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Determination of arylphenoxypropionic herbicides in water by liquid chromatography–electrospray mass spectrometry

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Abstract

A very sensitive and specific analytical procedure for determining arylphenoxypropionic herbicides in aqueous environmental samples, using pneumatically assisted electrospray (ESI) liquid chromatography–mass spectrometry (LC–MS) is presented. Arylphenoxypropionic acids are a new class of herbicides used for the selective removal of most grass species from any nongrass crop. These herbicides are commercialized as herbicide esters. It has been shown that the ester derivatives undergo fast hydrolysis in the presence of vegetable tissues and soil bacteria, yielding the corresponding free acid. The analytical procedure involves passing 1 l of surface or ground water and 2 l of drinking-water samples, through a 0.5-g graphitized carbon black (GCB) extraction cartridge. A conventional 4.6-mm I.D. reversed-phase LC C_{18}, operating with a 1 ml/min mobile phase flow-rate, was used for chromatographing the analytes. A flow of 200 μl/min of the column effluent was diverted to the ESI source. The ESI source was operated in positive-ion mode for neutral pesticides and in negative-ion mode for acid pesticides. For ion-signal optimization, the effect of the concentration of the acid in the mobile phase on the response of the ESI–MS detector was investigated. By evaluating the specificity and sensitivity of the method, the effects of varying the orifice plate voltage on the production of the diagnostic fragment and the response of the MS detector were also investigated. For the analyte considered, the response of the mass detector was linearly related to the amount of the analyte injected between 1 and 200 ng. In all cases, recoveries of the analytes were better than 91%. The limit of detection (signal-to-noise ratio=3) of the method for the pesticides considered in drinking water samples was estimated to be about 3–10 ng/l.

Keywords: Pesticides; Arylphenoxypropionic acids

1. Introduction

Arylphenoxypropionic (APPs) acids are a new class of herbicides used for selective removal of most grass species from any nongrass crop [1]. APPs are commercialized as herbicide esters. It has been shown that the ester derivatives undergo fast hydrolysis in the presence of vegetable tissues and soil bacteria, yielding the corresponding free acid, which is assumed to possess biological activity [2,3]. As shown in Fig. 1, the members of this class of herbicides have similar structural features centred around a phenoxypropionic moiety and an attached aromatic system bearing a halogen moiety.

There are relatively few methods available for the determination of APP herbicides in environmental matrices and current analytical methods for the determinations are targeted at individual members of the group. Therefore, the isolation procedures described in the literature are usually based on an

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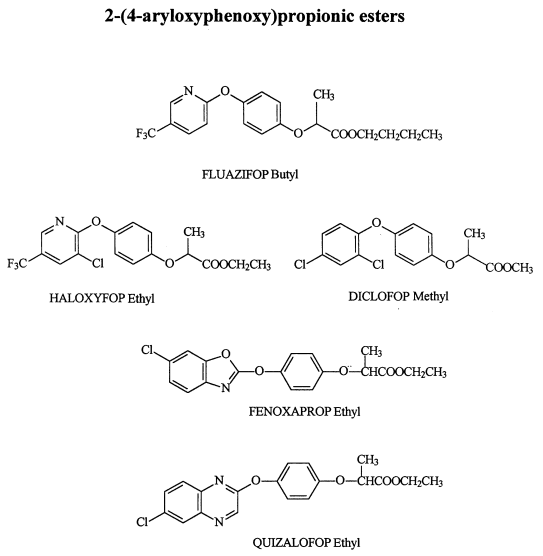

Fig. 1. Structure and common name of APPs herbicides.

alkaline treatment of the samples, thus isolating residues of the free acid such as salts, followed by suitable analytical methods for the acid, usually liquid–liquid extraction and determination by HPLC [4–6] or GC–ECD, after suitable derivatization [7,8], or GC–MS [9].

Although capillary column gas chromatography (GC) remains the major technique used to determine organic compounds present in water [10–12], the number of publications describing reversed-phase gradient elution high-performance liquid chromatography (HPLC) has increased steadily over the last ten years [13–17].

However, because of the legal implications of many environmental data, coupling HPLC with mass spectrometry (MS) represents a key element for the future of HPLC procedures.

