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Simultaneous determination of acidic and non-acidic pesticides in natural waters by liquid chromatography–mass spectrometry

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Abstract

There is increasing interest and demand for real multi-residue methods able to simultaneously determine pesticides with a broad spectrum of chemical characteristics in environmental and biological matrices. A method based on solid-phase extraction with a Carbograph 4 cartridge and liquid chromatography with electrospray mass spectrometry (LC–ES-MS) enabling simultaneous determination of non-acidic and acidic pesticides in real water samples is described. On repeatedly ($n=5$) extracting 4 l of drinking water (spike level 50 ng/l), 2 l of ground water (spike level 100 ng/l) and 1 l of river water (spike level 200 ng/l), recovery of 26 base/neutral pesticides and 13 acidic pesticides were equal to or better than 80%, except for carbendazim (67%), butocarboxim (73%), aldicarb (75%) and molinate (77%). Relative standard deviations ranged between 4 and 15%. Final extracts containing acidic and non-acidic pesticides were analyzed in a single chromatographic run while the ES-MS system was operated in both positive and negative ion modes. With the aim of finding the best operating conditions, in terms of sensitivity, the pH of the LC eluent was varied in the 2.9–8.4 range. Altogether, the best results were obtained by using an LC eluent containing 1 mmol/l formic acid. Over the entire pH range considered, well shaped peaks for both basic and acidic analytes were achieved by the use of a new generation LC column. By extracting selected ion current profiles from the total ion current mass chromatogram relative to analysis of 4 l of drinking water spiked with 50 ng/l of each of the 39 analytes, estimated limits of detection ranged between 0.05 and 1.5 ng/l, except for propyzamide (8 ng/l) and 2,4-DB (3 ng/l).

Keywords: Water analysis; Pesticides

1. Introduction

Over the last 20 years, in the United States alone, about $15 \cdot 10^6$ tons of pesticides were employed for pest control. This situation has urged local governments to enact more and more restrictive regulations for banning some dangerous pesticides and lowering the maximum admissible concentrations of pesticides in drinking water and foodstuffs. For example, a recently enacted European Community Directive states that a single pesticide cannot be present in water destined for human consumption in concentrations higher than 0.1 μg/l.

The complex matter of pesticide trace analysis can

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be afforded by developing/using multi-component methods (MCMs) able to determine as many as possible pesticides and pesticide metabolites having a broad range of polarity and structural properties in a wide array of sample matrices at the required sensitivity limit. Today, gas chromatography (GC) still remains the most popular technique for accomplishing MCMs, as demonstrated by the fact that the five principal MCMs invariably involve this technique as an effective identification/confirmation tool. After the pioneering work by Mills et al. in 1963, several other MCMs followed as analysts have attempted to deal with the increasing number of pesticides [1]. However, many pesticides and pesticide metabolites cannot be determined by these MCMs, because they are not amenable to direct GC analysis. Liquid chromatography (LC) does not suffer from those limitations typical of GC and any pesticide is a potential candidate for LC analysis. Over the last decade, an increasing number of publications describing the application of LC to pesticide trace analysis have appeared in the literature. The introduction of a new generation of robust, sensitive, versatile and relatively cheap LC–mass spectrometry (MS) instrumentation, has filled the gap existing between GC–MS and LC with UV detection and has further stimulated researchers to develop LC–MS methods for determining a large number of pesticides in various matrices. This matter has been reviewed in several articles [2–5].

Indeed, all the methods developed to monitor a large number of pesticides by LC–MS, analogously to those by GC–MS, are not really MCMs, as they are not tailored to simultaneous monitoring of acidic and non-acidic pesticides. Recently, we have designed some analytical procedures based on solid-phase extraction (SPE) with graphitized carbon black (GCB) cartridges and LC–MS for determining traces of acidic [6,7] and base/neutral pesticides [8,9] in natural waters. Both sample preparation procedures and instrumental conditions chosen, however, do not permit simultaneous determination of acidic and non-acidic pesticides.

The purpose of this work has been that of developing a MCM for simultaneously determining traces of pesticides having a broad spectrum of acidity strength in natural waters by suitably modifying previously reported analytical conditions [6–9]. Among the enormous number of existing pesticides, 39 acid/base/neutral pesticides were selected for this study. This selection was made with the criteria of including many of those pesticides that (1) are not amenable to GC analysis; (2) do not possess chromophores and thus cannot be analyzed by conventional LC–UV instrumentation; and (3) are widely used in both European and American countries.

2. Experimental

2.1. Reagents and chemicals

Pesticides were purchased in part from Alltech (Sedriano, Italy) and in part from Riedel-de Haën (Seelze, Germany). Table 1 lists trivial names of the pesticides used together with basicity/acidity strength of some of them. *sec*-Buthylazine (*s*-BA) was supplied by Alltech and 4-octylbenzenesulfonate (C_8-LAS) was purchased from Aldrich (Milwaukee, WI, USA). *s*-BA was used as internal standard for base/neutral pesticides, while C_8-LAS was used as internal standard for acidic pesticides. Individual standard solutions of the analytes and the two internal standards were prepared by dissolving 20 mg of them in 20 ml of acetonitrile. A composite working standard solution of the analytes was prepared weekly by suitably mixing the standard solutions mentioned above and further diluting them with acetonitrile to obtain a final pesticide individual concentration of 2 ng/μl. For studies of optimization of instrumental conditions, another composite working standard solution with the same pesticide concentration was obtained by diluting with water instead of acetonitrile. A water–methanol (60:40, v/v) solution acidified with formic acid (1 mmol/l) and containing both *s*-BA (2 ng/μl) and C_8-LAS (5 ng/μl) was prepared by suitably diluting the two solutions mentioned above. When unused, all solutions were stored at 4°C.

