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Rapid direct determination of pesticides and metabolites in environmental water samples at sub-μg/l level by on-line solid-phase extraction-liquid chromatography–electrospray tandem mass spectrometry

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Abstract

A very rapid, multi-residual, sensitive and specific procedure for determining 35 pesticides in environmental ground and surface water in proposed. It is based on the use of solid-phase extraction (SPE) combined on-line with liquid chromatography (LC) electrospray (ESI) tandem mass spectrometry (MS–MS). Simultaneous target analysis of 29 pesticides (1 fungicide, 16 insecticides, 10 herbicides and 2 acaricides) and 6 metabolites with positive or negative ionization was reached by the direct injection of only 1.3 ml of filtered water sample, with a total analysis time of 18 min. The SPE–LC–MS–MS method was validated, obtaining good results for all compounds at 0.5 and 0.1 μg/l. Most of them could be correctly quantified at a concentration level as low as 25 ng/l. Efficiency and applicability of this method was evaluated by the analysis of several samples included in a monitoring program.

Keywords: Water analysis; solid-phase extraction; Pesticides

1. Introduction

Contamination of natural waters with pesticides from agriculture is still a problem of primary concern. In order to evaluate possible impacts of pesticides on aquatic ecosystems and drinking waters supplies, analytical methods for the routine simultaneous determination of a several number of such compounds in water samples are required.

Several methods based on gas chromatography (GC) have been developed for pesticides determination [1,2], but in most cases a derivatization step and/or clean up are usually required. In order to decrease the analysis time, analytical procedures based on the on-line combination of liquid chromatography (LC) and mass spectrometry (MS) are often preferred for the analysis of pesticides and metabolites [3,4]. This technique allows the determination of many polar pesticides and metabolites avoiding pre-derivatization and minimising sample manipulation.

Moreover, high sensitivity of the analytical method is compulsory for its use in environmental water monitoring. A European Union Directive [5] limits

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the content of individual pesticides in drinking water to 0.1 μg/l, which means that methods have to achieve detection limits (LOD) lower than 0.1 μg/l and preferably lower than around 4 times this value in order to reduce the possibility of false positive findings. In this way, a high degree of detection selectivity is also advantageous.

In order to achieve these detection limits with LC–MS, a trace enrichment step is usually necessary. Solid Phase Extraction (SPE) is commonly chosen for this purpose [6–11], as it is a very simple way of preconcentration and also of removing some interferences. Some papers have been published [6–10] using SPE followed by LC–MS using volumes of sample between 0.5 and 20 litres which force these methods to perform an off-line SPE step. In the cases, the large volume used in the preconcentration step led to the enrichment of interferences making advisable an additional clean-up step [7–10], and the quickness and automation that can be reached are not suitable when high number of samples have to be analyzed as occurs in most of monitoring programmes. In LC–MS, on-line SPE has also been used in order to achieve an automated process, but large sample volume is also necessary to obtain desirable sensitivity. In this way, Aguilar et al. [11] achieve satisfactory detection limits using an automated on-line SPE step by preconcentrating 200 ml of sample with a total analysis time of around an hour.

Recently, tandem mass spectrometry detection (MS–MS) is gradually becoming more important for environmental analysis [3,12–20]. The MS fragmentation pattern is a powerful tool for obtaining such confidence in compound identification. MS–MS allows the analysis without chromatographic separation between analytes and, therefore, low chromatographic time can be used. On the other hand, this controlled fragmentation generate cleaner chromatograms improving the signal-to-noise ratio and then decreasing the LOD. This sensitivity permits, in order to achieve detection limits lower than 0.1 μg/l, the use of low samples volumes which allows a rapid and automated analysis. In this way, on-line LC–LC [15] or SPE [16–20] are usually chosen. Our previous work [15] shows that LC–LC is a suitable approach which allows rapid and automated determination of several polar herbicides in water achieving desired detection limits using only 250 μl of sample. However the LC–LC approach loses some of its characteristics when applied to multi-residual determination. When dealing with the SPE–LC technique, 4–100 ml of water sample are usually preconcentrated in order to achieve satisfactory detection limits, with analysis time between 11 and 60 min. Thus, Kienhuis et al. [16] preconcentrated 100 ml of water sample achieving LODs of 0.05–0.1 μg/l for 34 compounds in 37 min, and using full scan mode which allows the determination of target and unknowns compounds. Hartman et al. [17] used a new approach for the on-line preconcentration of pesticides in water samples; they reached satisfactory LODs for 11 compounds in 11 min injecting 20 ml sample in a coated capillary microextraction (CCME) combined with a LC–MS–MS system. The single-short-column approach is also used in order to reduce the total time in target analysis methods. In this case a single short (but high-pressure packed) LC column is used for both SPE and analytical separation. Thus, Hogenboom et al. [18–20] used this approach combined with MS–MS detection for determine 14 compounds in 15–20 min injecting 4 ml of sample and achieving LODs of 0.1–1 μg/l.

