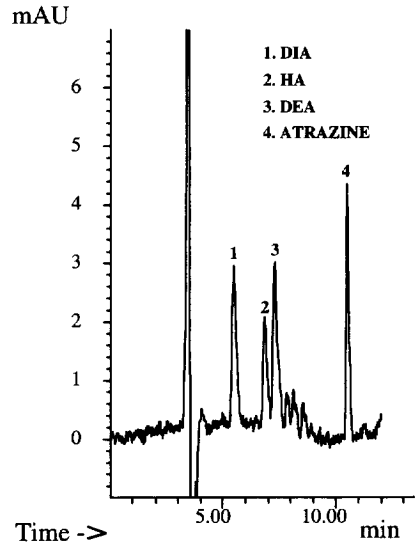


Fig. 7. LC–LC chromatogram of a surface water sample spiked at 2 μg l^{-1} with atrazine and metabolites registered at 220 nm. Volume of sample injected, 2 ml; clean-up time, 2.60 min; transfer time, 4.2 min. Blank subtracted.

and its metabolites) samples per day due to the short analysis time and the low sample handling. They were also greatly sensitive because of the direct injection of 2 ml of sample, and quite selective since early-eluting interferences were removed. With regards to the robustness of the method, the C_{18} columns maintained their performance during more than 6 months and re-adjustments of column-switching conditions (clean-up and transfer time) were not necessary. Thus, very rapid, sensitive, selective and robust methods useful for screening purposes in monitoring programs were developed.

Comparing these procedures with methods reported until now, it is relevant to emphasize that small sample volumes are used (2 ml), achieving similar LODs, compared to the large amounts of

Table 4
Recoveries and coefficients of variation for atrazine and its metabolites in different water samples spiked at three levels ($n=5$)

Compound	Drinking water			Surface water		
	1 μg l^{-1}	4 μg l^{-1}	20 μg l^{-1}	1 μg l^{-1}	4 μg l^{-1}	20 μg l^{-1}
DIA	99 (6)	102 (2)	102 (2)	96 (3)	103 (2)	100(1)
HA	98 (7)	101 (5)	89 (2)	104 (7)	102 (6)	97(4)
DEA	87 (7)	86 (2)	97 (1)	103 (5)	97 (2)	99 (2)
Atrazine	92 (6)	103 (1)	101 (2)	103 (2)	102 (2)	100 (2)

sample involved (up to 2000 ml) when on-line or off-line SPE techniques are used. SPE combined with HPLC is currently one of the main techniques used in residue analysis, due to its good sensitivity, in spite of the time required for sample preconcentration. Thus, detection limits down to 0.1 μg l^{-1} have been proposed for triazine and some of their metabolites in recent papers, although unfortunately the chromatograms of real water samples spiked at this low level of concentration are not always presented [8,10,13,16,17,19,21].

According to the EEC regulations for pesticide residues in drinking water, analytical methods with detection limits lower than 0.1 μg l^{-1} are required. Thus, more sensitive procedures have been developed in this paper adding a preconcentration step using a water sample of only 100 ml on SPE-bonded phase cartridges previous to the LVI–LC–LC analysis.

This SPE procedure was optimized for triazine herbicides previously [33] and applied to drinking water samples spiked at 0.1 μg l^{-1} yielding recoveries between 84 and 96%, with coefficients of variation between 2 and 5% (n=3). The performance of this procedure is illustrated in Fig. 8, which shows

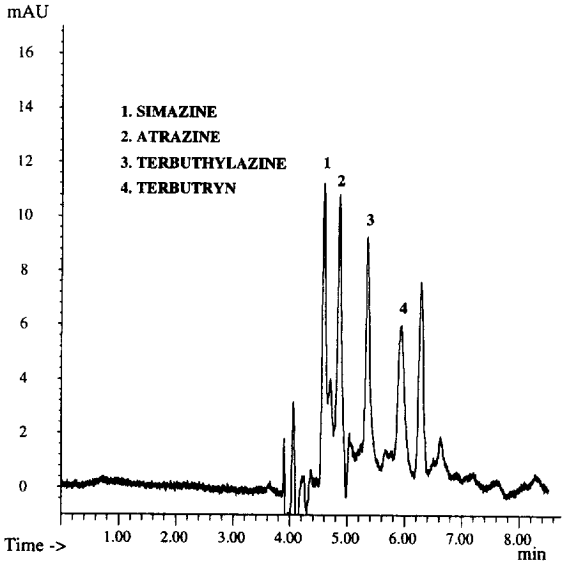


Fig. 8. LC–LC chromatogram of a drinking water sample spiked at 0.1 μg l^{-1} previously preconcentrated on C_{18} cartridges registered at 223 nm. Volume of extract injected, 2 ml; clean-up time, 2.90 min; transfer time, 0.7 min. Blank subtracted.

a drinking water sample spiked at 0.1 μg l^{-1}, preconcentrated on C_{18} cartridges, and analysed by LVI–LC–LC.