For LC, distilled water was further purified by passing it through the Milli-Q Plus apparatus (Millipore, Bedford, MA, USA). Methanol ''Plus'' of gradient grade was obtained from Carlo Erba (Milan, Italy). Other solvents were of analytical grade (Carlo Erba) and they were used as supplied.

Table 1
Analyte recovery by extraction from water samples of different origin with a Carbograph 4 cartridge

	Type of matrix		
	Drinking water	Ground water	River water
Volume (l):	4	2	1
Spike level (ng/l):	50	100	200
No. of replicates:	5	5	5
Pesticide		Recovery[a] (%)	
Base/neutral			
1. Butoxycarboxim	87	85	81
2. Demeton sulfone	91	92	84
3. Carbendazim (pK_a 4.2[b])	70	69	67
4. Dimethoate	85	87	82
5. Butocarboxim	73	74	76
6. Aldicarb	78	80	75
7. Cyanazine	88	85	84
8. Carbofuran	89	87	90
9. Simazine	95	97	89
10. Carbaryl	96	94	89
11. Monolinuron	92	90	88
12. Metazachlor	95	96	86
13. Methabenzthiazuron	87	87	86
14. Atrazine	99	97	91
15. Isoproturon	99	97	93
16. Diuron	92	95	89
17. Ametryne (pK_a 4.1)	84	85	80
18. Linuron	90	92	92
19. Propyzamide	96	92	96
20. Molinate	79	77	82
21. Prometryne (pK_a 4.1)	94	90	86
22. Terbutryn (pK_a 4.3)	90	87	83
23. Metolachlor	104	98	105
24. Neburon	96	97	91
25. Prochloraz	103	95	99
26. Pirimiphos methyl	89	88	89
Acidic			
27. Thifensulfuron (pK_a 4.0)	90	92	92
28. Triasulfuron (pK_a 4.6)	90	89	99
29. Metsulfuron (pK_a 3.3)	89	88	89
30. Chlorsulfuron (pK_a 3.6)	109	105	105
31. Rimsulfuron (pK_a 4.0)	92	90	98
32. Tribenuron (pK_a 4.0)	111	97	100
33. Bensulfuron (pK_a 5.2)	104	107	105
34. Primisulfuron (pK_a 3.5)	107	98	105
35. Bentazone (pK_a 3.3)	108	95	105
36. 2,4-D (pK_a 4.0)	95	97	102
37. Dichlorprop (pK_a 3.7)	102	99	104
38. Mecoprop (pK_a 3.8)	102	97	106
39. 2,4-DB (pK_a 4.8)	103	93	105

[a] For all the types of matrices, five replicate analyses gave RSDs ranging between 4 and 15%.
[b] p*K* values taken from Ref. [19].

2.2. Apparatus

SPE cartridges filled with 0.5 g of Carbograph 4 and PTFE pistons enabling back elution of the analytes [10] were supplied by LARA (Rome, Italy). Carbograph 4 is an example of GCB with a surface area of 210 m^2/g. The SPE cartridge was fitted into a side-arm filtration flask and liquids were forced to pass through the cartridge by vacuum (water pump). Before processing water samples, the cartridge was washed with 10 ml of the eluent phase for the analytes (see below), followed by 2 ml methanol, 10 ml of an HCl-acidified water (pH 2), and 10 ml distilled water.

2.3. Sampling

Drinking water samples were collected from the tap in the laboratory. Before spiking with the analytes, hypochlorite was eliminated by addition of $Na_2S_2O_3 \cdot 5H_2O$, 0.5 g/l. Grab samples of a river water (18 mg/l dissolved organic carbon, DOC) and a ground water were collected in brown bottles and kept at 4°C in the dark until analysis. One-liter aliquots of the pesticide-amended river water sample were extracted unfiltered (although with restricted flow-rates), as it did not contain large amounts of suspended materials.

2.4. Procedure

For recovery studies, 4 l of tap water, 2 l of ground water and 1 l of river water were fortified with 100 μl of the composite standard solution to produce pesticide concentrations of, respectively, 50, 100 and 200 ng/l. Water samples were agitated for 1 min and, after 2 min, poured into a glass bottle connected to the sorbent cartridge through a PTFE tube. From this point onward, the same procedure as reported elsewhere [8] was followed, with the exception that, after reversing the cartridge, analytes were back eluted by passing through the cartridge 1.5 ml of methanol followed by 8 ml of a methylene chloride–methanol (80:20, v/v) solution acidified with formic acid, 50 mmol/l. The eluate was dried in a water bath at 30°C under a gentle nitrogen stream. Precaution was taken to not allow the residue-containing vial to stay in the water bath for more than 30 s after solvents appeared to be completely removed. The residue was reconstituted with 200 μl of the water–methanol solution containing the two internal standards (see above) and one-fifth of it was injected into the LC column.