The aim of the present study was to develop a method for the simultaneous determination of several pesticides and metabolites of different physico-chemical properties in environmental water samples. SPE–LC–MS–MS has been chosen to attain the necessary sensitivity, selectivity and sample throughput. The need for washing step in SPE and chromatographic optimisation are also discussed. Furthermore, the efficiency and applicability of the developed method during a monitoring programme is tested analysing real environmental water samples.

2. Experimental

2.1. Reagents and chemicals

All pesticides and metabolites reference standards were purchased from Dr. Ehrenstorfer (Augsburg, Germany). HPLC-grade acetonitrile was purchased from ScharLab (Barcelona, Spain). LC-grade water was obtained by purifying demineralized water in a Nanopure II system (Barnstead Newton, MA, USA).

Formic acid (HCOOH, content >98%) were supplied by Fluka (Buchs, Switzerland).

Stock standard solutions were prepared dissolving 25 mg, accurately weighted, in 50 ml of HPLC grade acetonitrile obtaining a final concentration of 500 μg/ml. For LC–MS analysis, the stock solutions were mixed and diluted with acetonitrile or LC-grade water.

2.2. Liquid chromatography

A Quattro LC triple quadrupole mass spectrometer (Micromass, Manchester, UK) was interfaced to an HPLC system (Fig. 1) based on a 233XL autosampler with a loop of 1330 μl (Gilson, Villiers-le-Bel, France) and 2 pumps: an Agilent 1100 (Agilent, Waldbron, Germany) binary pump as P-1 and a Waters Alliance 2690 (Waters, Milford, MA, USA) quaternary pump as P-2. The SPE preconcentration was performed using a cartridge C_{18}, 10×2 mm (Teknokroma, Barcelona, Spain) as C-1.For the LC separation a column 100×2 mm with a polar embedded stationary phase ABZ+ 5 μm from Supelco (Bellefonte, PA, USA) was used as C-2. Mobile phases consisted in water and acetonitrile in P-1 and mixtures of 0.01% HCOOH in acetonitrile–0.01% HCOOH in water in P-2.

2.3. Mass spectrometry

A Quattro LC (quadrupole-hexapole-quadrupole) mass spectrometer with an orthogonal Z-spray-electrospray interface (Micromass, Manchester, UK) was used. Drying gas as well as nebulising gas was nitrogen generated from pressurized air in a NG-7 nitrogen generator (Aquilo, Etten-Leur, NL). The nebuliser gas flow was set to approximately 80 L/h and the desolvation gas flow to 800–900 L/h. Infusion experiments were performed using a Model 11 single syringe pump (Harvard, Holliston USA), directly connected to the interface.

For operation in MS–MS mode, collision gas was Argon 99.995% (Carburos Metalicos, Valencia, Spain) with a pressure of 5×10^{-4} mbar in the collision cell. Capillary voltages of 3 kV and 3.5 kV were used in negative and positive ionization mode respectively. The interface temperature was set to 350°C and the source temperature to 120°C. Dwell times of 0.1 s/scan were chosen.

2.4. Sample procedure

Ground and surface water samples were collected in selected sites from Spanish Mediterranean area (Castellon, Valencia, Alicante and Murcia provinces). After filtration through 0.45 μm (only in the case of surface water), 1330 μl of sample were directly injected into the SPE–LC–ESI–MS–MS system for the determination of pesticides and metabolites selected.

