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Determination of traces of pesticides in water by solid-phase extraction and liquid chromatography–ionspray mass spectrometry

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Abstract

A multi-residue analytical method for six pesticides (atrazine, hydroxyatrazine, carbofuran, promecarb, linuron and monolinuron) in drinking water has been developed. The method combines liquid chromatography and mass spectrometry using an ionspray interface. The linearity domain, as well as the limits of detection and quantification, were determined for each compound. Although satisfactory performance could be achieved, present drinking water regulations (0.1 $\mu g\ l^{-1}$ for single pesticide) requires a pre-concentration step. This was performed using solid-phase extraction with octadecyl-bonded silica cartridges. The analytical procedure was tested on water samples spiked at the 0.04 and 0.08 $\mu g\ l^{-1}$ levels, and allowed the determination of the investigated pesticides (except hydroxyatrazine) at these trace concentrations. © 1997 Elsevier Science B.V.

Keywords: Water analysis; Environmental analysis; Pesticides

1. Introduction

The detection and characterization of pesticides in drinking water in trace concentrations imposed by the European Community Drinking Water Directive (i.e., maximum admissible concentration of 0.1 $\mu g\ l^{-1}$ for single pesticide and 0.5 $\mu g\ l^{-1}$ for total pesticides) remain a challenging analytical problem. Gas chromatography–mass spectrometry (GC–MS) coupling remains one of the most extensively employed techniques. However, numerous pesticide residues are not amenable to GC–MS detection because of either thermal instability (e.g., carbamates and uron herbicides) and/or polarity. This drawback can be overcome by a derivatization step, however, the added sample treatment is often time consuming and generally leads to some interferences.

Therefore, pesticides are more frequently separated by liquid chromatography (LC), coupled to a conventional UV detector (e.g., a diode array detector), a fluorescent or an electrochemical detector. Nevertheless, interference and sensibility problems are also encountered, and these detectors suffer from a lack of structural information.

Unambiguous identification is achieved by coupling LC to mass spectrometry (LC–MS). Several recent publications have reviewed the different interfaces, their principles and application domains [1–3]. Only a few of them have so far been applied to pesticides [4,5]. The particle beam (PB) interface provides electron impact mass spectra, giving access to comparison with large data bases [5], and in particular, it was applied to the determination of carbamates [6]. Unfortunately, the method is not

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sensitive [5] and induces uncontrolled thermal degradation, besides electron induced fragmentation. The thermospray (TSP) interface has also been extensively applied [4], for example to carbamates and uron herbicides [7], or triazines [8]. However, problems of optimization and repeatability, and thermal degradation of some pesticides were encountered [9,10]. In addition, lack of structural information was due to the absence of abundant fragment ions [4,5].

The development of atmospheric pressure ionization (API) systems offers new opportunities for the determination of thermolabile and polar compounds, such as carbofuran [11]. Thus, heated nebulizers under atmospheric pressure chemical ionization mode (APCI) have been tested on few residues including: carbamates [12], phenylureas [13] and organophosphorus pesticides [14,15]. The main limitation of this interface is the process itself: ionization occurs in the gas phase, thus requiring sample volatilization by sufficient heating, and some pesticides may undergo thermal degradation prior to ionization by the corona discharge [1]. Unlike APCI, electrospray ionization is not prone to thermal degradation as the sample is ionized directly in the liquid phase at quasi-ambient temperature, thus leaving intact fragile pesticides such as sulfonylureas [10]. Pneumatically-assisted electrospray, or ionspray (ISP), allows the introduction into the API source of a significantly higher solvent flow-rate, thus increasing the ruggedness of the LC–MS interface [16]. Application work using ISP are numerous, for example [16,17], and a few of them concern environmental studies, for example the determination of labile and polar organophosphorus pesticides [9], and of triazines and phenylureas [18,19]. The performance of the LC–ISP-MS system was compared to that of LC–TSP-MS for carbamate determination, and showed a lower detection limit (e.g., 5 $\mu g\ l^{-1}$ for carbofuran) using the former method [20]. More recently, LC–ISP-MS–MS was used for the determination of sulfonylurea herbicides in soil extracts [21] and sulphonamide residues in food products [22]. Although the sensitivity is often in the low ppm concentration range, it is often insufficient for the direct analysis of real samples. The required preconcentration step is frequently achieved by solid-phase extraction (SPE) using hydrophobic supports [5,7–11,15,16,19,20,23].

In this work, an ionspray LC–MS interface and a narrow-bore HPLC system were used for the determination and the characterization of six pesticides, belonging to three major pesticide classes: carbamates (carbofuran, promecarb), triazines (atrazine, and its major degradation product, hydroxyatrazine), and ureas (linuron, monolinuron). The MS instrument parameters were optimized in order to increase the method selectivity and sensibility. To meet the requirements of the maximum admissible concentration in drinking water, pre-concentration of water samples was performed using solid-phase extraction on C_{18} bonded silica particles.

