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Journal of Chromatography A, 777 (1997) 81–90

JOURNAL OF CHROMATOGRAPHY A

Rapid target analysis of microcontaminants in water by on-line single-short-column liquid chromatography combined with atmospheric pressure chemical ionization tandem mass spectrometry

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Abstract

The applicability of trace enrichment and separation of microcontaminants on a 10 mm×2 mm I.D. high-pressure packed (8 μm C_{18} bonded silica or 10–15 μm PLRP-S) column combined on-line with an atmospheric pressure chemical ionization MS–MS system is demonstrated for the target analysis of herbicides in river water. Tailor-made procedures are obtained for a limited number of analytes by tuning the chromatographic efficiency of the short LC column and the specificity of tandem MS, in order to minimize the analysis time. With the on-line short-column LC–MS–MS method, good linearity is obtained for the herbicides in the range of 0.1–10 μg/l. The relative standard deviations of peak areas are less than 5% and, with only 4-ml samples, detection limits of 0.01–0.1 μg/l can be achieved. The total analysis time is 10–15 min. The 10 mm×2 mm I.D. LC columns packed with 8 μm particles show good stability and can be used for at least 40 analyses. Target compound analyses of river water allowed the confirmation of the presence of herbicides such as diuron, simazine, atrazine and terbutylazine at sub-μg/l levels. © 1997 Elsevier Science B.V.

Keywords: Water analysis; Environmental analysis; Tandem mass spectrometry; Pesticides; Triazines; Phenylureas

1. Introduction

In recent years, considerable attention has been paid to the development of screening methods for the determination of microcontaminants in surface water [1–3]. Monitoring of organic microcontaminants in environmental water requires analytical methodology capable of providing reliable data at very low concentration levels. Sample concentration prior to analysis therefore is a necessity. Generally, on-line solid-phase extraction (SPE) is the method of choice. For confirmation purposes, column liquid chromatography (LC) combined with mass spectrometry (MS) is increasingly used [4–9]. Recently, on-line SPE–LC–diode array detection (DAD) UV and/or MS has been applied for the (provisional) identification and/or confirmation of microcontaminants of widely different polarity in surface water at or below the legislative levels (0.5 μg/l for total compound concentration) [10–15]. However, for a number of environmental screening and monitoring purposes, the high separation power and selectively of such a system is not required. Especially in target screening, a significant gain in analysis time, i.e., 15 min instead of 60 min per sample, can be achieved by reducing the selectivity of the LC separation step,

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0021-9673/97/$17.00
PII S0021-9673(97)00558-X

especially when it is used in combination with (tandem) mass spectrometric detection.

One way of reducing the analysis time is by reducing the column length, e.g., from 250 mm to 20 mm. In addition, by using this short 20-mm LC column for both SPE (trace enrichment) and analytical separation, a further reduction of the analysis time can be achieved [16,17]. We demonstrated the practicality of the single-short-column approach (20 mm) coupled to either DAD UV [16,17], particle beam [16], or atmospheric pressure chemical ionization (APCI) [18] (tandem) mass spectrometry (MS–MS) with the analysis of a number of pesticides from different compound classes at or below the 0.5-μg/l level in surface water.

As a continuation of our single-short-column studies, we now investigate the possibility of reducing the column length from 20 mm to 10 mm. Preliminary results showed the feasibility of using such a 10-mm column packed with 5 μm material coupled on-line to a thermospray (TSP)-MS–MS system [19] for the rapid target analysis of triazines in surface water. Although the primary aim was to separate the unretained peak and other interferences from the compounds of interest, the six triazines could actually be separated from each other within 5 min using the separation efficiency of the LC column and specificity of MS–MS detection. The total analysis time was 15–20 min. There were, however, two problems. Firstly, although some of the 10-mm columns packed with 5 μm C_{18} bonded silica could be used for quite a number of consecutive runs, this was not true for most of them. Secondly, in order to achieve concentration levels of 1 μg/l for these herbicides in surface water, on-line preconcentration of volumes up to 48 ml was necessary with, consequently, a seriously increased total analysis time. This somewhat disappointing result was mainly due to the rather poor detection performance of the TSP-MS–MS instrument used. With these two aspects in mind, coupling a better-packed 10-mm column to a modern MS–MS via an APCI interface seems to be a logical step to considerably reduce the required sample volume and improve the ruggedness of the total procedure.

In the present project, we especially studied the possibility of tuning the separation efficiency of a 10-mm LC column and the additional specificity of tandem MS, in order to minimize the analysis time and consequently increase sample throughput. To what extent the chromatographic resolution can be minimized, largely depends upon the application at hand, the number of analytes and the detection system used. In this study, six triazine and eight phenylurea herbicides were selected as model compounds to demonstrate that, for target analysis of a limited number of compounds in aqueous samples, single-short-column LC–APCI-MS–MS is a viable and reliable approach.