2.5. SPE–LC procedure

The conditioning of the C_{18} cartridge was achieved with acetonitrile at a flow-rate of 2 ml/min for 2 min, following by 2 min more with water. An aliquot of 1330 μl of water sample was preconcentrated into the cartridge and washed with 4 ml of water at 2 ml/min. After washing, the sample was back flush transferred to the C-2 column and a

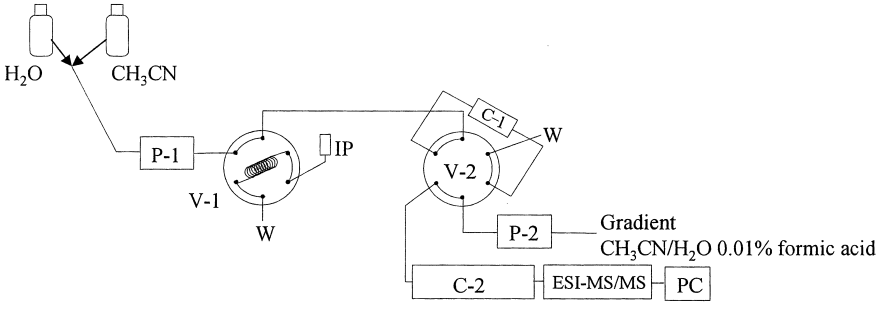

Fig. 1. SPE–LC set-up. AS=sample injector with 1300 μl loop; HV=six-port high-pressure valve; P-1=binary LC pump; P-2=quaternary LC pump; C-1=SPE cartridge; C-2=separation column; MS/MS=tandem mass spectrometer detector; PC=data system; W=waste.

Table 1
Steps of the SPE–LC–ESI–MS–MS

Time (min)	P-1	AS	P-2	PC
0–2	Conditioning[a] 2 ml/min acetonitrile	Wait	Wait	Wait
2–3	Conditioning 2 ml/min water			
3–5		Loop charge		
5–9	Washing 2 ml/min water	Preconcentration		
9–15	Wait 0.3 ml/min acetonitrile	Transferring	Gradient	Data acquisition
15–18		Wait		
18–20	Conditioning[b] 2 ml/min acetonitrile			

[a] Sample 1.
[b] Sample 2.

gradient in P-2 started. (See Table 1). Pesticide standard solutions used for quantification were also preconcentrated by SPE using the same procedure as for samples.

2.6. Validation study

The precision (expressed as coefficient of variation, in %) was evaluated within-day by determining all pesticides in three standard solutions prepared at 25, 100 and 500 ng/l ($n=8$). The calibration curve was obtained by analyzing standards solutions at eight concentrations between 0 and 500 ng/l.

The recoveries were obtained by analyzing all pesticides in ground and surface water samples spiked at three concentration levels each (25, 100 and 500 ng/l). In all cases, experiments were performed in quintuplicate ($n=5$).

The limit of quantitation (LOQ) was taken as the lowest concentration level assayed, for which adequate recoveries (between 70 and 120%) and precision (below 15%) were obtained. The limit of detection (LOD), defined as the lowest concentration that the analytical process can reliably differentiate from background levels, was obtained when the signal was three times the background noise in the chromatogram at the lowest analyte concentration assayed.

Masslynx NT v 3.4 (Micromass, Manchester, UK) software was used to process the quantitative data obtained from calibration standards and from water samples.

3. Results and discussion

3.1. Infusion experiments

The full-scan mass spectra and the MS–MS spectra of the 35 compounds were obtained from infusion of 5 μg/ml 50:50 acetonitrile–water solutions of each compound at a flow-rate of 10 μl/min. These experiments showed that 3 of 35 compounds (bromacil, terbacil and carbofuran-7-phenol-3-keto) present only negative ionization meanwhile the rest shows positive ionization.

It is interesting to show that carbofuran-7-phenol-3-keto presents an MS–MS spectra without any important fragment, nevertheless Andreoli et al. have reported an approach for compounds without abundant fragmentations [21]. Precursor ion is also measured with low collision energy as product ion, breaking interferences but not the analyte ion; therefore cleaner chromatograms are obtained [22]. In this case, precursor ion and product ion were both selected at m/z 177 and a collision energy of 15 eV was set in order to break interferences preserving this molecule.

On the other hand, azinphos-methyl was not measured as a fragment of its protonated molecule

$[M+H]^+$ ion at m/z 318. A more sensitive transition was obtained under cone fragmentation; azinphos-methyl is broken in the cone to obtain a fragment at m/z 160 which generate a product ion at m/z 132 in the collision cell.

The mass spectrometry parameters selected as precursor ion and product ion for selected compounds are shown in Table 2.