For atrazine and its main metabolites, two different sorbents were assayed: a non-polar bonded-phase C_{18} and a strong cation exchanger, SCX. Several drinking water samples were spiked at 0.5 μg l^{-1} and analysed by the proposed SPE–LVI–LC–LC procedure (Table 5) yielding satisfactory results regarding both recovery and reproducibility in the case of the C_{18} material, although a two-step elution was required in order to recover atrazine completely. With regards to the SCX sorbent, results were satisfactory for all the compounds except HA, which was not recovered, although different eluent solvents were assayed consisting of mixtures of 1 M NH_4Ac–acetone with buffer pH ranging between 7 and 11 and percentage of organic modifier between 0 and 30%.

The chromatograms of two samples preconcentrated on C_{18} and on SCX cartridges are shown in Fig. 9 and, as can be seen, significant differences in the background of the chromatogram were also found between the two sorbents. With C_{18} cartridges, recoveries were acceptable even for the more polar metabolite (DIA), in contrast to the unsuccessful results reported in recent papers [19,23]. In relation to this, it is relevant to emphasize that LVI–LC–LC methods are quite sensitive and, consequently, they do not require preconcentration of large sample volumes, so breakthrough of polar analytes is more easily avoided and the analysis time reduced.

In this way, limits of detection down to 0.02–0.1 μg l^{-1} were reached for all the analytes. In comparison to previous procedures involving solid-phase extraction, a considerable gain in reliability and sample throughput was obtained.

Table 5
Recoveries and coefficients of variation for atrazine and its metabolites in drinking water samples (100 ml) spiked at 0.5 μg l^{-1} and preconcentrated by means of SPE (n=5)

	SCX	C_{18}
DIA	93 (2)	99 (2)
DEA	102 (1)	98 (5)
HA	nr	98 (6)
Atrazine	103 (3)	103 (2)

nr, not recovered.

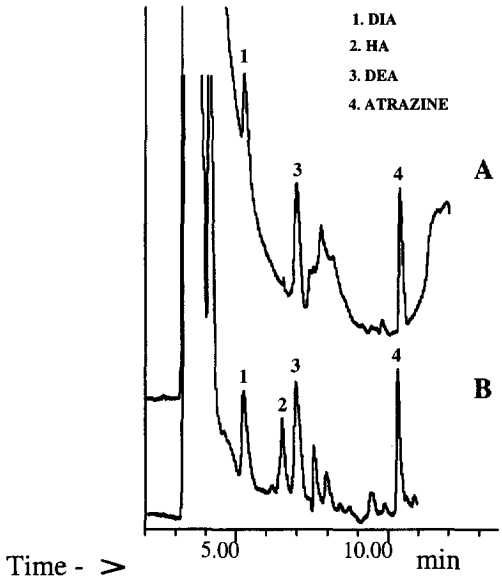


Fig. 9. LC–LC chromatograms (λ=220 nm) of a drinking water sample spiked at 0.5 μg l^{-1} previously preconcentrated on SCX (A) and C_{18} (B) and SPE cartridges. Volume of extract injected, 2 ml; clean-up time, 2.60 min; transfer time, 4.2 min.

4. Conclusions

The combination of coupled-column LC with large-volume injection allowed the development of rapid, sensitive and selective procedures for the trace-level determination of triazine compounds, as well as some of the most important atrazine metabolites in environmental water samples. In comparison to previous works, the proposed procedures are robust and rapid, large sample volumes and preconcentration steps are not required and sample throughput is estimated in more than 30 samples per day. All these characteristics make the method very suitable for monitoring programs, where a high number of samples must be analyzed. The selectivity of the procedures are also important since they allow automated removal of early-eluting interferences. The procedures were also quite sensitive due to the direct injection of up to 2 ml of the aqueous sample, yielding detection limits between 0.1 and 0.5 μg l^{-1}, which can be decreased down to 0.02–0.1 μg l^{-1} by adding a rapid preconcentration step of 100 ml of water sample on C_{18} SPE cartridges before the chromatographic determination by LVI–LC–LC.

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