2. Experimental

2.1. Chemicals and reagents

HPLC-gradient-grade methanol, acetonitrile and water were from J.T. Baker (Deventer, Netherlands). The triazine and phenylurea herbicide standards were from Riedel-de Haën (Seelze, Germany), and were over 95% pure.

Stock standard solutions were prepared by dissolving 1000 μg of each compound in 1 ml of acetonitrile and were stored in the dark at −20°C. Because of its lesser solubility in acetonitrile, for simazine a standard stock solution of 200 μg/ml was prepared. Standard mixtures were prepared by dilution of the stock solutions with HPLC-grade water to give concentrations ranging from 5 ng/ml to 5 μg/ml, except for simazine the concentrations of which were 75% of those of the other triazines. The mixtures were used for standard injections and spiking of the surface water samples. During the entire study, the standard mixtures were stored at 4°C.

Tap water was sampled (Nieuwegein, Netherlands, April and August 1996) after letting the tap run for 10 min. The tap water samples were analysed without any prior clean-up. Surface water was collected from the river Lek/Rhine (Nieuwegein, Netherlands, April and August 1996). Before use, an aliquot (1 l) of water sample was filtered over a 0.45 μm membrane filter (Schleicher and Schuell, Dassel, Germany). Spiking was done by adding a proper amount of a standard mixture solution to 100-ml samples.

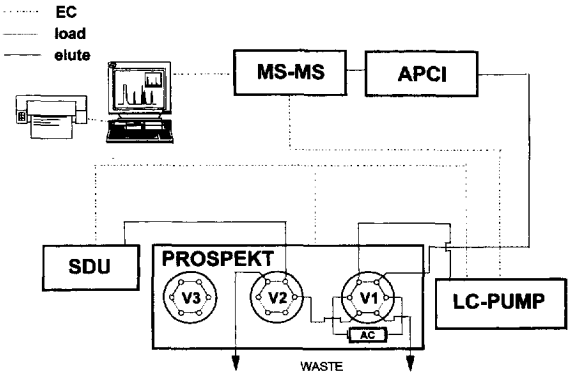

Fig. 1. Set-up of the single-short-column LC–MS–MS system. V1, V2 and V3, high-pressure six-port valves of the Prospekt. SDU, solvent delivery unit containing methanol, water and sample; AC, single-short-column. APCI, atmospheric pressure chemical ionization interface; MS–MS, a triple stage quadrupole: TSQ 7000. EC= electronic connections.

2.2. Instrumentation and columns

2.2.1. Short-column LC

In this study, two types of short columns (10 mm×2 mm I.D.) were used, one packed with 8 μm C_{18} bonded silica and the other with 10–15 μm PLRP-S, which is a styrene–divinylbenzene copolymer. All columns were high-pressure-packed SPE cartridges from experimental batches kindly provided by Spark Holland (Emmen, Netherlands). Standard SPE cartridges (packed with 20–40 μm C_{18} bonded silica) were used as a means of comparison.

2.2.2. LC set-up

The LC eluent was delivered by an HP 1050 LC system equipped with a quaternary solvent delivery system (Hewlett-Packard, Waldbronn, Germany). The eluents were degassed by bubbling helium through the eluents in the LC system. Automated sample handling, including conditioning and washing of the 10-mm column and loading of the water sample onto the column was done by a Prospekt (Spark Holland) sample handling module equipped with three six-port switching valves and a solvent delivery unit (SDU). Fig. 1 shows a schematic diagram of the on-line single-short-column LC–APCI-MS–MS system.

An additional six-port switching valve, inserted between the Prospekt and the APCI interface, was used to switch the APCI-MS–MS part of the system off-line during conditioning and sample loading. 30 s after the start of the elution programme, the APCI-MS–MS was switched in-line by automated switching of the valve. This step was included in order to remove interferences such as humic acids and inorganic salts which are still present even after washing of the column with water, to waste.

2.2.3. MS–MS

Tandem mass spectrometry was performed on a Finnigan MAT (San José, CA, USA) TSQ 7000 triple-stage quadrupole equipped with an APCI interface. The interface was operated with the heated capillary at a temperature of 225°C. The temperature of the vaporizer was set at 400°C and the nitrogen sheath gas was set at 80 p.s.i. (1 p.s.i.=6894.76 Pa). For positive ions, the corona discharge was maintained at a potential of 5.0 μA. The manifold temperature was maintained at 70°C.