3.2. SPE optimization

The determination of pesticides in real water samples by HPLC involves the use of a trace enrichment step in order to reach the concentration levels required for environmental analysis. SPE is usually chosen in order to achieve these levels and additionally it removes interferences. When using

Table 2
Mass spectrometry optimized parameters for the determination of 35 pesticides and metabolites. Analytical characteristics of the developed SPE–LC–ESI–MS/MS method

Compound	Precursor Ion (m/z)	Cone voltage (V)	Collision energy (eV)	Product ion (m/z)	Chrom. group[b]	Repeatability[c] (%) ($n=8$) 25 ng/l	100 ng/l	LOD (ng/l)
2-Aminobenzimidazol	134	45	25	92	A	–	6	25
Carbendazim	192	35	20	160	A	6	2	0.5
Carbofuran 3-OH	238	20	15	163	B	18	10	4
Dimethoate	230	30	10	199	B	19	11	6
Pyrimicarb	239	30	20	72	B	3	4	1
Imidacloprid	256	35	15	209	B	16	14	9
4-Chloroaniline	128	40	20	93	B	14	8	5
Simazine	202	35	20	132	B	3	2	1
Carbofuran	222	30	15	165	B	7	4	4
Terbumeton	226	35	18	170	B	5	2	0.5
Carbofuran 7-phenol-3-keto[a]	177	45	15	177	B	5	6	12
Bromacil[a]	259	40	20	203	B	6	3	10
Terbacil[a]	215	35	18	159	B	9	8	20
Azinphos-methyl	160	25	15	132	C	9	5	4
3,4-Dichloroaniline	162	40	20	127	C	13	9	8
Molinate	188	30	15	126	C	2	2	4
Ethiofencarb	226	20	15	107	C	9	7	2
Methiocarb	226	20	20	121	C	7	4	10
Terbuthylazine	230	30	20	174	C	4	2	0.5
Fenthion	279	30	20	169	C	21	10	21
Diuron	233	30	16	72	C	6	5	5
Terbutryne	242	30	20	186	C	4	5	0.5
Quinalphos	299	35	20	147	C	10	7	6
Methidathion	303	20	8	145	C	10	5	7
Diazinon	305	30	15	169	C	9	8	8
Malathion	331	30	10	127	C	–	6	33
Pyridaphenthion	341	40	25	189	C	14	8	7
Thiobencarb	258	30	18	125	D	4	6	4
Pirimiphos-methyl	306	35	22	164	D	8	7	4
Buprofezin	306	25	12	201	D	–	8	50
Chlorpyrifos-methyl	324	30	18	125	D	10	11	9
Pendimethalin	282	20	10	212	D	–	10	34
Pyriproxyfen	322	30	15	96	D	–	12	40
Chlorpyrifos	352	30	20	200	D	–	12	40
Hexythiazox	353	25	16	228	D	–	11	60

[a] Polarity ESI negative.
[b] Chromatographic group based in t_R.
[c] Expressed as Relative Standard Deviation.

electrospray interface in LC–MS, matrix interferences can reduce the signal of analyte making more difficult the quantitation [23]. Inorganic salts are among the usual interferences in water samples, and thus, a washing step with water is often required in order to decrease this effect. However, the washing volume could be a critical parameter specially in the analysis of polar compounds as they could be also washed out with the interferences if the washing time or volume is too long.

The effect of different washing water volumes were studied, and finally 4 ml was selected as a compromise. In this way, the signal suppression produced by salts for the most polar analytes was removed and satisfactory recoveries obtained. For example, recoveries for 2-aminobenzimidazol in ground and surface waters increased from 60% (2 ml washing volume) up to 97% (4 ml washing step).

3.3. LC optimization

Usually the use of tandem mass spectrometry does not require chromatographic separation between analytes, as is very rare to find molecules which share the same unique transition. However, simultaneous analysis of high number (35) of compounds by MS–MS at least requires enough chromatographic separation between groups of analytes.

This group separation is required in order to ensure enough points for defining the chromatographic peak, as the detection is performed sequentially. The smaller the group, the higher the number of points available for defining the peak, improving the quality of data.

In our case, we have only used one transition for qualification, as the use of another transition for confirmation implies the use of at least 70 channels. These high number of channels, as stated above needs longer chromatographic times in order to increase the data points available per peak, decreasing the sample throughput of the developed procedure.

As our objectives were multi-residuality and fastness, we have kept only one channel per analyte. Moreover, for some analytes is difficult to find more product ions in the spectra capable of being used for confirmation, as the energy involved in the collision cell of triple quads is small, and there is a lack of abundant fragmentation.