2. Experimental

2.1. Chemicals and materials

Methanol (HPLC grade) was obtained from Prolabo (Fontenay-sous-Bois, France), and was filtered through a 0.22 μm filter from Millipore (St. Quentin-en-Yvelines, France). Deionized water was purified using a Milli-Q system (Millipore). Ethyl acetate (HPLC grade) was from Merck (Darmstadt, Germany); formic acid (purity 99%) was from Sigma (St. Louis, MO, USA). The pesticide standards (Fig. 1), in methanol solution (1000 mg l^{-1}, except hydroxyatrazine 100 mg l^{-1}), were purchased from Interchim (Montluçon, France), and were further diluted in methanol–water (50:50) to obtain 50 mg l^{-1} stock solutions.

Disposable solid-phase extraction cartridges (Supelclean ENVI-18), containing 0.5 g octadecyl-bonded silica (with a 3 ml cartridge volume) were obtained from Supelco (Supelco, Bellefonte, PA, USA). They were successively conditioned with 2 ml methanol, 2 ml ethyl acetate, 2 ml methanol and 2 ml deionized water, taking care not to let the cartridge dry out. Nitrogen (THP-grade) from Carboxyque (Aubervilliers, France) was used for solvent evaporation of the extracts.

2.2. Liquid chromatography–ionspray mass-spectrometry

The eluent was delivered by a microgradient

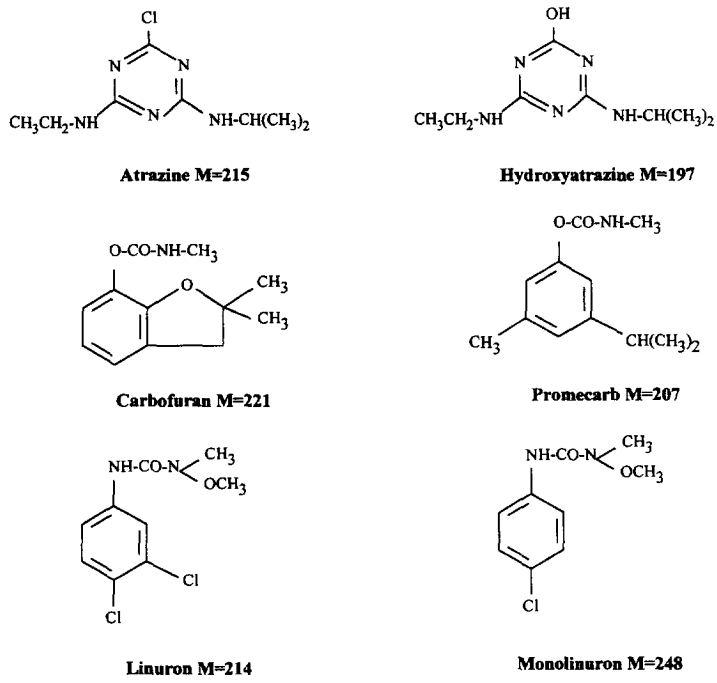

Fig. 1. Formulas and masses of the investigated pesticides.

system from Applied Biosystem, Model 140 C (Perkin-Elmer, Foster City, USA), fitted with a 5 μl loop injector. The separating system comprised a 15 mm×1.0 mm I.D. pre-column (Optiguard, Interchim, Montluçon, France) and a 100 mm×1.0 mm I.D. column, packed with 5 μm C_{18} bonded particles (Spheri-5, Applied Biosystem). Gradient elution was carried out with methanol and water acidified with 0.3% formic acid: from 45% methanol and 55% water (held for 10 min) to 70% methanol and 30% water in 25 min. Then, the column was flushed for 10 min with 100% methanol and equilibrated for 15 min with the LC initial conditions.

The LC column was connected to a single quadrupole LC–MS system, Model Perkin-Elmer/Sciex API 100 (Perkin-Elmer/Sciex, Thornhill, Canada) equipped with an Ionspray probe. The post-column effluent was split through a zero-dead volume T-union, delivering 20% to the ionspray probe, and the rest to waste. Splitting was achieved using appropriate lengths of 75 μm I.D. capillary tubing, (35 cm to the API probe and 7 cm to waste), or of 50 μm I.D. tubing (taking 60 cm and 12 cm, respectively).

MS tuning parameters were optimized using direct injection of atrazine in methanol–water 50:50 acidified with 0.3% formic acid. A voltage of 6 kV was applied to the Ionspray needle, 380 V to the ring electrode. The flow-rates for the nebulizing gas (air), and curtain gas (nitrogen) were 1.46 l min^{-1} and 1.44 l min^{-1}, respectively. The cone orifice voltage (OR) was alternatively set, in periods of 1 s, at 20 V (low OR mode) and 60 V (high OR mode). A solution of polypropylene glycol oligomers was used for mass calibration.