2.3. Analytical conditions and procedures

Gradient LC elution was performed using water–methanol (95:5, v/v) (A) and water–methanol (5:95, v/v) (B) as eluents. The analytical conditions are given in Table 1.

The trace-enrichment procedure used in the single-short-column LC–MS–MS experiments is summarized in Table 2. The procedure consists of con-

Table 1
Analytical conditions

Compounds	Column	Linear gradient conditions[1]	Flow-rate (ml/min)
Triazines	C_{18}	A–B (80:20, v/v) to (40:60, v/v) in 5 min	0.5
Triazines	C_{18}	A–B (90:10, v/v) to (50:50, v/v) in 5 min	1.0
Phenyureas	PLRP-S	A–B (95:5, v/v) to 100% B in 5 min	1.0

[1] Eluent A: water–methanol (95:5, v/v) and eluent B: water–methanol (5:95, v/v).

Table 2
Time schedule for the Prospekt sample preconcentration procedure

C_{18}/PLRP-S		PLRP-S		SDU Solvent	Prospekt				
Time (min:s)	Purge flow (ml/min)	Time (min:s)	Purge flow (ml/min)		Event	Valve			Auxillary
						1	2	3	5
0:00	1.0	0:00	2.0	MeOH	Cond.	Purge	Purge	Purge	
2:00	1.0	1:00	2.0	Water	Cond.				
4:00	1.0	2:00	2.0	Sample	Load				
8:00	1.0	4:00	2.0	Water	Wash				
9:00	1.0	5:00	2.0		Start LC	Elute			ON
9:01	1.0	5:01	2.0		Flush				OFF
9:05	2.0	7:05	2.0	MeOH					
11:05	0.0	9:05	0.0						
15:00		10:00			End of run				

Event: cond.: conditioning of column with methanol and water; load: load surface water sample on column; wash: remove inorganic salts from column; elute: desorb analytes with eluent to MS; start LC: contact closure to start LC programme; flush, SDUs (solvent delivery unit) lines are flushed with methanol.

ditioning of the column methanol to wet the packing material and to remove hydrophobic compounds left from the previous run and, next, with water to obtain suitable conditions for analyte sorption, loading of surface water sample onto the column, washing with water and finally desorption with the LC eluent. Total sample preparation time varied between 5 and 10 min, depending on the sampling flow-rate. The total analysis time depends on the sample volume needed for a certain application and the chromatographic run time.

MS–MS experiments were carried out with an argon pressure of approx. $2.0 \cdot 10^{-3}$ Torr (1 Torr= 133.322 Pa) in the collision cell, using a (optimized) collision energy of −20 eV for the phenylureas and −25 eV for the triazines for multiple reaction monitoring (MRM). Product ions were recorded with quadrupole 1 (Q1) set at a fixed m/z value representing $[M+H]^+$ and with quadrupole 3 (Q3) scanning from m/z 10 to 300 u at 0.5 s/scan with Q3 set at 0.6 u. For MRM experiments, both Q1 and Q3 were set at fixed m/z values, viz. $[M+H]^+$ for Q1 and two of the most intense product ions for Q3. The resolution of Q1 was decreased to give a peak width at the base of the peak of about 4 u and the scan time was optimized to 0.3 s/scan. The protonated molecule and the two product ions of each of the herbicides used in the MRM experiments are included in Table 3.

2.3.1. Automated on-line analysis

During trace enrichment, the LC and MS are in the "waiting" position. After the enrichment procedure has been completed, a contact closure signal is given to the HP1050 to start the LC analysis. At the same time the HP1050 will give a contact closure signal to the tandem MS, which is kept in operation during the complete analysis. At the end of run, a signal is given to the tandem MS by the HP1050, and the former returns to the "waiting" position for the next analysis. One of the advantages of the Prospekt is that it enables for the automated exchange of the short columns. Time-consuming experiments such as, e.g., column-to-column stability studies, can therefore be performed (overnight) in an automated way.