2.5. LC–electrospray (ES) MS analysis

LC was carried out with a Thermoquest (Manchester, UK) Model P2000 equipped with a Rheodyne Model 7125 injector with a 50-μl loop. The analytes were chromatographed on an Hypersil 25 cm×4.6 mm I.D. column filled with 5 μm C_{18} HyPurity Elite reversed-phase packing (Thermoquest). For fractionating the analytes, phase A was methanol and phase B was water. The effect of the pH of the LC eluent on the LC–MS analysis of the pesticides considered was evaluated by adding varying amounts of formic acid and ammonia so as to obtain pH values of 2.9, 3.2, 3.5, 3.9, 5.3, 7.0, 8.4, as measured (pH meter) for water. After adding suitable amounts of the additives to water to obtain the desired pH value, the same amounts of them were added to methanol. The first three pH conditions were obtained by amending water, respectively, with 20, 5 and 1 mmol/l of formic acid. The other pH conditions were generated by first adding 1 mmol/l of formic acid to water and then adjusting the pH of water by suitable volumes of 1 mol/l ammonia. Under any pH condition, the initial composition of the LC eluent was 20% A which was linearly increased to 100% in 35 min. The flow-rate of the LC eluent was 1 ml/min and 500 μl of the column effluent was diverted to the ES source. A Finnigan AQA benchtop mass spectrometer (Thermoquest) consisting of a pneumatically assisted ES interface and a single quadrupole was used for detecting and quantifying target compounds in the LC column effluent. During the chromatographic run, the ES-MS system was operated in both positive ion (PI) and negative ion (NI) modes. Instrumental MS conditions were as follows (when not specified, conditions were common to both acquisition modes): probe temperature, 300°C; capillary voltage, 3.5 kV; skimmer cone voltage, 30 V; mass scan range, 75–380 (PI), 139–470 (NI); scan duration, 1.5 s; interchannel delay, 0.5 s. In order to obtain in-source collision-induced dissociation (CID) spectra display-

ing both fragment and parent ions for many of the pesticides considered, 30 V of skimmer cone voltage was found to be the best compromise.

Percentage recovery of each acidic and non-acidic pesticide in water was calculated by measuring the peak area resulting from the sum of the ion currents relative to parent and fragment ions (when available), relating this area to that of the internal standard and comparing this result with that obtained from standard solutions. These were prepared by dissolving known and appropriate volumes of the working standard solution in the eluent phase used for eluting analytes from the Carbograph 4 extraction cartridge and then following the rest of the procedure reported above. It has to be pointed out that the response of the ES-MS system was linearly related to injected amounts of the analytes up to 50–60 ng.

The MS data handling system used was the MassLab software from Thermoquest.

3. Results and discussion

3.1. General remarks

In the past, some MCMs based on SPE with a GCB cartridge and LC with UV detection were proposed for trace determination of acidic and non-acidic pesticides in water [11–13]. By taking advantage of the peculiarity of the GCB material of adsorbing specifically anionic compounds by electrostatic interactions [14], analyte re-extraction was performed by differential elution so that base/neutral pesticides were isolated from acidic ones. The two final extracts were then analyzed by using different chromatographic conditions. The rationale behind this procedure was that of simplifying interpretation of the chromatograms and minimizing the probability of false positives. The use of recently introduced LC–MS instrumentation that, besides offering a high confirmation power, allows simultaneous monitoring of positive and negative ions, could make the acid/non-acid fractionation cited above unnecessary.

3.2. Recovery studies

In this vein and still using a GCB extraction cartridge, we modified previously reported sample preparation procedures [11,12] in that both acidic and non-acidic pesticides were eluted together from the SPE cartridge with a suitably acidified eluent phase (see the Experimental section). In terms of analyte recovery, we checked the feasibility of this procedure by repeated analyses ($n=5$) of pesticide-amended samples of drinking water, ground water and river water. Results are reported in Table 1, while typical mass chromatograms for drinking water are visualized in Fig. 1. Except for carbendazim, butocarboxim, aldicarb and molinate, recoveries of the other analytes were equal to or better than 80% with relative standard deviations (RSDs) ranging between 4 and 15%. As reported elsewhere [8], the relatively low recovery of carbendazim was due to some effect of irreversible adsorption taking place on the GCB surface, while some uncontrollable loss of butocarboxim, aldicarb and molinate occurred during the solvent removal step. This loss could be avoided by taking care of stopping the solvent removal process when the extract reached the volume of about 100 μl [8]. However, in order to simplify the analytical procedure, we avoided this precaution.

Under the extraction conditions reported in the Experimental section and when analyzing pesticides in the river water sample, the final extract had a very pale yellow color, this indicating that humic acids were not substantially co-eluted with the analytes. Evidently, the complex structure of humic acids contains highly acidic functional groups able to interact so strongly with positively charged sites on the GCB surface that formic acid is unable to displace them. This is an important feature of this analytical procedure as repeated injections of extracts containing large amounts of humic material can contaminate the ES ion source, thus gradually decreasing its efficiency. Moreover, analyte signals can be depressed by co-elution of humic acids [15].

3.3. Effect of varying the pH of the LC eluent on the performance of the LC–MS system

In previous works [6–9], diverse chromatographic conditions have been in turn proposed to analyze final extracts by LC–MS, according to whether they contained acidic or non-acidic pesticides. In this study, we varied the pH of the LC eluent (see the Experimental section) in order to find the best