In the full scan mode, a mass spectrum was acquired in one second (corresponding to either low or high OR mode), from m/z 100 to m/z 300, in step size of m/z=0.2 and a dwell time of 0.884 ms. In time scheduled selected ions monitoring mode, two ions were monitored for each time window. The dwell time was 1 s for each ion at a given OR voltage. The respective acquisition windows for each pesticide were: 0–6.35 min (hydroxyatrazine); 6.35–8.85 min (carbofuran); 8.85–11.95 min (monolinuron); 11.95–18.15 min (atrazine); 18.15–22.95 min (linuron); 22.95–29.95 min (promecarb).

2.3. Sample preparation

Deionized water (250 ml) was spiked at the 0.04 and 0.08 μg l^{-1} levels, using stock solutions of five pesticides (2000 μg l^{-1}) in methanol (the C_{18} extraction of hydroxyatrazine was not evaluated as its retention on this support is very low; some authors recommend the use of graphitized carbon black cartridges [19]). The sample was passed through disposable C_{18} solid-phase extraction cartridges at a moderate flow-rate (around 4 ml min^{-1}), using vacuum aspiration, but taking care to avoid cartridge dry out. After complete sampling, the cartridge was allowed to dry using vacuum for 15 min, then the pesticides were eluted using 2 ml of ethyl acetate. Next, the extracts were dry evaporated under a gentle stream of nitrogen at 40°C, and again diluted in 500 μl of methanol–water (50:50). The overall concentration factor should be 500, assuming 100% recoveries, thus leading to final solutions at 20–40 μg l^{-1} concentrations, i.e., above the limits of quantification (LOQs). Loop injection of the final solution delivered 5 μl to the LC column. Each sample extraction was made in duplicate, giving always similar final results for all the investigated pesticides.

2.4. Quantification

Calibration graphs were constructed using nine points, (from 10 ng to 0.005 ng injected on column, using pesticide solutions at 2000, 1375, 1000, 500, 100, 50, 10, 5 and 1 μg l^{-1} concentrations). The more concentrated solutions (i.e., 2000, 1375 and 1000 μg l^{-1}) were prepared by appropriate dilution of the 50 mg l^{-1} stock solutions. Intermediate concentrated mixtures (500, 100 and 50 μg l^{-1}) were obtained upon dilution of the 2000 μg l^{-1} solution. The 100 μg l^{-1} mixture was used again to obtain the 10 and 5 μg l^{-1} solutions; finally the 10 μg l^{-1} solution was diluted to provide the 1 μg l^{-1} solution. The final volume of all samples was 2 ml. The low concentrated mixtures were prepared in pure water, as water injection in reversed-phase chromatography can provide sample pre-concentration onto the column head; thus improving both chromatographic resolution and sample detection. Pesticide standards were detected by selected ion monitoring of their MH^+ and major fragment ions. For each solution, repeatability of peak area measurements was evaluated from five consecutive injections. Reproducibility tests were carried out over a 5 day period, injecting solutions at different concentrations. Recoveries from solid-phase extraction were evaluated by external calibration.

3. Results and discussion

3.1. Optimization of the ISP interface parameters

The possible parameters affecting the formation and stability of the spray in the ISP interface are the nebulizer gas flow-rate, the needle voltage, the LC eluent flow-rate, the percentage of organic modifier in the mobile phase [20]. We found that the nebulizer gas (air) flow-rate and the needle voltage had negligible influence, around the typical values of 1.46 l min^{-1} and 6 kV, respectively, thus optimization was rather focused on the liquid flow-rate entering the interface. Direct infusion of 1 mg l^{-1} atrazine in water–methanol 50:50 acidified with 0.3% formic acid, at different flow-rates (from 10 μl min^{-1} to 60 μl min^{-1}) was delivered to the ionspray probe, while monitoring differences in the atrazine MH^+ ion intensity. Although the signal response remained unchanged, the use of the lower flow-rates improved the base line stability in the full scan mode, thereby increasing the signal/noise ratio. This confirms the general observation that sample detection under ISP conditions is sensitive to the concentration, and not to the sample mass flow-rate delivered to the source. In the following LC–MS experiments, the LC eluent was held at 60 μl min^{-1} for proper retention time and resolution conditions, and only 20%, i.e., 12 μl min^{-1} was split to the interface.

Methanol was the best organic modifier because of its protic nature. Positive ion recording mode and use of acidic solutions (0.3% formic acid) gave the optimum responses for the investigated pesticides, all known to contain easily protonable sites.

3.2. Structure identification

Ionspray provides direct information on the ana-

lyte molecular masses from the determination of their adduct ions (protonated or/and cationated ions). Collision-induced dissociation (CID) combined with mass analysis (CID-MS) can be obtained by simply increasing the orifice voltage (OR) in front of the mass analyzer [16,24]. The resulting fragments are comparable to those observed by CID using other types of experimental set-up [20], and are easily and reproducibly obtained [2].