For performing the group separation, a 0.01% HCOOH in acetonitrile:0.01% HCOOH in water gradient was optimized. An acidified mobile phase has been used in order to enhance the sensitivity in positive electrospray mode. The percentage of organic modifier was changed linearly as follows: 0 min, 5%; 6 min, 70%; 9 min, 70%; 10 min, 90%; 14 min, 90%; 15 min, 5%, 18 min 5%. Chromatographic groups of less than 14 coeluting compounds (14 transitions) were obtained with this gradient and therefore good peak shape were achieved for all compounds. These chromatographic groups are shown in Table 2. Group A includes compounds which retention time is less than 5 min, Group B includes compounds with retention times between 5 and 8 min, compounds with retention times between 8 and 10 min are included in Group C, and Group D presents the most non polar compounds, with retention times higher than 12 min.

3.4. Analytical characteristics

Standard curves showed excellent linearity, with correlation coefficients greater than 0.997. Repeatability and detection limits are reported in Table 2, which were obtained for standard solutions. The method was precise (RSD$<$15%) for all compounds at 500 and 100 ng/l level. Even at concentration as low as 25 ng/l level, 24 out of 35 compounds still presented good repeatability.

Limits of detection were calculated from the most diluted standard analyzed and ranged from 0.5 ng/l for some compounds like carbendazim, terbumeton, terbuthylazine and terbutryne to around 50 ng/l for other as buprofezin, chlorpyrifos, pyriproxyfen and hexythiazox. For 28 out of 35 compounds the limits of detection were lower than 25 ng/l, using only 1.3 ml of sample, and 23 compounds presented detection limits lower than 10 ng/l.

Fig. 2 shows typical chromatograms for standards at 10 ng/l level. The highest sensitivity was reached mainly for nitrogen-containing compounds which generate easy positive ionization.

3.5. Method validation

Precision and accuracy for surface and ground water samples analyzed by the developed SPE–LC–ESI–MS–MS method were performed at 25, 100 and

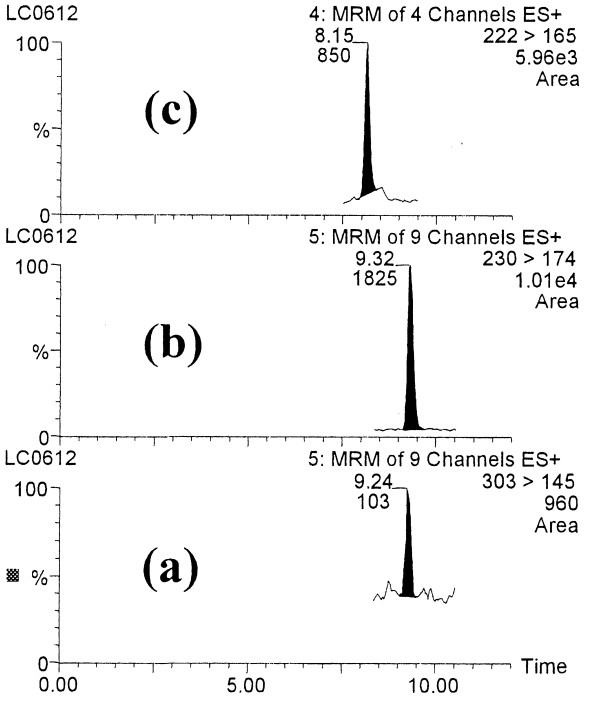

Fig. 2. SPE–LC–ESI–MS–MS chromatograms from a 10 ng/l standard for (a) Methidathion, (b) Terbuthylazine, and (c) Carbofuran.

500 ng/l level. Table 3 only reports the data for 25 and 100 ng/l in order to make it more readable, as at 500 ng/l level the results were similar to 100 ng/l level.

As this table shows, at 100 ng/l level, the method was found to be precise (RSD<15%) for all the 35 compounds studied. Besides, recoveries were satisfactory (between 70 and 120%) in ground water except for the metabolite carbofuran 3-hydroxy (65%). As regards surface water, the presence of more interferences resulted in lower recoveries (50 and 68%) for only two additional compounds (methiocarb and malathion, respectively).

At the 25 ng/l spiking level, 28 compounds could be still quantified, and only one presented an unacceptable precision (carbofuran 7-phenol-3-keto). This fact possibly occurred because this compound was measured with a ''pseudo-MRM'' transition (where precursor and product are the same ion) and chromatograms in ''pseudo-MRM'' were noisier than ''real-MRM'' making more difficult fine integration.