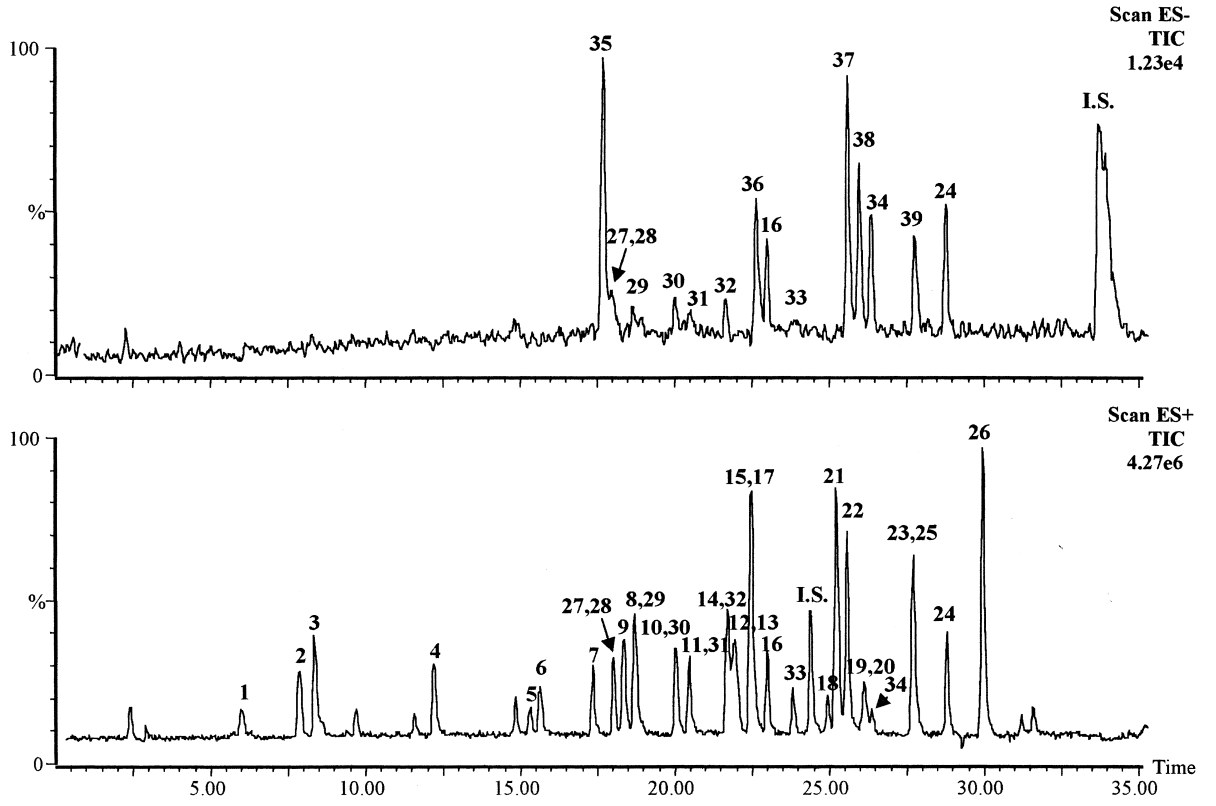

Fig. 1. Typical mass chromatograms obtained by simultaneous acquisition of positive and negative ions and relative to analysis of 4 l of drinking water spiked with 39 pesticides at an individual level of 50 ng/l. LC eluent: water–methanol (gradient elution) both acidified with 1 mol/l formic acid. Peak numbering: see Table 1.

compromise, in terms of sensitivity, analyte separation and peak shape, for simultaneously analyzing both acidic and non-acidic pesticides.

Under the instrumental conditions reported in the Experimental section and at any pH value considered, the average S/N for each analyte was calculated by injecting three times 20 μl of the aqueous working standard solution containing each analyte at the 2 ng/μl level (see the Experimental section). The S/N for each analyte was evaluated by extracting from the total ion current (TIC) chromatogram the sum of the ion currents relative to the molecular ion plus those of the most abundant product ions (when available) and measuring the resulting peak height against average background noise. The peak to peak noise was measured on the baseline close to the analyte peak. The various S/N values were then plotted against pH. For the sake of clarity, results for only some selected non-acidic analytes are presented in Fig. 2. In any case, S/N variations were mostly due to variations of the ion signals for the analytes rather than to noise variations. By increasing the pH from 2.8 to 3.5, a general steady enhancement of the S/N values was observed. This behavior is consistent with previous findings [8,16,17] indicating that non-ionophore species are charged with high efficiency even when the electrosprayed solution contains very small amounts of protons and that a decrease of the analyte ion intensity occurs by increasing the acid concentration in the LC eluent. At pH values between 3.5 and 7.0 ion signal intensities of most of the analytes decreased as the result of a decreasing availability of protons in the electrosprayed solution. An unexpected result was that ion signals of many of the analytes again increased significantly by raising the pH to 8.4. This finding was not thoroughly