In this work, double information was provided from the same experiment. The chromatogram (Fig. 2) from the injection of a synthetic mixture of six standard pesticides (sampling 10 ng per peak to the column) shows total ion current traces recorded at two different orifice voltages: a low OR voltage mode at 20 V, and a high OR voltage mode at 60 V. Repetitive jumps between the two modes were produced every second: the low voltage mode gives peaks for the protonated molecule $[M+H]^+$ and the sodium adduct $[M+Na]^+$ for each pesticide; the high voltage mode generates fragment ions from these precursor ions. As an example, two spectra of atrazine and promecarb were acquired with the orifice voltage set either at 20 V or at 60 V (Fig. 3). The latter spectrum clearly indicates that fragmentation had occurred, by expulsion from the protonated or cationated molecule of small stable neutral fragments. Masses and relative abundances for each pesticide, at two orifice voltage values are reported in Table 1. Similar results and ion types have been reported previously from more conventional MS–MS experiments [18].

3.3. Performance of the LC–ISP-MS

Selected ion monitoring (SIM) of major ions can often increase sensitivity up to a three order of magnitude factor, however, compound selectivity for samples in complex matrices is reduced when only one ion is monitored. Conventional MS–MS experi-

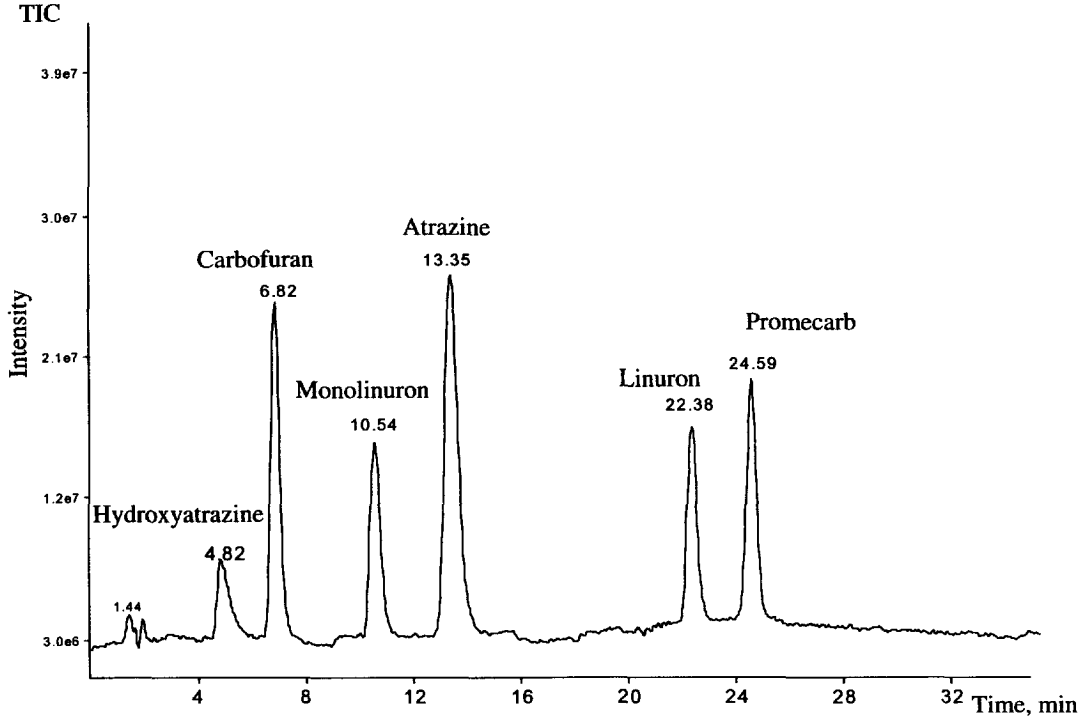

Fig. 2. Total ion current trace (m/z 100–300) from the LC–MS analysis of a synthetic pesticide mixture (10 ng/peak). Cone orifice voltage steps from 20 to 60 V at 1 s intervals. LC, 5 μl injection; 100 mm×1.0 mm I.D. ODS (5 μm) column at 60 μl min^{-1}; see text for gradient conditions. Capillary tube between the post-column flow splitter and the API source, 35 cm×75 μm I.D.; input flow-rate to the API source 12 μl min^{-1}.