3. Results and discussion

3.1. General aspects

Recently, a single short 10-mm LC column coupled to TSP-MS–MS was used for the target analysis of six herbicides in surface water [19]. Part of the problems that were observed were related to the insufficient stability and efficiency of the experimental LC columns used. High-pressure packing of the small-particle, i.e., 5-μm, C_{18} bonded silica in 10

Table 3
Retention times, protonated molecules and two product ions (monitored in MRM experiments) using single-short-column LC–APCI-MS–MS of 5-ng loop injections

Compound	t_R	$[M+H]^+$	Two major product ions[1]
1. Simazine	102	202	124 (100) 132 (82)
2. Cyanazine	124	241	96 (14) 214 (100)
3. Atrazine	168	216	96 (42) 174 (100)
4. Propazine	236	230	146 (100) 188 (65)
5. Sebutylazine	230	230	132 (10) 174 (100)
6. Terbutylazine	260	230	96 (34) 174 (100)
7. Desmethylmetoxuron	59	201	123 (95) 156 (100)
8. Metoxuron	105	229	46 (70) 72 (100)
9. Monuron	114	199	46 (60) 72 (100)
10. Chlorotoluron	143	213	46 (68) 72 (100)
11. Diuron	153	233	46 (76) 72 (100)
12. Linuron	204	249	160 (58) 182 (100)
13. Chlorobromuron	281	293	182 (88) 204 (100)
14. Neburon	225	275	57 (100) 88 (80)

[1] Numbers in parentheses give relative abundances of the two product ions used in MRM experiments.

mm×2 mm I.D. columns did not provide good column-to-column reproducibility. Furthermore, with our in-laboratory constructed MS–MS set-up, 40–50-ml samples had to be used to obtain detection limits of ca. 1 μg/l in surface water in the MRM-mode. One item of interest, therefore, was to find more stable and efficient columns. Recently, batches of columns packed with 8 μm (instead of 5 μm) C_{18} bonded silica were made available to us. Since, simultaneously, we were given the opportunity to couple the short columns to a state-of-the-art APCI-MS–MS, which should provide distinctly improved analyte detectability (cf. [18]), several preliminary experiments were conducted to assess the sample volume typically required under these optimized conditions. A 10-fold improvement appeared to be a reliable estimate (also see Section 3.2 Section 3.3 Section 3.4). So instead of the earlier 40–50-ml volumes, ca. 4-ml samples could now be used; this would, of course, significantly enhance the speed of analysis.

Before starting a systematic research on the quality of the 8-μm packed short columns (and the total set-up), it was thought prudent to find out whether it would be possible to use 10 mm×2 mm I.D. cartridges packed with even larger, i.e., conventional 20–40 μm C_{18} bonded silica. The results of a short study on the behaviour of the two types of packing material which are shown in Fig. 2, are rather obvious. Whereas the six triazines are completely resolved on the 8-μm packed short column, with the set-up using the conventional, larger particles, essentially no separation at all is found.

3.2. Characteristics of 8-μm C_{18} bonded silica short columns

Using on-line LC–APCI-MS–MS, we tested a number of short columns high-pressure packed with 8-μm C_{18} bonded silica. First, with a single short column the influence of the flow-rate was studied by performing target analysis on 4-ml water samples and six triazines as model compounds spiked at the 0.5 μg/l level. Twenty consecutive runs were performed, viz. ten runs at a sampling and elution speed of 0.5 ml/min, and ten at 1 ml/min. In both cases the repeatability was good with relative standard deviations (R.S.D.s) of less than 1.5 and 5% for the retention times and peak areas of all analytes, respectively. No deterioration in terms of loss of chromatographic efficiency of the column was observed even after 40 analyses. Next, four target analyses (at the 0.1-μg/l spiking level) were carried out with ten short columns, using a flow-rate of 1 ml/min for both sampling and elution. The column-to-column reproducibility of the ten 8-μm columns was fully satisfactory with R.S.D.s of peak areas of 4–9% for all six herbicides.