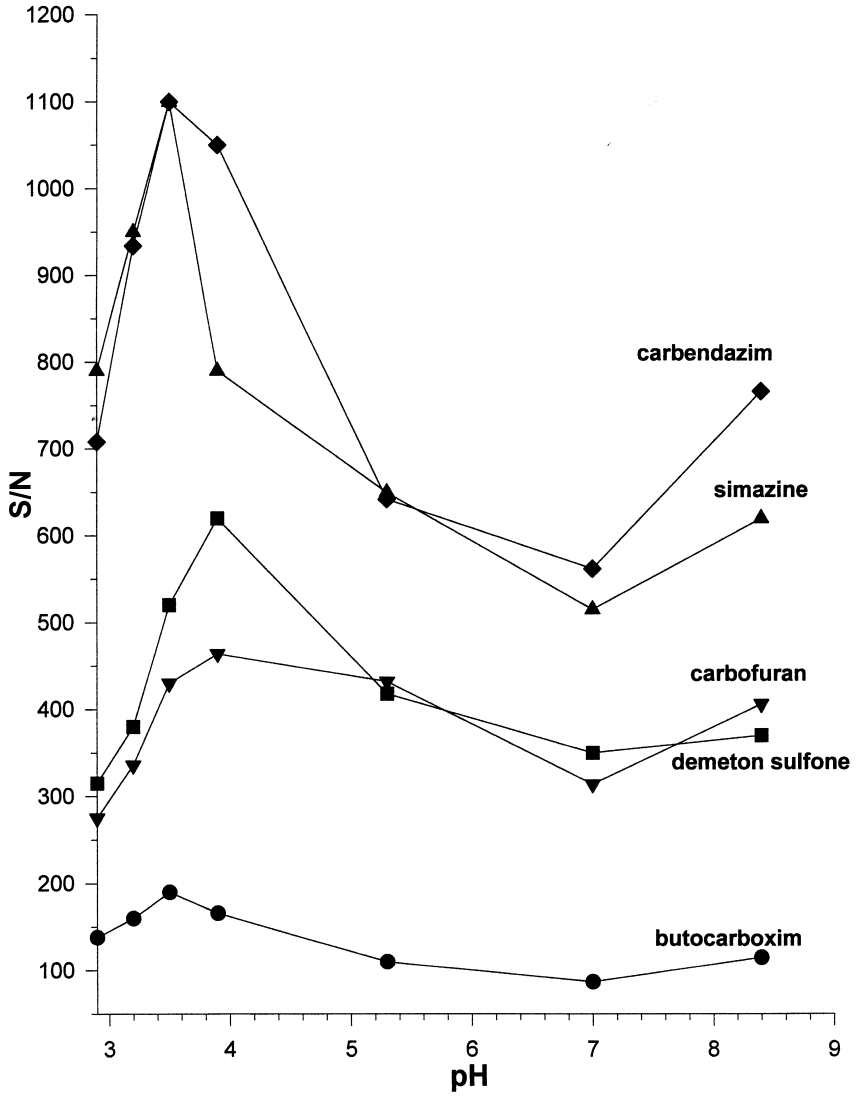

Fig. 2. Signal-to-noise ratio vs. pH of the LC eluent for some selected base/neutral pesticides.

understood. pH values higher than 3.5 were obtained by adding increasing volumes of ammonia to the 1 mmol/l HCOOH-containing LC eluent. At pH 8.4 all of the formic acid should be neutralized and the LC eluent should contain an excess of ammonia. This species is in equilibrium with its protonated form. Then, it can be hypothesized that the proton of the NH_4^+ ion is partially abstracted by the analyte molecules in the electrosprayed solution. The extent of this process depends upon the proton affinity of the analyte molecules relative to that of ammonia. This conjecture was substantiated to some extent by chromatographing targeted compounds with two different LC eluents still having a pH 8.4, but obtained in different ways. In one case, this pH value was generated by replacing ammonia with NaOH, while in the second case the pH of the water–methanol LC eluent was adjusted to 8.4 by adding only ammonia. Results reported in Table 2 for some representative non-acidic pesticides show that when operating with a LC eluent whose pH was adjusted to 8.4 by adding only ammonia, S/N values for

Table 2
Ion signal intensities (arbitrary units) for some selected pesticides by elution with LC eluents at pH 8.4 prepared in different ways

Compound	LC eluent A[a]	LC eluent B[b]	LC eluent C[c]
Carbendazim	140	95	12
Ametrine	210	160	52
Simazine	110	70	6
Carbofuran	150	80	5
Diuron	110	50	2
Pirimiphos methyl	170	70	7

[a] MeOH–water+HCOOH+NH_3.
[b] MeOH–water+NH_3.
[c] MeOH–water+HCOOH+NaOH.

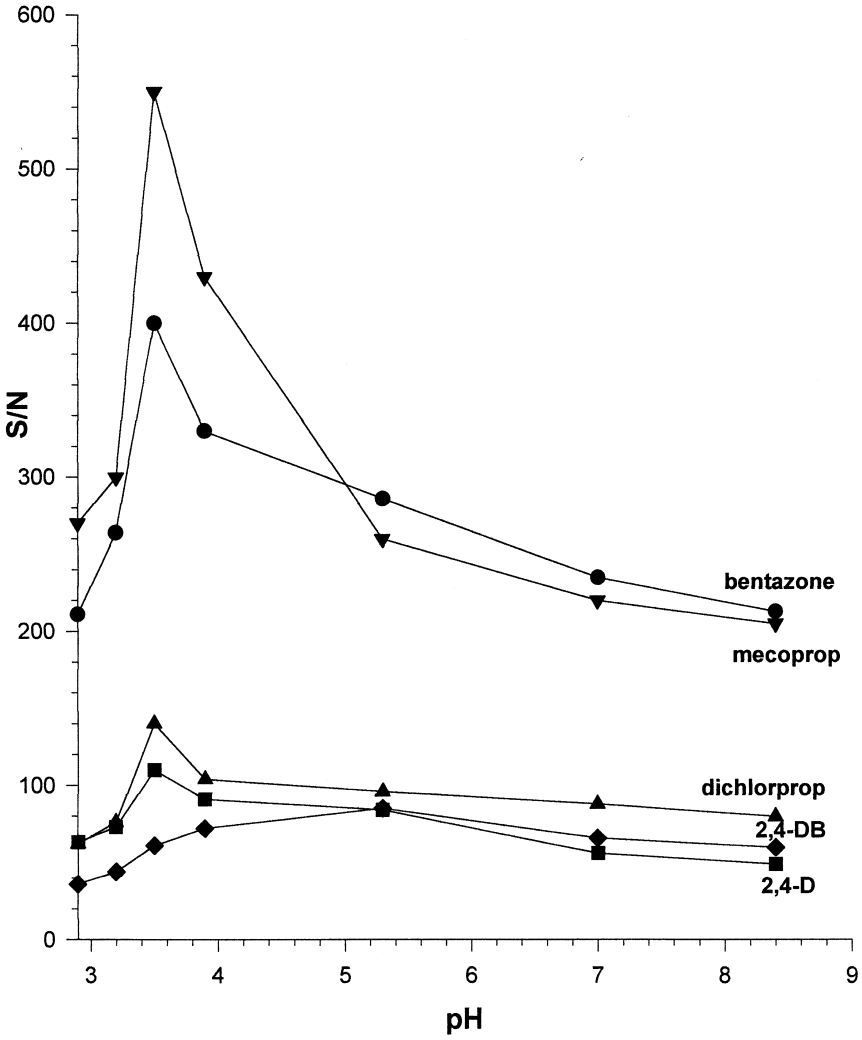

Fig. 3. Signal-to-noise ratio vs. pH of the LC eluent for some selected acidic pesticides.

non-acidic pesticides were not greatly different from those obtained by the addition of appropriate amounts of both formic acid and ammonia. Vice versa, very weakly ion signals were observed when formic acid was neutralized with NaOH.