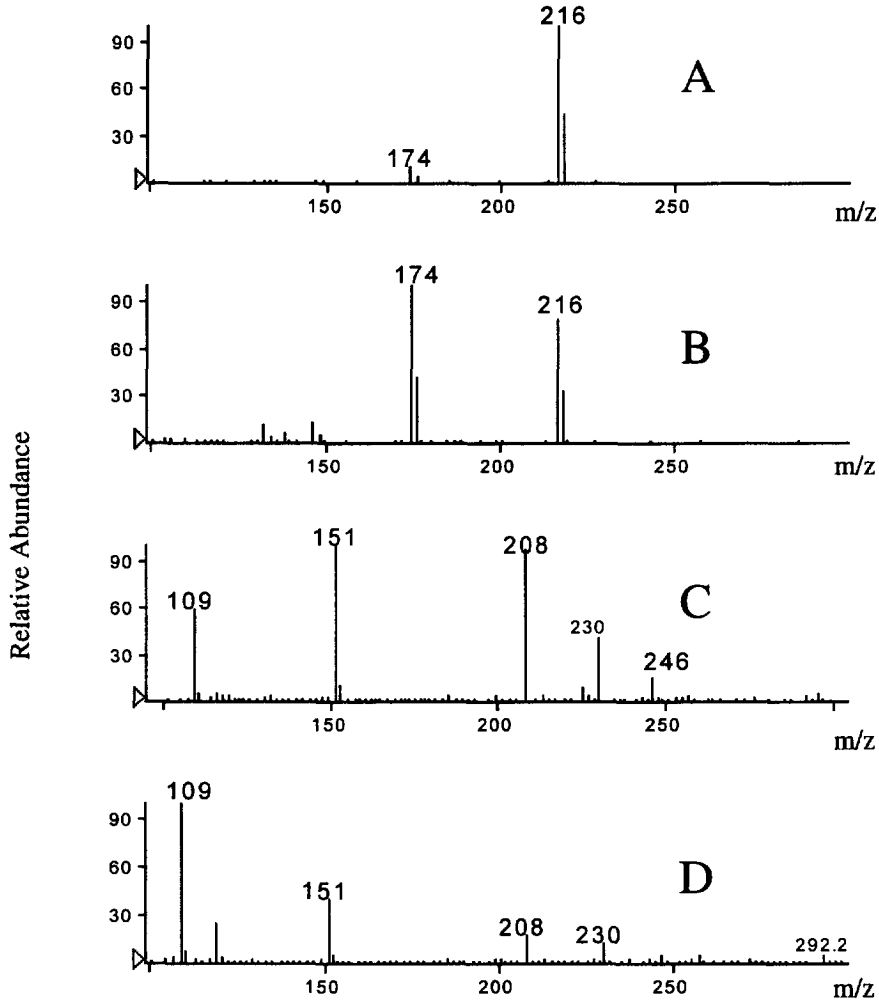

Fig. 3. ISP mass spectra (m/z 100–300) of atrazine (panels A, B) and promecarb (panels C,D) recorded at orifice voltage of 20 V (panels A,C) and 60 V (panels B,D). See Table 1 for ion identity. LC conditions as in Fig. 2.

ments using tandem analyzer instrument generally requires selection of a precursor parent ion in the first analyzer, collision induced fragmentation into an intermediate zone, and determination of the product ions by the second analyzer, either under full scan or under ion selective recording mode. An API source combined with a triple quadrupole analyzer is ideally suited to this purpose, with CID produced into the second quadrupole. However, some similar results can also be obtained from an API source fitted to a simple quadrupole analyzer, when ISP ionization only generates singly charged species derived from the intact molecule, as is the case for pesticide samples.

The selectivity of our single quadrupole MS was considerably increased by monitoring two ions: the precursor ion derived from the intact molecule at 20 V orifice voltage, e.g., the MH^+ ion, and its major fragment ion produced at 60 V orifice voltage, thus allowing unambiguous pesticide identification. A

Table 1
Summarized ionspray mass spectra of six pesticides recorded at two cone orifice voltages (20 V, 60 V)

Pesticide	M_r (DA)	m/z	Most abundant ions	Relative intensity (%)	
				20 V	60 V
Atrazine	215	216	$[M+H]^+$	100	100
		174	$[M+H\text{-}C(CH_3)_2]^+$	–	89
Hydroxyatrazine	197	198	$[M+H]^+$	100	91
		156	$[M+H\text{-}C_3H_6]^+$	–	100
Carbofuran	221	222	$[M+H]^+$	100	17
		244	$[M+Na]^+$	67	32
		165	$[M+H\text{-}O{=}C{=}N\text{-}CH_3]^+$	59	43
		123	$165^+\text{-}C_3H_6$	–	100
Promecarb	207	208	$[M+H]^+$	83	21
		230	$[M+Na]^+$	61	14
		151	$[M+H\text{-}O{=}C{=}N\text{-}CH_3]^+$	100	32
		109	$151^+\text{-}C_3H_6$	58	100
Monolinuron	214	215	$[M+H]^+$	100	35
		237	$[M+Na]^+$	18	–
		127	$[M+H\text{-}(CO_2+C_2H_5N)]^+$	–	100
Linuron	248	249	$[M+H]^+$	100	50
		271	$[M+Na]^+$	26	25
		161	$[M+H\text{-}(CO_2+C_2H_5N)]^+$	–	100

third criterion that completes pesticide identification is the LC retention time under the same elution conditions. The two monitored ions and the retention time for all pesticides are listed in Table 1. The peak detection specificity was improved compared to selective ion monitoring of the $[M+H]^+$ ions under low orifice voltage, without a significant loss of sensibility.