LC–MS methods are especially attractive owing to their inherent high specificity. A review of the use of LC–MS techniques for polar pesticides was published very recently by Slobodnik et al. [18], covering both the principles of ionization and applications of the most frequently used LC–MS techniques (thermospray particle beam and atmospheric pressure ionization). Of these LC–MS interfaces, the authors underlined the potential of atmospheric pressure ionization (API) for pesticide analysis both in terms of sensitivity and the possibility of achieving structural information, in spite of the comparatively small number of studies of LC–API-MS published so far. API is a term covering several different principles of ionization [19,20], e.g. electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI). ESI, introduced only a few years ago, is a soft ionization method, typically generating only ionized molecules $[M+H]^+$ (in positive mode) or $[M-H]^-$ (in negative mode). However, if structural information is desired, some fragmentation can be achieved through preanalyzer collision-induced dissociation (CID) by increasing the voltage difference between the two regions of the ESI interface.

The specific objective of this work was to develop a sensitive and specific assay for monitoring APP ester and acid pesticides, in environmental aqueous samples in order to obtain LODs below 100 ng/l needed for pesticide compliance with the Commission of the European Communities – Drinking Water Directive (CEC–DWD). APPs, both esters and acids, were simultaneously extracted using a Carbograph cartridge from water samples without any sample pretreatment.

By passing two suitable solvent systems sequentially through the cartridge, isolation of acidic pesticides from nonacidic ones was successfully achieved by differential elution [21–23]. Class fractionation was made possible because the GCB surface was contaminated by some positively charged adsorption sites that enabled this material to behave as both a nonspecific sorbent and an anion-exchanger [24].

In this way it was possible to perform extraction, preconcentration and class fractionation of analytes using a single cartridge.

The neutral and acid fractions were analyzed by HPLC–ESI-MS. The combined attributes of SPE coupled with HPLC–ESI-MS techniques, under selected-ion monitoring (SIM) conditions, provide a very sensitive and highly specific method for analysing these compounds in an environmental matrix.

2. Experimental

2.1. Reagents and chemicals

There are 14 commercial products for this class of herbicides, but only 5 active principles.

For instance, there are 5 different commercial

esters of quizalofop free acid. For the present work we selected five of the most common commercial herbicides. The structures and common names are shown in Fig. 1.

Authentic arylphenoxypropionic acids and esters were purchased from LabService (Bologna, Italy). They are as follows: Haloxyfop, Diclofop, Fluazifop, Fenoxaprop free acid, Fenoxaprop ethyl ester and Quizalofop ethyl ester. Fluazifop butyl ester, Diclofop methyl ester and Haloxyfop ethyl ester were kindly provided by AgrEvo (Frankfurt am Main, Germany).

Quizalofop free acid was obtained by hydrolysis from Quizalofop ethyl ester [25]. Individual standard solutions were prepared by dissolving 10 mg of each in 10 ml of acetonitrile. Composite working standard solutions were prepared by mixing 0.1 ml of each standard solutions and diluting to 50 ml with acetonitrile (2 ng/μl). When not being used, all standard solutions were stored at 4°C.

For HPLC, distilled water was further purified by passing it through the Milli-Q RG apparatus (Millipore, Bedford, MA, USA). Acetonitrile 'plus' and methanol 'plus' of LC gradient grade were from Carlo Erba (Milan, Italy). Formic acid and tetrabutyl ammonium fluoride (TBAF) were purchased respectively from Merk (Darmstadt, Germany) and from Aldrich Chemicals (Milwaukee, WI, USA). All other solvents were of reagent grade (Carlo Erba) and were used as received.

2.2. Apparatus.

Extraction cartridges were filled with 0.5 g of Carbograph 1 (120–400 mesh size, Carbochimica Romana, Rome, Italy), while the other materials for preparing extraction cartridges were from Supelco (Bellefonte, PA, USA). The preparation and pretreatment of the reversible extraction cartridge were carried out as previously reported [26].

The trap was fitted into a side-arm filtering flask, and liquids were forced through the cartridge by means of the vacuum produced by a water pump.

2.3. Sampling.

Grab samples of surface and ground waters (various sources near Rome) were collected in brown bottles and kept at 4°C in the dark until analyzed. Unless they contained a large amount of suspended sediments, water samples were extracted unfiltered. When necessary, Whatman GF/C glass-fiber pads (pore size 10 μm) were used. Rome municipal drinking water samples were taken after the water had been allowed to flow for 30 min.