Fig. 3 visualizes S/N variations for bentazone and the four phenoxy acids as the solvent pH was varied. Except for the weakly acidic 2,4-DB herbicide, the LC eluent at pH 3.5 afforded the best S/N values even for acidic pesticides. This result seems to be counterintuitive. By increasing the pH of the solution in which acidic compounds are dissolved, one would expect a gradual enhancement of the ion signal intensity, as the result of increased deprotonation of the acidic species. Our finding could be explained by considering that the very small droplets of the electrosprayed solution contain large amounts of ammonium ions as the result of droplet shrinking due to heat exchange with the drying gas and coulombic explosions. In this situation, part of the deprotonated acidic analytes could be expelled from the droplets as ammonium salts. Another factor to be considered is that high pH values favor the formation of the deprotonated form of an acidic species. This reflects

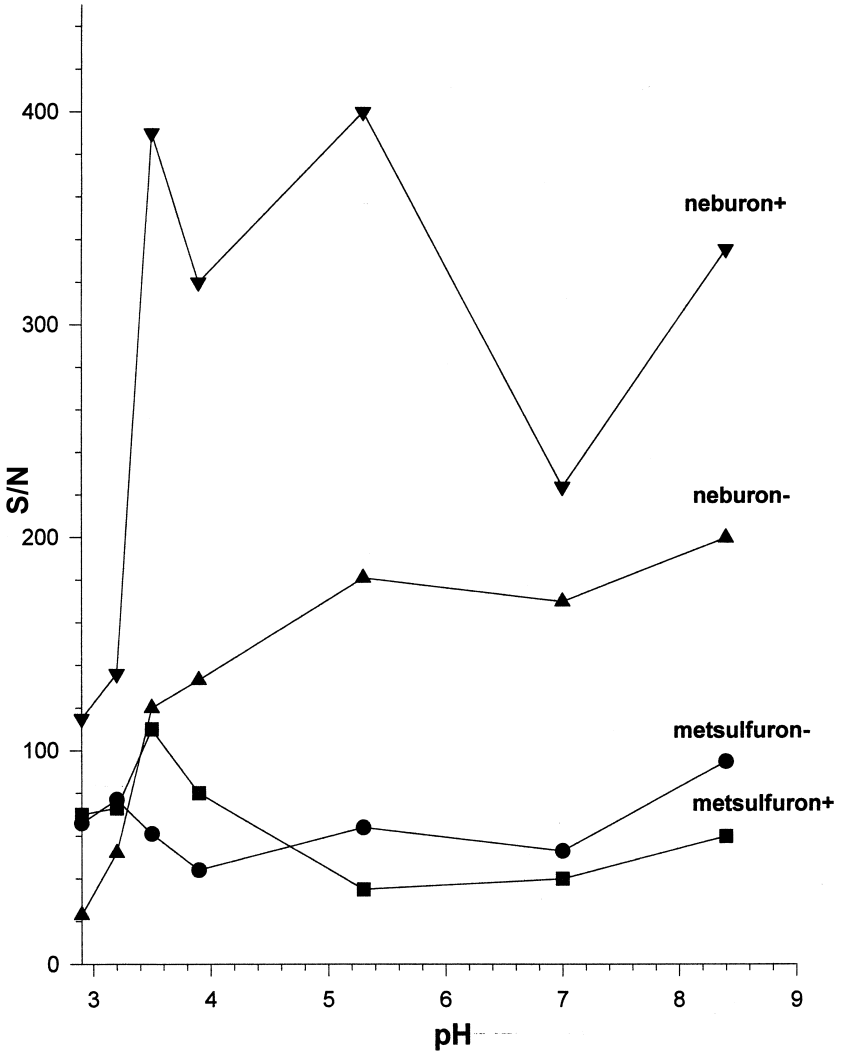

Fig. 4. Signal-to-noise ratio vs. pH of the LC eluent for two of those pesticides able to produce both positive and negative ions. Symbols + and − following the name of the pesticide stand for acquisition in the positive and negative ion modes, respectively.

in a decreased affinity for the reversed-phase stationary phase. It follows that, when the LC column is operated in the gradient elution mode, the analyte leaves the LC column and enter the ES ion source dissolved in a solution richer of water. This makes a decrease of the ion signal intensity, as the response of the ES-MS system depends on the water content in the electrosprayed solution.

The results reported above indicate that simultaneous analysis of acidic and non-acidic analytes can be for the best performed at pH 3.5 by adding a small amount of an acidic additive to the LC eluent. It has to be pointed out that this result was attained also on account of recent improvements in column technology. In the past, we observed that the weakly basic methylthiotriazine class of herbicides as well as carbendazim were eluted as tailed and broad peaks when using an acidified LC eluent. Vice versa, the LC column selected for this study was able to give sharp peaks for weakly basic compounds at any pH value of the LC eluent we considered.