In general the majority of pesticides and metabolites could be satisfactorily determined at sub-ppb levels in both ground and surface water. The poorest recoveries were obtained for carbofuran-3-hydroxy, methiocarb and malathion. Moreover, the different matrix of surface water in relation to ground water seemed not to affect in a great deal to the robustness of the method.

As an example, in Fig. 3, representative chromatograms for two compounds are shown, molinate at 25 ng/l level and hexythiazox at 100 ng/l level in both type of water samples studied.

3.6. Monitoring of pesticides in environmental waters

This method was successfully applied in the analysis of several ground and surface water samples from Mediterranean area in Spain. As a consequence, several pesticides and metabolites were detected at relatively high levels (μg/l). Fig. 4 shows the chromatograms for several compounds detected in surface and ground water samples. The high sensitivity of the method applied allows to detect some pesticides at very low levels. As an example, the ground water analyzed (sample a) contained several compounds at concentrations lower than the LOQ of the method (25 ng/l). The good peaks in Fig. 4 for pirimicarb, diuron and terbuthylazine would allow us the quantitation of the analytes, although the method was not validated at concentration <25ng/l. Thus, concentrations of around 10 ng/l could be estimated for these compounds.

In general, herbicides were the most commonly detected pesticides, and triazines were found in around 75% of samples. As an example, 15% of samples contained more than 0.1 μg/l of terbuthylazine and/or terbumetone. Bromacil, terbacil and diuron were detected in around 50% of samples (35% of samples contained more than 0.1 μg/l of terbacil). Molinate was also frequently detected. In relation to insecticides, pyrimicarb, carbofuran and ethiofencarb were detected in around 25% of samples, but never in levels higher than 0.1 μg/l. Morevover, any of the acaricides investigated were detected in the samples. The fungicide carbendazim was detected in most of the samples. As regards metabolites, 2-aminobenzimadole (and carbofuran) were the most commonly detected compounds in the samples.

Table 3
Validation study for ground water (GW) and surface water (SW) samples

Compound	Recovery *(n=5)*			
	25 ng/l		100 ng/l	
	GW	SW	GW	SW
2-Aminobenzimidazol	–	–	113[a](7)[b]	115(3)
Carbendazim	92(4)	115(8)	94(4)	95(8)
Carbofuran 3-OH	66(5)	43(14)	65(8)	55(9)
Dimethoate	97(9)	55(12)	90(13)	112(6)
Pyrimicarbe	108(6)	92(6)	98(3)	96(4)
Imidacloprid	94(14)	83(18)	101(5)	90(14)
4-Chloroaniline	102(7)	88(10)	87(9)	95(12)
Simazine	99(6)	96(9)	98(9)	98(3)
Carbofuran	100(4)	89(5)	93(7)	90(3)
Terbumeton	101(6)	100(4)	95(5)	101(6)
Carbofuran 7-phenol-3-keto	100(26)	102(18)	95(10)	98(4)
Bromacil	99(6)	81(6)	102(4)	98(3)
Terbacil	108(9)	96(6)	101(12)	103(13)
Azinphos-methyl	101(6)	78(8)	93(6)	100(7)
3,4-Dichloroaniline	94(12)	113(12)	116(5)	104(5)
Molinate	104(4)	96(8)	95(4)	100(6)
Ethiofencarb	118(8)	83(11)	98(3)	91(5)
Methiocarb	78(11)	45(8)	75(9)	50(4)
Terbuthylazine	101(7)	99(5)	85(7)	97(3)
Fenthion	83(13)	94(13)	100(8)	81(9)
Diuron	85(12)	89(9)	94(5)	95(6)
Terbutryne	102(9)	89(7)	87(5)	92(5)
Quinalphos	80(12)	99(11)	103(9)	103(6)
Methidathion	109(12)	88(12)	90(6)	87(6)
Diazinon	88(13)	94(19)	99(9)	98(4)
Malathion	–	–	87(9)	68(12)
Pyridaphenthion	93(6)	96(7)	101(8)	97(8)
Thiobencarb	98(4)	99(9)	100(4)	96(4)
Pirimiphos-methyl	116(7)	83(12)	95(8)	102(6)
Buprofezin	–	–	98(8)	96(5)
Chlorpyrifos-methyl	95(12)	94(11)	90(9)	95(2)
Pendimethalin	–	–	115(11)	91(7)
Pyriproxyfen	–	–	105(5)	87(12)
Chlorpyrifos	–	–	95(9)	93(6)
Hexythiazox	–	–	103(11)	104(12)

[a] Recovery (%).
[b] Relative Standard Deviation (%).