2.4. Procedure

For recovery studies, aqueous samples were fortified with known amounts of the composite standard solution. Water samples were then agitated strongly for about 1 min. and poured into a glass reservoir connected to the sorbent cartridge. Water was forced through the cartridge at flow-rates of ca. 100 ml/min by reducing the pressure in the vacuum apparatus to a minimum. After the sample had passed through the column, the pump was disconnected, and the cartridge filled with 7 ml of distilled water, which was allowed to pass through the cartridge at flow-rates of 5–7 ml/min. Most of the water was removed from the cartridge by forcing room air through it for 1 min. and 1 ml of methanol was poured into the cartridge, and slowly passed through the sorbent bed to eliminate part of the residual water. Following the passage of methanol, the pressure was reduced to a minimum for 1 min.

APP esters and co-extracted neutral compounds were eluted by passing through the cartridge, 2 ml of methanol followed by 8 ml of a methylene chloride–methanol (80:20, v/v) solution, at a flow-rate of ca. 8 ml/min obtained by suitably regulating the vacuum. Thereafter, a suitably drilled cylindrical teflon piston with one conically indented base and a Luer tip was forced into the cartridge until it reached the upper frit. The trap was turned upside down, a 1.4 cm I.D. glass vial with a conical bottom was placed below the trap, and the analytes were back eluted by passing through the trap, 8 ml of a methylene chloride–methanol (80:20, v/v) solution acidified with formic acid at 50 mmol/l. The flow-rate at which the eluent phase percolated through the cartridge was about 6 ml/min. The last few drops of this mixture were collected by further decreasing the pressure inside the flask.

2.5. Evaporation step

To the acid fraction was added, 100 μl of metha-

nol containing TBAF 0.4 *M*, and the mixture dried over a water bath at 40°C under a gentle nitrogen stream. The residue was reconstituted with 200 μl of a water–acetonitrile solution (80:20, v/v) acidified with 10 m*M* HCOOH. A volume of 50 μl of the final extract was injected into the LC column. If TBAF was not added to the solvent mixture, severe loss of the APP acids was observed on drying the extract. Being a comparatively nonvolatile compound, TBAF probably plays a role in inhibiting the methylation of the carboxylic group that formed at the given temperatures in an acid media [27].

The neutral fraction was concentrated down to about 200 μl in a water bath at 30°C under a nitrogen stream to remove the solvent. In these conditions, no trace of methylene chloride was present in the final extract [28]. The final extract was measured using a 500 μl syringe, and 50 μl were injected into the HPLC apparatus.

2.6. HPLC–ESI-MS analysis

Liquid chromatography was carried out using a Perkin Elmer series 200 binary pump (Perkin Elmer, Norwalk, CT, USA) equipped with a Rheodyne 7125 injector with a 50-μl loop and a Perkin Elmer Series 200 vacuum degasser. The analytes were chromatographed on an Alltima 25 cm×4.6 mm I.D. column filled with 5-μm C_{18} reversed-phase packing (Alltech, Deerfield, IL, USA). Electrospray mass spectrometry was performed on a Perkin Elmer/Sciex API I single-stage quadruple instrument equipped with an TurboIonspray interface (Sciex. Thornton, Canada).

In order to separate the analytes into a neutral and an acid fraction, phase A was acetonitrile and phase B was water. Both solvents contained 25 mmol/l of HCOOH.

2.6.1. Acid fraction analysis

Gradient elution was performed by linearly increasing the percentage of the organic modifier from 40 to 85% in 25 min. The flow-rate of the mobile phase was 1 ml/min. A 200-μl portion of the column effluent was diverted to the ES source. Postcolumn addition (after splitting) of 10 μl/min of CH_3COONH_4 (50 mmol/l acetonitrile–water, 85:15 v/v, pH 8) was carried out using a Harvard model 11 syringe pump (Harvard Apparatus, South Natick, MA). The mass spectrometer was operated in negative ion (NI) mode by applying, to the capillary, a voltage of 4000 V. The orifice voltage was set at 70 V and the interface temperature at 62°C. Nitrogen was used as curtain gas with a flow-rate of 1.1 l/min and air as nebulizer gas with a pressure setting of 42 psi. Mass spectra collected in full-scan mode were obtained by scanning over the range 50–410 m/z in 1.8 s.