Under CID-MS mode, 12 ions should be repetitively monitored (two ions for each of the six pesticides), with a corresponding low dwell time on each peak. However, the dwell time, and consequently the sensitivity, can be increased by dividing the chromatogram in six time windows corresponding to the elution of a given pesticide. Within these windows, only two preset ions need to be monitored. Separation and identification under those conditions can be obtained using mixtures corresponding to the on-column sampling of 2.5 ng/constituent (Fig. 4). Absolute signal intensities in Figs. 2 and 4 should not be directly compared, as they were recorded on different days, with a different gain to the signal amplifier, however, the signal/noise ratio (S/N) in Fig. 4 was ca. 500, compared to a S/N ratio of 22 in Fig. 2, although using a more concentrated sample solution (10 instead of 2 ng/constituent). This corresponds to a 100 fold gain in sensitivity when comparing the CID-MS mode to the full scan TIC mode.

Table 2 lists the calibration line equations for the different pesticides, along with their limit of detection (LOD) and LOQ. Linearity was observed for all the pesticides in the injected 0.025–10 ng range (except 0.5–10 ng for hydroxyatrazine, partly because of a distorted chromatographic peak shape). Other authors have reported a loss of linearity for carbamates above 0.4 mg l^{-1} concentrations [20]. We observed that the response factors for the two carbamates are very similar. The same conclusion applies to the phenylureas. On the contrary, the calibration equations are different for atrazine and its degradation product (the slopes differ by a factor of 3.3). The LODs (S/N=4.65) ranged from 7 pg (atrazine) to 25 pg (hydroxyatrazine). These values are in agreement with recent reported LODs (S/N= 3) of 10 pg and 30 pg for atrazine and hydroxyatrazine respectively, using 5 μl injections onto a very narrow bore LC column (0.1 mm I.D.) directly