4. Conclusion

This work has shown that SPE–LC–ESI–MS–MS is a rapid, sensitive and selective technique for the multi-residue determination of pesticides and metabolites in environmental water samples. The developed procedure allows the simultaneous determination of 35 pesticides and metabolites in both ground and surface water with a global analysis time of 18 min using only 1.3 ml of sample. All of these compounds are correctly quantified at 100 ng/l which is the strict regulatory level in drinking water. Besides, most of them (24 out of 35) are also correctly quantified at 25 ng/l. Detection limits are for most compounds (23 out 35) even lower than 10 ng/l. Good precision and recoveries are obtained and

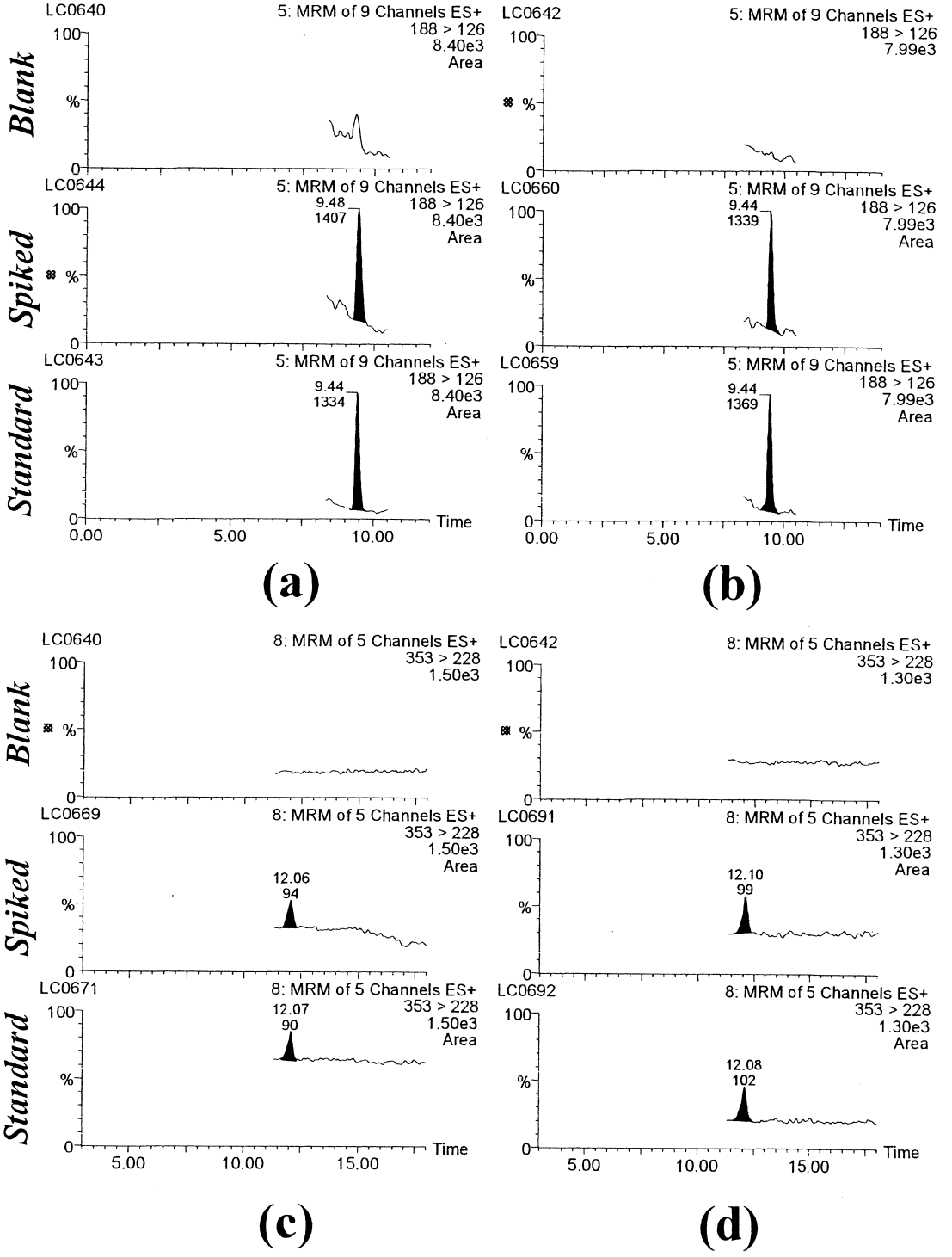

Fig. 3. SPE–LC–ESI–MS–MS chromatograms from blank and spiked water and standards. Molinate at 25 ng/l in ground water (a) and surface water (b) Hexythiazox at 100 ng/l in ground water (c) and surface water (d).