2.6.2. Neutral fraction analysis

In order to separate neutral analytes, phase A was acetonitrile and phase B was water. Gradient elution was performed by linearly increasing the percentage of organic modifier from 60 to 90% in 25 min. The flow-rate of the mobile phase was 1 ml/min. A 200-μl portion of column effluent was diverted to the ES source. The mass spectrometer was operated in positive-ion mode by applying, to the capillary, a voltage of 5000 V. The orifice voltage was set at 70 V and the interface temperature at 62°C. Nitrogen was used as curtain gas with a flow-rate of 1.1 l/min and as nebulizer gas with a pressure setting of 46 psi. Mass spectra collected in full-scan mode were obtained by scanning over the range 50–410 m/z in 1.8 s.

Time-scheduled selected-ion monitoring (SIM) LC–MS was performed using the procedure described in Table 1.

Table 1
Time-scheduled SIM condition for monitoring APPs esters and free acid in water samples (orifice plate voltage=70 V; dwell time=0.1 s; width=1)

Analyte	Channel mass m/z	Retention window (min)
Neutral fraction		
Fluazifop butyl	254+281+383	from 0 to 12.0
Fenoxaprop ethyl	259+289+363	
Quizalofop ethyl	269+299+373	from 12.0 to 17.0
Haloxyfop ethyl	289+317+391	from 17.0 to 19.0
Diclofop methyl	255+283+343	from 19.0 to 22.0
Acid fraction		
Fluazifop	69+253+325	from 0 to 11.0
Fenoxaprop	152+260+332	from 11.0 to 15.3
Quizalofop	270+342	
Haloxyfop	69+288+360	from 15.3 to 17.1
Diclofop	254+326	from 17.1 to 22.0

For recovery studies, the concentrations of the analytes were calculated by measuring peak areas from extracted-ion current profiles (XIC) and comparing them with those obtained from standard solutions. For any analyte, the selected XIC was the one from the most abundant ion. Standard solutions were prepared by dissolving suitable known volumes of the working standard solution in the eluent phase used for eluting analytes from the Carbograph 1 cartridge and then following the rest of the procedure as described above. Peak-area ratio for selected ions were determined automatically using the PE Sciex package Multiview 1.3.

3. Results and discussion

3.1. Recovery experiments

Recovery experiments were performed as reported in the Section 2.4. The resulting data are shown in Table 2. They consist of the average of the recovery values obtained by analyzing each water sample six times.

No problems were caused by the organic material found in water samples (mainly composed of humic and fulvic substances). In spite of the large volume of the water samples utilized in this experiment, and/or their high organic matter content, also neutral pesticides were totally retained on the GCB cartridge. Results in Table 2 show no evidence of any break-through loss of analytes. Analyte recoveries were invariably higher than 90% and were unaffected by the nature of the aqueous matrix in which analytes were dissolved.

Table 2
Recovery and relative standard deviation (R.S.D.) of APPs herbicide added to 2 l of drinking water and 1 l of ground water and surface water

Analyte	Recovery[a] (%)±R.S.D.		
	Drinking water 100 ng/l[b]	Ground water 200 ng/l[b]	Surface water 500 ng/l[b]
Fluazifop butyl	93±4	92±6	92±9
Fenoxaprop ethyl	94±4	96±5	93±4
Quizalofop ethyl	92±7	91±5	93±3
Haloxyfop ethyl	97±7	93±6	98±5
Diclofop methyl	92±5	92±5	91±5
Fluazifop	96±4	93±6	94±4
Fenoxaprop	93±7	92±4	94±5
Quizalofop	92±5	92±7	91±7
Haloxyfop	96±7	97±8	98±5
Diclofop	95±4	96±6	97±4

[a] Mean values from six determinations.
[b] Spike level for each pesticide.

3.2. Ion signal optimization.

With a view to optimizing the sensitivity of the ES-MS detector, the dependence of the ion signal intensities for APPs upon the composition of the LC mobile phase was evaluated.