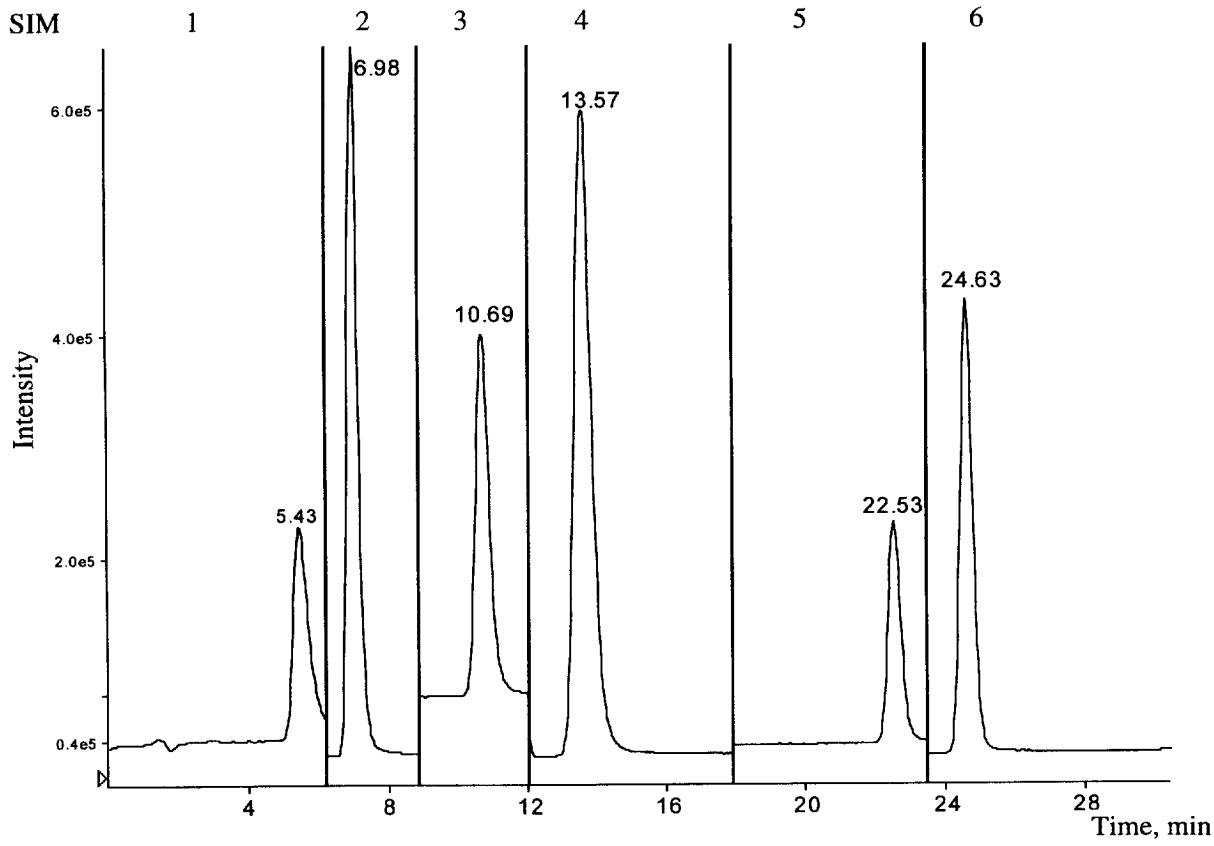

Fig. 4. Time-scheduled selective ion monitoring from the LC–MS analysis of a synthetic pesticide mixture (2.5 ng/peak). LC conditions as in Fig. 2. Monitored ions: (1) *m/z* 198 and *m/z* 156 for retention time 0–6.35 min (hydroxyatrazine); (2) *m/z* 222 and *m/z* 123 for retention time 6.35–8.85 min (carbofuran); (3) *m/z* 215 and *m/z* 121 for retention time 8.85–11.95 min (monolinuron); (4) *m/z* 216 and *m/z* 174 for retention time 11.95–18.15 min (atrazine); (5) *m/z* 249 and *m/z* 161 for retention time 18.15–22.95 min (linuron); (6) *m/z* 208 and *m/z* 109 for retention time 22.95–29.95 min (promecarb). LC conditions as in Fig. 2.

coupled to a LC–ESP-MS [19]. Comparable LOD values of 15 pg and 5 pg for carbofuran and promecarb have also been reported, from 10 μl sample injection onto a 125×3.0 mm I.D. column [20].

The major drawback of our method, compared to conventional MS–MS in a triple analyzer instrument, is that chemical noise is not removed from the parent and fragment ion signals. Thus sensitivity performance using a single quadrupole MS are lower than those with a triple quadrupole MS. Relative standard deviations (R.S.D.s) of the peak areas for concentration equal or superior to LOQ ranged from 1.7 to 14% (n=5). A single mass spectrometer under CID-MS mode (high orifice voltage) provides acceptable accuracy and reproducibility, compared to conventional single ion monitoring mode (low orifice voltage, no fragmentation). Nevertheless the sensitivity in CID-MS mode is somewhat lower, as the absolute fragment ion current was slightly weaker than that of the MH^+ ion in low voltage mode.

3.4. Sample pre-concentration by solid-phase extraction prior to LC–ISP-MS analysis

Despite the achievement of low LODs and LOQs with the LC–ISP-MS system, they are still far above the maximum admissible concentration in drinking water (0.1 μg l^{-1}). In addition, quantification capability within 25% of this level has been recom-

Table 2
Calibration data from LC–ISP-MS analyses in time scheduled SIM mode, after repeated direct injection of six pesticides in the range: 0.025–10 ng (5–2000 μg l^{-1})

Compounds	t_R (min) (R.S.D.%) $n=33$	m/z targets	Calibration equation (R.S.D.% of the slope) $n=5$	r^2	LOD[a] (pg) (R.S.D.%) $n=5$	LOQ[b] (pg)
Atrazine	13.3	216	$y=9\,432\,306x-773\,032$	0.997	7	35
	(2.9)	174	(2.3)		(26)	
Hydroxyatrazine	5.29	198	$y=2\,852\,325x-342\,975$	0.994	25	125
	(2.7)	156	(3.4)		(18)	
Carbofuran	6.9	222	$y=5\,053\,723x+186\,665$	0.999	11	55
	(3.5)	123	(1.3)		(3)	
Promecarb	24.5	208	$y=4\,501\,490x-191\,793$	0.998	22	110
	(1.5)	109	(2.1)		(8)	
Monolinuron	10.6	215	$y=2\,931\,153x+322\,383$	0.999	11.5	57.5
	(3.0)	121	(1.3)		(3)	
Linuron	22.5	249	$y=2\,995\,765x+212\,812$	0.997	21.5	107.5
	(1.5)	161	(2.3)		(5)	

Calibration lines correspond to peak area (y) vs mass (ng) of injected sample (x). Linearity domain starts at 0.025 ng for all pesticides except for hydroxyatrazine (0.25 ng).
[a] LODs are for $S/N=4.65$ [7].
[b] LOQs are derived from LODs. Repeatability for concentrations equal or superior to LOQ is from 1.7 to 14%.

mended. Consequently, pre-concentration using solid-phase extraction was performed to improve the overall performance. The extracts were determined using the same LC–MS procedure as above (time-scheduled CID-MS mode of two pre-selected ions for each pesticide).

For example, spiked water extracts, at the 0.04 and 0.08 μg l^{-1} levels, were determined after pre-concentration on C_{18} cartridges (Fig. 5). The slight change in absolute retention times was due to the change of the capillary tubes in the post-column splitter, using a different inner diameter capillary tubing (50 μm instead of 75 μm). Precise extract quantitation was achieved, by external calibration. The estimated recoveries from the 0.04 μg l^{-1} level solution were: atrazine 97.3%, carbofuran 101.1%, promecarb 91.7%, monolinuron 100.3%, linuron 92.2%. For the 0.08 μg l^{-1} level, the percent recoveries were: atrazine 99.4%, carbofuran 87.1%, promecarb 91.9%, monolinuron 75.1%, linuron 98.5%.