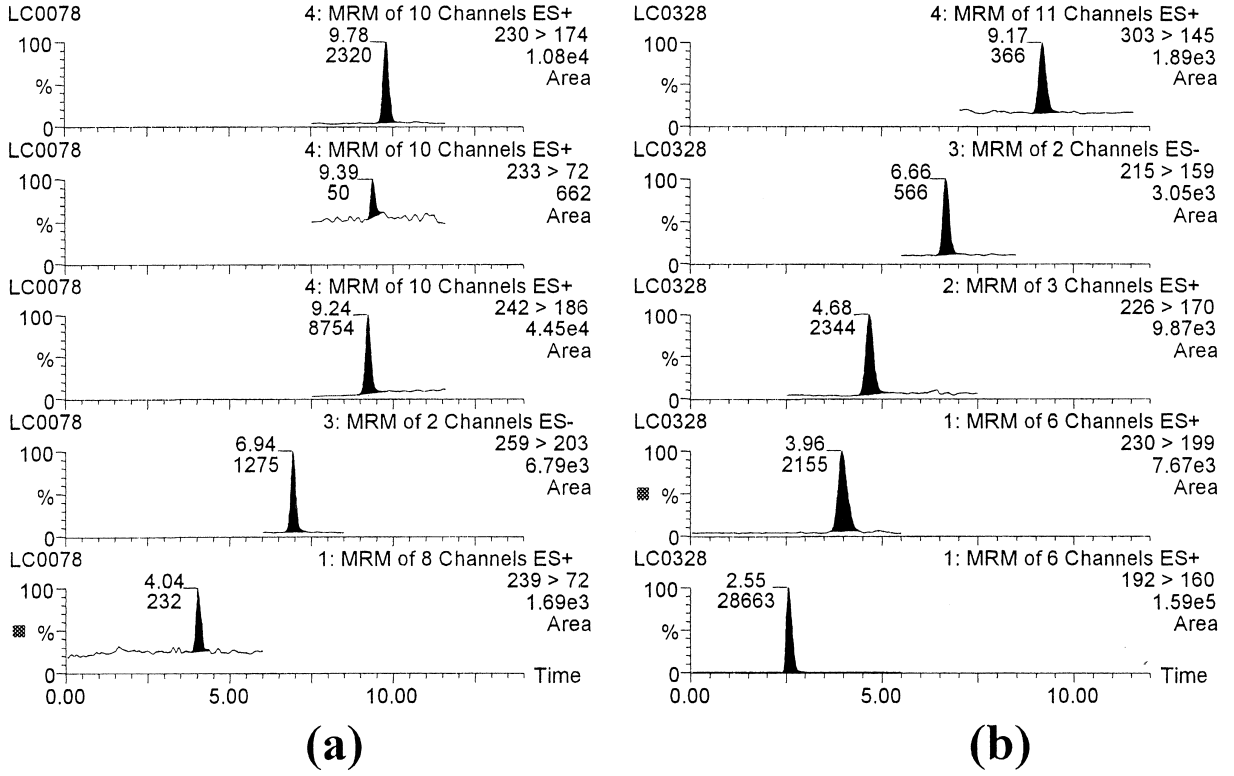

Fig. 4. Typical SPE–LC–ESI–MS–MS chromatograms from positive real water samples. (a) ground water containing 9 ng/l of pyrimicarb (239>72), 650 ng/l of bromacil (259>203), 95 ng/l of terbutryne (242>186), 13 ng/l of diuron (233>72) and 10 ng/l of terbuthylazine (230>174) and (b) surface water containing 620 ng/l of carbendazim (192>160), 150 ng/l of dimethoate (230>199), 27 ng/l of terbumeton (226>170), 170 ng/l of terbacil (215>159) and 25 ng/l of methidathion (303>145).

sample preparation is not required, rendering a fast and robust assay.

These characteristics (quickness, sensitivity, automation, multi-residuality and absence of sample manipulation) make the SPE–LC–ESI–MS–MS method, one of the most powerful analytical tools for monitoring of pesticide residues in water, where the analysis of many samples in a short time is compulsory.

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