3.2.1. Acid fraction

An improvement in sensitivity in the determination of acidic herbicides by HPLC–ESI-MS in the NI mode can be achieved by postcolumn addition of a base or buffer. Since a good separation of the acidic herbicides is feasible using a C_{18} silica column with an acidic mobile phase, the postcolumn addition of neutralization buffer was required in order to form ions in solution and to facilitate the charging of droplets. In a recent paper, Barcelo [29] develops a method for the determination of acid pesticides in water based on HPLC–ESI-NI-MS with a neutralization of the formic acid mobile phase by an equimolar amount of tripropylamine added postcolumn.

For this research, a partial neutralization of the mobile phase by a 10 μl/min addition of 50 m*M* CH_3COONH_4 was utilized since a further increase of buffer did not produce any improvement in sensitivity (unpublished data) and because we were thus able to improve the ruggedness of the method.

Our results agree with previous work by Wang and Cole [30], who observed a loss of signal intensity for phenoplphtalein diphosphate (free acid form) when increasing the ionic strength of the mobile phase.

3.2.2. Neutral fraction

Ion spectra for esters displayed major peaks for MNa^+, MK^+ and MH^+ ions, the latter generally being more abundant than the former two.

MNa^+ and MK^+ adducts are formed as a result of the presence of salt impurities in organic solvents, especially in methanol, which are used as organic

modifiers of the LC mobile phase. The formation of adduct ions other than MH^+ ions is not a favorable condition for two reasons. One is that batch-to-batch and manufacturer-to-manufacturer variations of the salt content in the organic solvents may lead to variations in the abundance of both fragment and parent ions, thus making CID spectra unreproducible. The second reason is that, with some exceptions which further complicate the interpretation of the spectra, the only fragment ion produced by decomposition of a MNa^+ adduct is generally the sodium ion itself. We observed that, in good agreement with the results of Pleasance et al. [31], the addition of HCOOH to the LC mobile phase suppressed production of Na^+ and K^+ adduct ions.

To make the analytical method as simple as possible, we used the same mobile phase, for the separation and analysis of the APPs esters, as for the acids, even if a slight increase in the signal-to-noise ratio is caused by using the methanol-like organic modifier.

3.3. Specificity and sensitivity

In the development of trace methods of pesticide analysis in complex aqueous matrices by LC–MS instrumentation, the presence in the spectra of peaks for characteristic fragment ions is necessary to avoid false positives and analyte overestimation. In addition, it must be considered that legal criteria for testing contaminants in a variety of matrices usually accept spectra displaying the molecular ion species plus two typical daughter ions. As mentioned above, fragment ions can be generated by the CID process of protonated adduct ions with residual drying gas molecules present in the ES-MS transport region. With our instrumentation, molecular ion decomposition can be achieved by increasing the voltage between the interface plate and orifice plate (OR) in the desolvation chamber. The effects of varying the OR voltage on both the response of the MS detector, and the production of diagnostic ions were investigated. For the pesticides considered, the effects of increasing the potential difference in the desolvation chamber by increasing the OR voltage from 50 to 90 V on both the response of the ESI-MS detector and the production of fragment ions were evaluated. This experiment was conducted by injecting 10 ng of each pesticide considered into the LC column. At each OR voltage selected, background-subtracted spectra were taken from the average of the chromatographic peaks. Ion-signal intensities were calculated by measuring the peak areas for each analyte from the total ion-current (TIC) chromatograms. Results are reported in Table 3. The product-ion spectrum of the Quizalofop free acid and Haloxyfop ester are shown in Fig. 2.

In terms of specificity, the CID process was able to produce the same patterns of fragmentation for both the ester and the acid of the APPs. The most abundant fragment ion derives from loss of the propanoic chain. Diclofop and Quizalofop free acids display only one significant fragment ion. In this case, we were able to use only two ions (fragment and $[M-H]^-$) to identify these compounds in an environmental matrix.

Abundant fragmentation of the analyte was obtained in the 50–90 V range. We selected OR=70 V as the working condition. The data in Table 3 show that the OR voltage could be varied with only negligible fluctuations of sensitivity.