These results suggest that concentrations lower than 0.04 μg l^{-1} in drinking water could be determined using our method. They confirm the high potential of off-line SPE–LC–ISP-MS for the determination of carbamates, triazines and phenylureas in surface waters. However, extraction and pre-concentration could be much more difficult due to possibly interfering substances from the complex water matrix, including humic substances. As already reported [18], significantly higher LODs of 450 pg and 500 pg for atrazine and linuron, respectively, were measured from the direct injection of water samples containing humic substances.

4. Conclusions

We have demonstrated the potentials of LC–ISP-MS for the analysis of trace pesticides levels in water. The system offers very low detection limits (7–25 pg) for all the investigated pesticides. Collision induced fragmentation into the MS analyzer by simply raising the orifice voltage improves the selectivity during target compound determination.

A multi-residue method has been developed for the trace analysis of high usage pesticide groups that are commonly found in water sources, at concentrations 0.04–0.08 μg l^{-1}, i.e., lower than the maximum admissible level in drinking water. Nevertheless, hydrophilic pesticide residues such as hydroxyatrazine cannot be pre-concentrated on C_{18} bonded silica, and therefore, they cannot be determined at such low concentration levels. Investigation of solid-phase extraction of polar pesticides on a mixed adsorbent packing, with different selec-

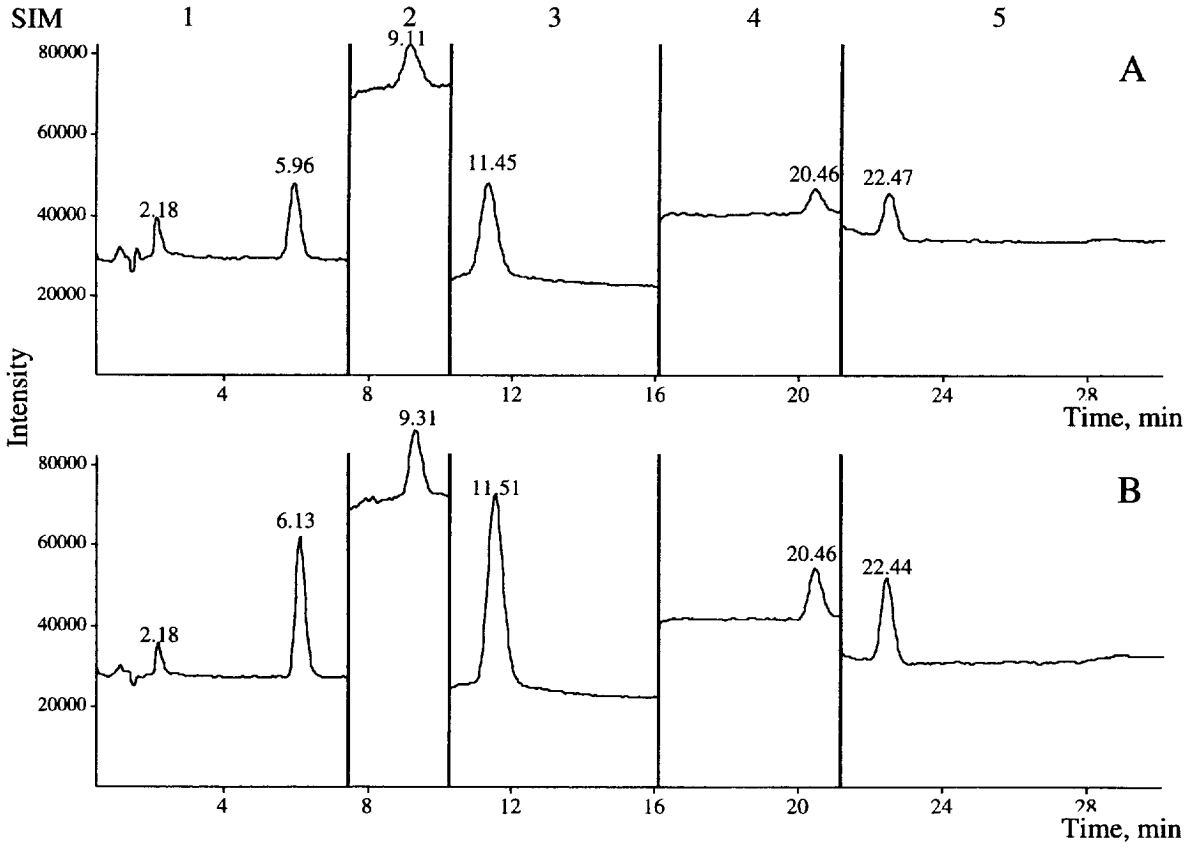

Fig. 5. Time-scheduled SIM LC–ISP-MS chromatograms of spiked water samples, after sample pre-concentration by solid-phase extraction onto C_{18} cartridges. (A) 0.04 μg l^{-1} level; (B) 0.08 μg l^{-1} level. LC conditions as in Fig. 2, except for the capillary tube between the post-column flow splitter and the API source: 60 cm×50 μm I.D. MS conditions as in Fig. 4.

tivities, e.g., C_{18} bonded silica and carbon black, are now in progress to overcome this limitation.

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