For some of the pesticides considered, that is the

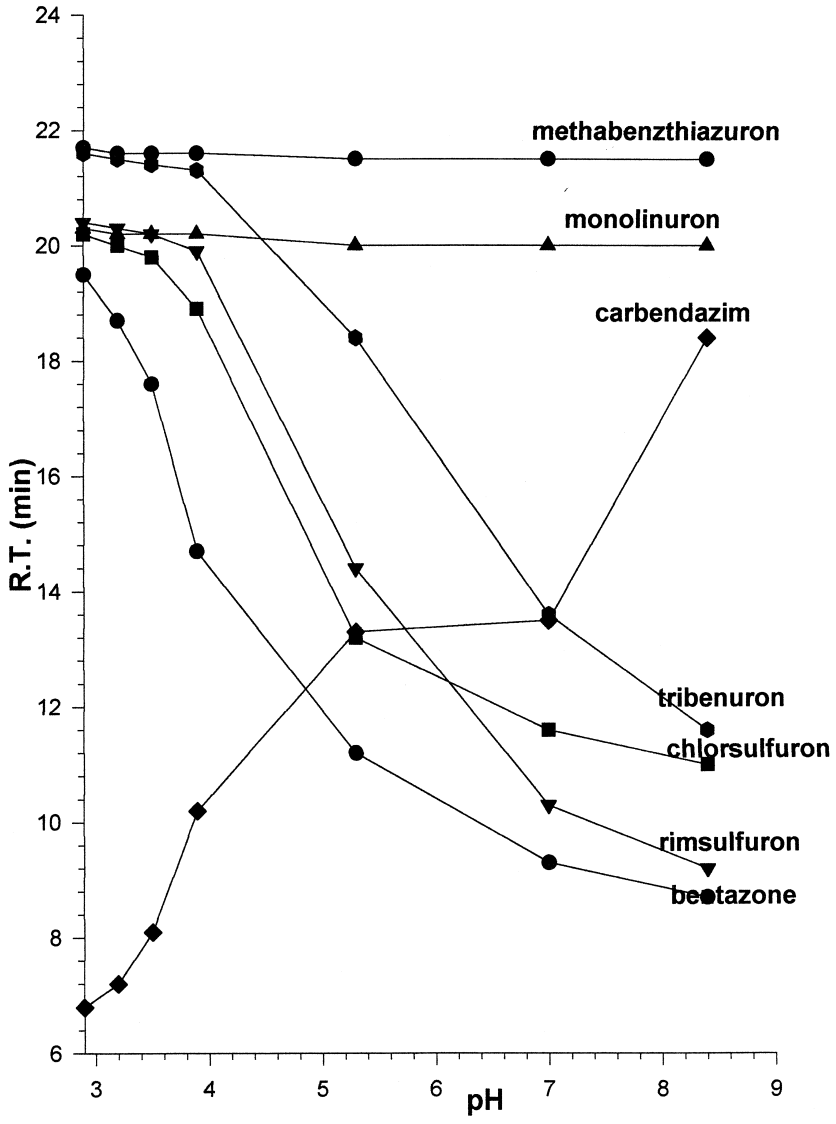

Fig. 5. Retention time vs. pH of the LC eluent for some selected pesticides.

eight sulfonylureas and two of the phenylurea herbicides considered, i.e., diuron and neburon, the electrospray process is able to form both $[M-H]^-$ and $[M+H]^+$ ions. Of the other phenylureas, linuron gave a poor signal in the NI mode, while no distinct signal was detected on injecting 40 ng of both monolinuron and isoproturon. Over the pH range considered, S/N data in both NI and PI modes for the above compounds were calculated and a S/N vs. pH plot for one representative sulfonylureas as well

Table 3
Limits of detection (LODs) estimated for 39 selected pesticides in drinking water by extracting current profiles of selected related ions from the total ion current mass chromatogram[a]

Compound	Positive ion mode		Negative ion mode	
	Selected ions	LOD (ng/l)	Selected ions	LOD (ng/l)
Base/neutral				
Butoxycarboxim	106, 166, 245 (MNa^+)	0.6		
Demeton sulfone	169, **263**[b]	0.3		
Carbendazim	160, **192**	0.1		
Dimethoate	88, 199, **230**	0.6		
Butocarboxim	75, 116, 213 (MNa^+)	0.8		
Aldicarb	89, 116, 213 (MNa^+)	0.6		
Cyanazine	214, **241**	0.2		
Carbofuran	165, **222**	0.2		
Simazine	**202, 204**	0.1		
Carbaryl	145, **202**	0.2		
Monolinuron	126, 148, **215**	0.2		
Metazachlor	134, 210, **278**	0.6		
Methabenzthiazuron	165, **222**	0.6		
Atrazine	174, **216**	0.1		
Isoproturon	**207**	0.2		
Diuron	**233, 235**	0.3	**231, 233**	1
Ametryne	**228**	0.1		
Linuron	128, **249, 251**	1.5		
Propyzamide	190, **257**	8		
Molinate	126, **188**	0.6		
Prometryne	200, **242**	0.1		
Terbutryn	186, **242**	0.2		
Metolachlor	252, **284**, 306 (MNa^+)	0.2		
Neburon	88, **275, 277**	0.4	**273, 275**	1
Prochloraz	308, 340, **376**	0.2		
Pirimiphos, methyl	**306**	0.05		
Acidic				
Thifensulfuron	167, **388**, 410 (MNa^+)	0.5	139, **386**	6
Triasulfuron	167, **402**	1	139, **400**	3
Metsulfuron	167, **382**	1.5	139, **380**	4
Chlorsulfuron	167, **358, 360**	1.5	139, **356, 358**	5
Rimsulfuron	182, **432**, 454 (MNa^+)	1.5	186, **430**	4
Tribenuron	155, 364, **396**	0.5	153, **394**	3
Bensulfuron	149, 182, **411**	1	254, **409**	9
Primisulfuron	254, 437, **469**	1.5	226, **467**	1.5
Bentazone			**239**	0.4
2,4-D			161, **219**	1.5
Dichlorprop			161, **233**	1
Mecoprop			141, **213**	0.3
2,4-DB			161, **249**	3