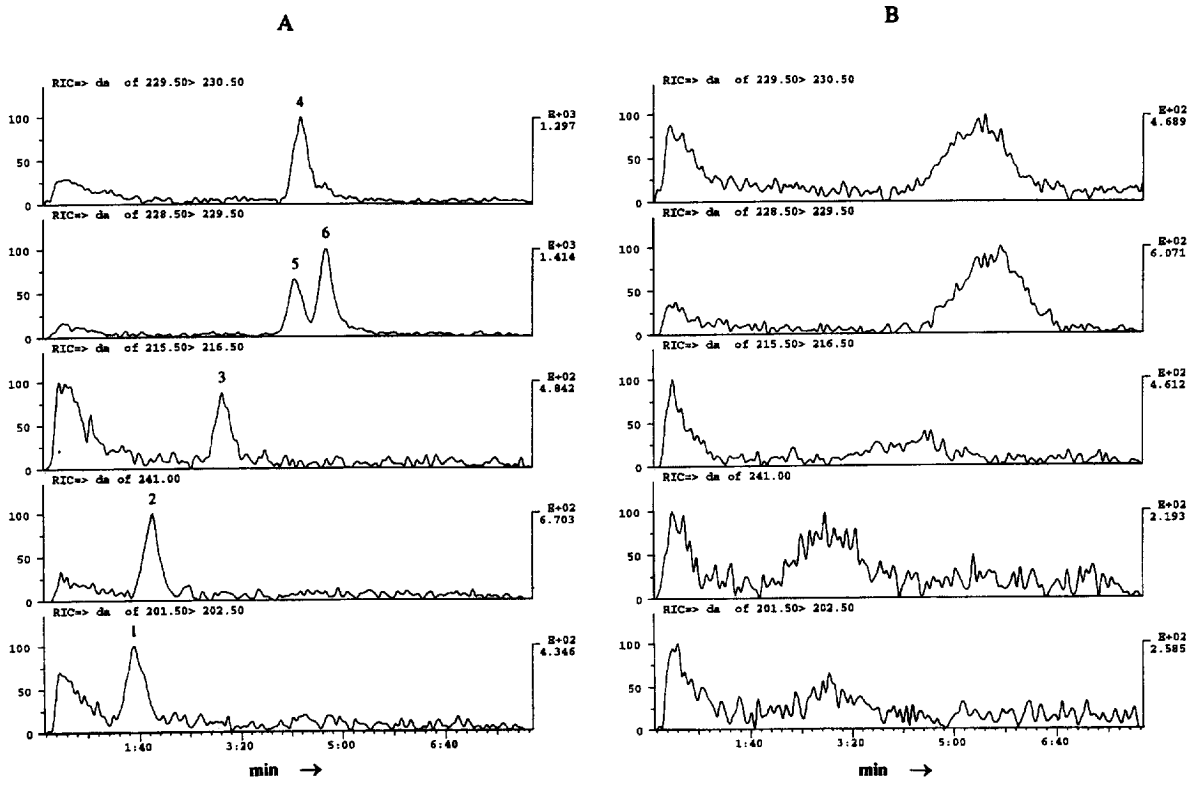

Fig. 2. Target analysis of six triazines at 0.1 μg/l in 4-ml water sample on a 10 mm×2 mm I.D. C_{18} bonded silica column packed with (A) 8-μm particles and (B) 20–40-μm particles. All sampling flow-rates were 1 ml/min. Conditioning with 2 ml of methanol and 2 ml of water; clean-up with 1 ml of water (Table 2). Linear gradient from A–B (80:20, v/v) to (40:60, v/v) in 5 min at a flow-rate of 0.5 ml/min (Table 1). For peak assignment and precursor and product ions selected for each analyte, see Table 3. MRM conditions: 0.3 s/scan. For other conditions, see Section 2.2 Section 2.3.

Experiments similar to the above were also carried out for 10 mm×2 mm I.D. columns packed with 10–15 μm PLRP-S. The repeatability and reproducibility again were good, with R.S.D.s of peak areas of 1–9% when using a flow-rate of 1 ml/min, and 2–8% when using 2 ml/min during the entire procedure. Even after more than 100 analyses of 4-ml surface water samples and when using both sampling flow-rates, no deterioration of the PLRP-S column or loss of performance of the entire short-column LC–APCI-MS–MS system was observed.

3.3. Short-column LC–APCI-MS–MS of triazines

Although isocratic elution of the triazines was used before [19], it was decided to apply gradient elution in the present study to obtain better peak shapes and, consequently, enhanced analyte detectability. The currently used gradient (see Table 1) meets our main criteria, viz. an LC run time of 5 min or less with a clear separation of the first eluting test analyte from the solvent front and a "minimum" separation of the analytes from each other (cf. Fig. 2).

First, 10-μl loop injections of the triazine mixture on a short column packed with 8-μm C_{18} bonded silica were performed at concentration levels ranging from 5 to 5000 pg/μl (50 pg to 50 ng injected). The MS–MS was operated in the MRM positive-ion mode by monitoring two product ions for each individual precursor ion selected. Each analysis (5

data points) was performed in duplicate and average peak areas were plotted against the concentrations of the triazines. The plots were linear with R^2 values of 1.000 for all test analytes. The detection limits of six analytes were in the range of 30–100 pg.