[a] pH of the LC eluent: 3.5.
[b] m/z values in boldface refer to quasi-molecular ions.

as neburon is visualized in Fig. 4. In all cases, mass chromatograms recorded in the PI mode gave the most satisfactory results. For those substances able to give both $[M-H]^-$ and $[M+H]^+$ ions, however, simultaneous acquisition in both PI and NI modes is of additional information when, under the instrumental conditions chosen, their spectra display only signals for the molecular ions. For example, working at 30 V of cone voltage, the CID process did not give rise to product ions of the $[M-H]^-$ and $[M+H]^+$ ions of diuron. Nevertheless, the appearance of two peaks having the very same retention times on extracting the current profiles at m/z 233 and 231 from the mass chromatograms in the PI and NI modes, respectively, affords a high confirmation power (see peak 16 for diuron in Fig. 1, top and bottom traces).

Variations of the retention times for some selected analytes by varying the pH of the LC eluent are shown in Fig. 5. As expected, retention times of the acidic pesticides decreased with increasing the pH of the LC eluent, as a consequence of the shift of the acid-conjugated base equilibrium towards deprotonated species. The reverse was obtained with weakly basic pesticides. When the ES-MS system is operated in the PI mode, co-elution of two substances can affect their ionization process [18]. Competition effects in picking up positive charges present in the electrosprayed solution can severely depress the ion signal of that species being much less abundant or having scarce tendency to be charged. In this case and provided that one of the two compounds is weakly acidic or basic, a variation of the pH of the LC eluent provides an easy way to avoid peak overlapping that may result in analyte underestimation. As an example, peaks for the triplet monolinuron, rimsulfuron and chlorsulfuron as well as those for the pair methabenzthiazuron–tribenuron were partially overlapped at pH 3.5. By exploiting the weakly acidic character of sulfonylureas, a satisfactory separation of all the above compounds could be achieved by raising the LC eluent pH at 3.9. Under this condition, all the five compounds still give intense ion signals.

3.4. Limits of detection (LODs)

Considering that this method involves analysis of 4 l of drinking water, reconstitution of the residue with 200 μl, and 40-μl injection of it into the LC column, LODs (S/N 3) were estimated for the 39 pesticides considered (Table 3). These data highlight that the MCM developed by us has the potential for analyzing simultaneously acidic and non-acidic pesticides in drinking water at few ng/l without appealing to the selected-ion monitoring acquisition mode. Data reported in Table 3 refer to 4 l of drinking water. Thus, LODs for groundwaters and river waters can be estimated by increasing LODs for drinking water by a factor 2 and 4, respectively (see Experimental section).

References

[1] S.M. Walters, in: G. Zweig, J. Sherma (Eds.), Analytical Methods for Pesticides and Plant Growth Regulators, Vol. XV, Academic Press, New York, 1986, p. 67.
[2] M. Linscheid, Int. J. Environ. Anal. Chem. 49 (1992) 1.
[3] M.H. Lamoree, R.T. Ghijsen, U.A.Th. Brinkman, Tech. Instrum. Anal. Chem. 13 (1993) 521.
[4] J. Slobodnik, B.L.M. van Baar, U.A.Th. Brinkman, J. Chromatogr. A 703 (1995) 81.
[5] M. Careri, A. Mangia, M. Musci, J. Chromatogr. 754 (1996) 347.
[6] C. Crescenzi, A. Di Corcia, S. Marchese, R. Samperi, Anal. Chem. 67 (1995) 1968.
[7] A. Di Corcia, C. Crescenzi, R. Samperi, L. Scappaticcio, Anal. Chem. 69 (1997) 2819.
[8] C. Crescenzi, A. Di Corcia, E. Guerriero, R. Samperi, Environ. Sci. Technol. 31 (1997) 479.
[9] A. Di Corcia, C. Crescenzi, E. Guerriero, R. Samperi, Environ. Sci. Technol. 31 (1997) 1658.
[10] A. Di Corcia, A. Bellioni, M. Diab Madbouly, S. Marchese, J. Chromatogr. A 733 (1996) 383.
[11] A. Di Corcia, M. Marchetti, Anal. Chem. 63 (1991) 1991.
[12] A. Di Corcia, M. Marchetti, Environ. Sci. Technol. 26 (1992) 68.
[13] T.D. Bucheli, F.C. Grüebler, S.R. Müller, R.P. Schwarzenbach, Anal. Chem. 69 (1997) 1569.
[14] A. Di Corcia, S. Marchese, R. Samperi, J. Chromatogr. 642 (1993) 163.
[15] R.J.C.A. Steen, A.C. Hogenboom, P.E.G. Leonards, R.A.L. Peerboom, W.P. Cofino, U.A.Th. Brinkman, J. Chromatogr. A 857 (1999) 157.
[16] M.G. Ikonomou, A.T. Blades, P. Kebarle, Anal. Chem. 62 (1990) 957.
[17] M.G. Ikonomou, A.T. Blades, P. Kebarle, Anal. Chem. 63 (1991) 1989.
[18] A. Di Corcia, C. Crescenzi, A. Laganà, E. Sebastiani, J. Agric. Food Chem. 44 (1996) 1930.
[19] C.D.S. Tomlin (Ed.), The Pesticide Manual, 11th ed., British Crop Protection Council, 1997.