Although APCI-MS–MS is reported to be a very sensitive and selective detection procedure for the determination of microcontaminants in water, trace enrichment is still necessary. From the loop injection data it was concluded that 4-ml sample volumes should be sufficient to detect the compound of interest at the required level of 0.1 μg/l (for individual compounds) [10,11]. Initial experiments with 4 ml of river Rhine water spiked at the 0.05-μg/l level using a C_{18} bonded silica short column and detection in the MRM positive-ion mode showed that the calculated sample volume indeed was sufficient (cf. Fig. 2A). Next, the linearity of the procedure was evaluated using 4-ml samples spiked with concentrations levels ranging from 0.1 to 5 μg/l. Peak integration was performed over the signal (sum of abundances of two most intense product ions of each individual triazine). For all analytes, the calibration curves were linear with R^2 values of at least 0.999 (Table 4). The precision of the method was tested by ten consecutive analyses of 4-ml samples spiked at the 0.5 μg/l level. All R.S.D.s of the retention times and peaks areas were less than 1.5 and 5%, respectively. The detection limits of the six triazines in 4 ml of surface water were between 10 and 30 ng/l (Table 4). This is about 10–50 times lower than the threshold levels typically laid down by regulatory bodies.

3.4. Short-column LC–APCI-MS–MS of phenylurea herbicides

Using the same criteria as for the triazines, a "minimum" separation of the eight phenylurea herbicides could be obtained on a 10–15-μm PLRP-S column using a linear gradient from A–B (95:5, v/v) to 100% B in 5 min. Analytical performance data were obtained from 10-μl loop injections. With regard to linearity, all plots of peak areas against analyte concentration were linear with R^2 of at least 0.999 (5 data points in duplicate). The detection limits were in the range of 30–200 pg.

With regard to trace enrichment, Fig. 3 shows a typical result obtained after short-column LC–APCI-MS–MS of 4 ml of river water spiked with the eight phenylurea herbicides at the 0.2-μg/l level, gradient elution and detection in the MRM mode. Repeated analysis of spiked samples in the range between 0.1 and 10 μg/l showed good linearity (Table 5). In addition, a repeatability study was performed at the 0.5-μg/l spiking level by analysing ten samples of each 4 ml of river water. The R.S.D.s of the retention times were less than 1% for all phenylureas, except desmethylmetoxuron. As regards the peak areas, the R.S.D.s were less than 4%, with desmethylmetoxuron (9%) again as exception. Obviously, for this first eluting compound insufficient separation from the solvent front has been achieved. During passage of the solvent front, the stability of the ionization conditions is distorted which results in a loss of reproducibility which cannot be dealt with by MRM. The detection limits for the phenylurea

Table 4
Analytical data[a] for short-column LC–APCI-MS–MS in MRM-mode of analysis of triazines in river Rhine water (4 ml)

Compound	t_R (s)	R.S.D. values		Calibration equation[b]	R^2	Detection limits (ng/l)
		t_R (%)	Peak area (%)			
1. Simazine	101	1.5	2.1	$y=34\,444\ (163)x+1428\ (374)$	1.000	20
2. Cyanazine	124	<0.1	1.9	$y=58\,656\ (355)x-2295\ (815)$	1.000	30
3. Atrazine	168	<0.1	5.2	$y=68\,143\ (639)x+14\,759\ (1466)$	0.999	20
4. Propazine	236	<0.1	0.8	$y=103\,477\ (460)x+1990\ (1055)$	0.999	10
5. Sebutylazine	230	0.5	2.4	$y=88\,406\ (840)x-5007\ (1927)$	0.999	10
6. Terbutylazine	260	<0.1	1.8	$y=90\,797\ (462)x-2760\ (1060)$	0.999	10

[a] R.S.D.s at 0.5 μg/l level ($n=10$); calibration range, 0.1–5 μg/l (5 data points in duplicate); detection limits at $S/N=3$.
[b] y=area, x=concentration (μg/l): $y=b(s_b)x+/-a(s_a)$.

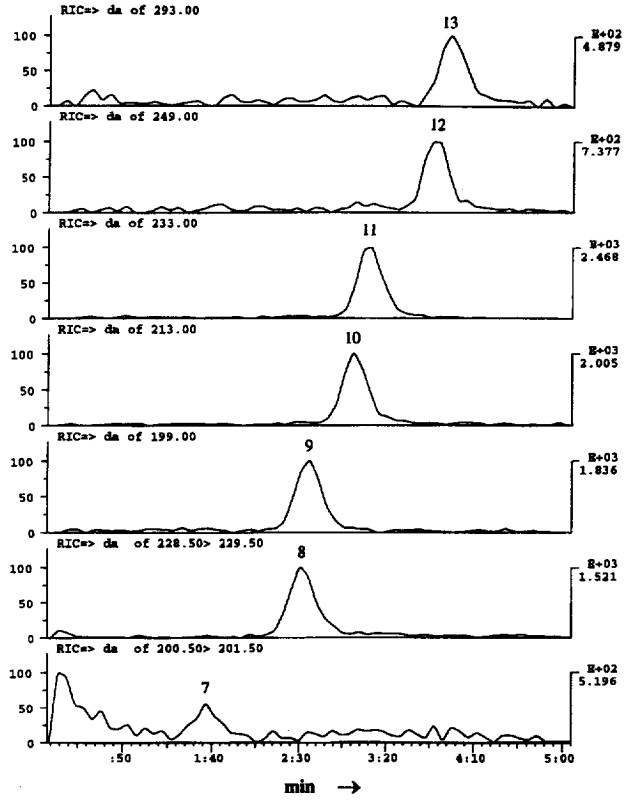

Fig. 3. Short-column LC–APCI-MS–MS MRM chromatogram of trace enrichment of 4 ml river Rhine water spiked with eight phenylurea herbicides at the 0.2-μg/l level on a 10–15-μm PLRP-S column. All sampling and elution flow-rates, 1 ml/min. Conditioning with 2 ml of methanol and 2 ml of water; clean-up with 1 ml water (Table 2). Linear gradient from A–B (95:5, v/v) to 100% B in 5 min. Peak assignment and precursor and product ions selected for each analyte, see Table 3. MRM conditions: 0.3 s/scan. For other conditions, see Section 2.2 Section 2.3.

Table 5
Analytical data[a] for short-column LC–APCI-MS–MS in MRM-mode of analysis of phenylureas in river Rhine water (4 ml)

Compound	t_R (s)	R.S.D. values		Calibration equation[b]	R^2	Detection limits (ng/l)
		t_R (%)	Peak area (%)			
7. Desmethylmetoxuron	59	2.2	9.4	y=5970 (115)x+8213 (404)	0.996	100
8. Metoxuron	105	1.0	2.0	y=65 466 (614)x−493 (2650)	0.999	10
9. Monuron	114	<0.1	1.9	y=68 020 (542)x+4411 (2340)	0.999	10
10. Chlorotoluron	143	<0.1	1.5	y=70 240 (819)x+9917 (3533)	0.998	10
11. Diuron	153	<0.1	2.1	y=66 641 (563)x+4552 (2429)	0.999	10
12. Linuron	204	0.7	2.3	y=24 133 (222)x+201 (958)	0.999	50
13. Chlorobromuron	218	<0.1	4.1	y=21 504 (320)x−993 (1379)	0.998	50
14. Neburon	225	0.9	2.9	y=64 895 (409)x+153 (1767)	0.999	50

[a] R.S.D.s at 0.5 μg/l level (n=10); calibration range, 0.1–10 μg/l (7 data points in duplicate); detection limits at S/N=3.
[b] y=area, x=concentration (μg/l): $y=b(s_b)x+/-a(s_a)$.

herbicides were in the range of 10–100 ng/l for 4 ml river water samples (see Table 5). The total time of analysis (trace enrichment, separation and detection) was 15 min. Actually, if the flow-rate of the sampling procedure was increased to 2 ml/min, the total time of analysis could be reduced to 10 min. In that case the time of sampling and elution were the same (5 min).

3.5. Real sample target analysis

The applicability of the single-short-column LC approach was demonstrated by the analysis of surface water taken from the river Rhine on 15 August 1996 (near WRK, Nieuwegein, Netherlands). Target analysis allowed the rapid tentative identification of diuron, simazine, atrazine and terbutylazine. Fig. 4 shows the target analysis and subsequent confirmation of the four microcontaminants. The concentration levels were calculated from the calibration data. They were about 80 ng/l for diuron and 20 ng/l, 180 ng/l and 30 ng/l for simazine, atrazine and terbutylazine, respectively.

4. Conclusions

On-line trace enrichment and separation on a single short 10 mm×2 mm I.D. LC column combined with APCI-MS–MS detection can successfully

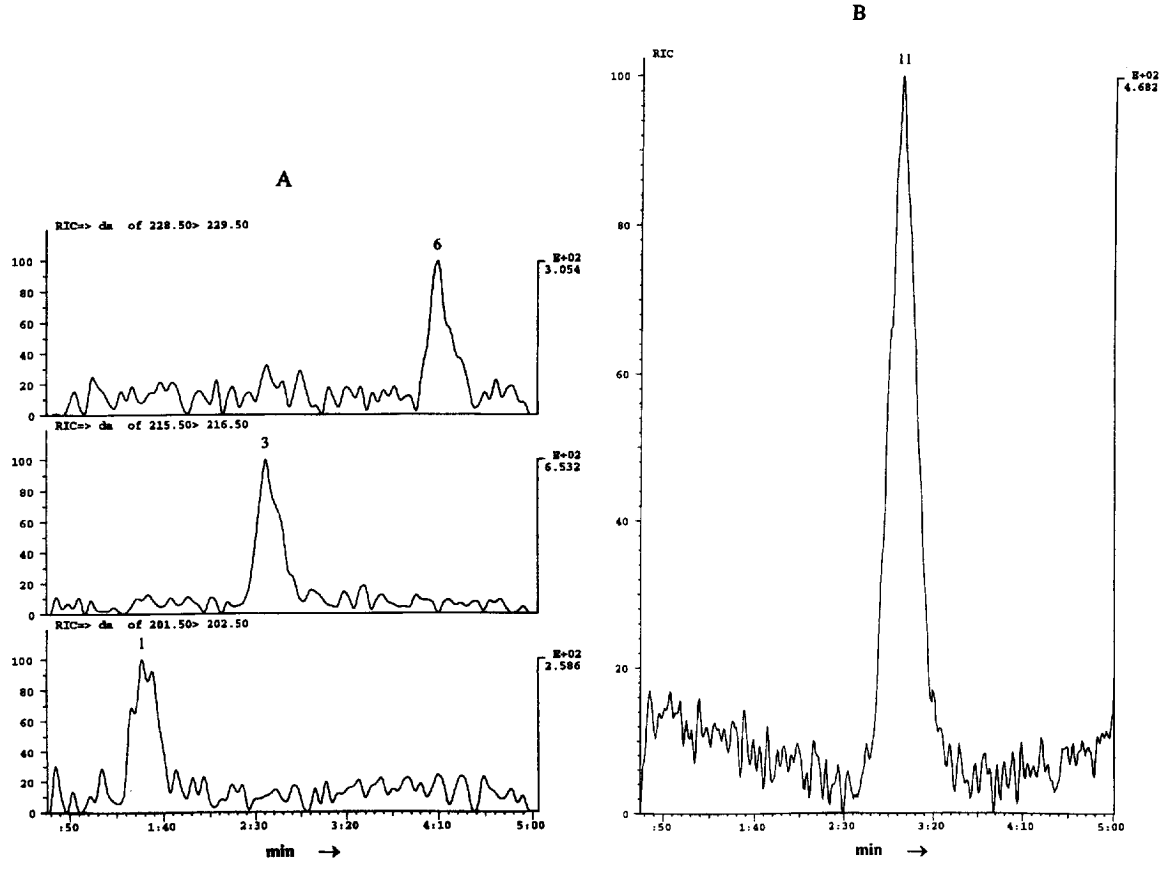

Fig. 4. Short-column LC–APCI-MS–MS MRM chromatogram of 4 ml of river Rhine water on a 10 mm×2 mm I.D. column (A) packed with 8 μm C_{18} bonded silica: identification of simazine, atrazine and terbutylazine (concentrations of ca. 20, 180 and 30 ng/l, respectively), and (B) packed with 10–15 μm PLRP-S: confirmation of the presence of diuron (concentration, ca. 80 ng/l). Conditions: (A), linear gradient elution with A–B (90:10, v/v) to (50:50, v/v) in 5 min at 1 ml/min; for all other conditions, see Fig. 2 and Section 2.2 Section 2.3; (B), see Fig. 3 and Section 2.2 Section 2.3. For peak assignment, see Table 3.

be used for the rapid target analysis of relevant microcontaminants in surface water. With the 8-μm C_{18} bonded silica columns recently made available to us, and also with the 10–15-μm PLRP-S columns, stability and efficiency do not pose real problems anymore. At least 40 analyses can be performed with a single column, without deterioration in terms of column stability or chromatographic efficiency. Column-to-column reproducibility also is fully satisfactory with R.S.D.s of peak areas of less than 9% for all herbicides tested (ten columns; four runs per column).

In the present study, the LC separation on the 10 mm×2 mm I.D. columns was tuned to the specificity of the MS–MS instrument to achieve the target analysis of a limited number of compounds within 5 min. With APCI-MS–MS, the required sample volumes could easily be reduced by a factor of 10 compared with an earlier study [19], viz. to 4 ml, to obtain minimum detectable concentrations of 0.01–0.1 μg/l. Since linearity in the concentration range of 0.1–10 μg/l (MRM mode) was fully satisfactory, quantification could confidently be performed at the trace level. Total analysis times typically were 10–15 min.

In view of the above, it seems safe to state that tailor-made applications such as the identification or confirmation of a limited number of target analytes in a few millilitres of an aqueous sample or sample extract can now be developed for a wide variety of analytes. Current research is devoted to the application of this approach to bioanalytical and food analysis.

Acknowledgments

The authors thank Spark Holland for supplying the high-pressure-packed 10 mm×2 mm I.D. C_{18} bonded silica and PLRP-S short columns.

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