3.4. Limits of detection (LODS)

Limits of detection (LOD) and the limit of quantitation (LOQ) were evaluated in this study. The LODs and LOQs were calculated using criteria established by Parker [32]. These data were obtained by measuring peak heights for any analyte against the averaged background noise from the TIC chromatogram relative to analysis of 2 l of a drinking water sample spiked with analytes at the individual level of 50 ng/l. The LODs calculated in TIC for drinking water ranged between 3 and 10 ng/l and LOQs are less than 30 ng/l. Figs. 3 and 4 show TIC and XIC chromatograms for esters and acids of APPs. From these results, it is apparent that this method can potentially be used for analyzing pesticides present in drinking water at only a few nanograms per liter.

Fig. 5 shows the time schedule SIM chromatogram for analytes. The LODs calculated in time-scheduled SIM for drinking water are less than 2 ng/l. By means of the time-scheduled SIM, we achieved two goals simultaneously: the best sensitivity of the method and the identification of the

Table 3
Effects of increasing orifice plate voltage on both signal intensities and production of fragments ions for APPs herbicides

Analytes	Orifice plate voltage (V)[a]		
	50	70	90
Fluazifop butyl	98 254(21), 281(38), 383(100)[b]	107 254(55), 281(65), 383(100)[b]	95 254(31), 281(90), 383(100)[b]
Fenoxaprop ethyl	92 259(28), 289(31), 363(100)[b]	90 259(62), 289(58), 363(100)[b]	101 259(88), 289(100), 363(85)[b]
Quizalofop ethyl	161 269(15), 299(33), 373(100)[b]	168 269(21), 299(78), 373(100)[b]	174 269(42), 299(100), 373(98)[b]
Haloxyfop ethyl	77 289(32), 317(25), 391(100)[b]	80 289(54), 317(59), 391(100)[b]	76 289(61), 317(88), 391(100)[b]
Diclofop methyl	52 255(18), 283(44), 343(100)[b]	55 255(65), 283(74), 343(100)[b]	59 255(75), 283(100), 343(89)[b]
Fluazifop	19 69(10), 253(23), 325(100)[b]	22 69(40)253(66), 325(100)[b]	22 69(78)253(100), 325(79)[b]
Fenoxaprop	10 152(32),260(35), 332(100)[b]	12 152(62), 260(81), 332(100)[b]	12 378(99), 260(100), 332(96)[b]
Quizalofop	7 270(29), 342(100)[b]	8 270(62), 342(100)[b]	8 270(95), 342(100)[b]
Haloxyfop	15 69(-), 288(50), 360(100)[b]	15 69(29), 288(78), 360(100)[b]	17 69(52), 288(100), 360(75)[b]
Diclofop	21 254(38), 326(100)[b]	20 254(71), 326(100)[b]	18 254(100), 326(98)[b]

[a] The signal (arbitrary units) is given in the first line. The relative abundance of ions (%) is given in second line.
[b] Values for protonated molecular ions.

compounds by selection of the characteristic ions of the analytes to their retention time.

This method could thus largely satisfy the strict requirements imposed by the 80/778 European Community directive setting 100 ng/l as the maximum admissible concentration of an individual pesticide in water intended for human consumption.

3.5. Linear dynamic range

The linear dynamic range of the ESI-MS detector for Quizalofop ethyl, Diclofop ethyl, Haloxyfop, and Fluazifop free acids was estimated under the conditions reported in Section 2.4. This set of measurements was performed by injecting, into the LC column, different known amounts of analytes. For each amount injected, measurements were made in triplicate. The average peak areas of each set of injections were plotted against the amount injected, and the resulting plot (Fig. 6) indicates that a fairly good linear response could be obtained for two model compounds from 1 to 200 ng/l for esters and a very good linear response for acid compounds.

3.6. Precision

For the selected pesticides, the repeatability and reproducibility of the signal intensities were assessed, together with those of the CID spectra. The intra-day precision was estimated by injecting 20 ng of each pesticide drawn from a standard solution into the LC column five times during a working day. The inter-day precision was evaluated by analyzing daily, the standard solution four times over 1 working week. The instrumental conditions were the same as those reported in the Section 2. For each analyte, the ion-signal intensity was assessed by measuring the peak area from XIC of the most abundant ion. The variation of the abundance of the ion in the CID process at an OR of 70 V ranged from 3 to 7%. The intra- and the inter-day variations of the signal intensities for the analytes lay within the ranges 4–6% and 7–10%, respectively. These data show

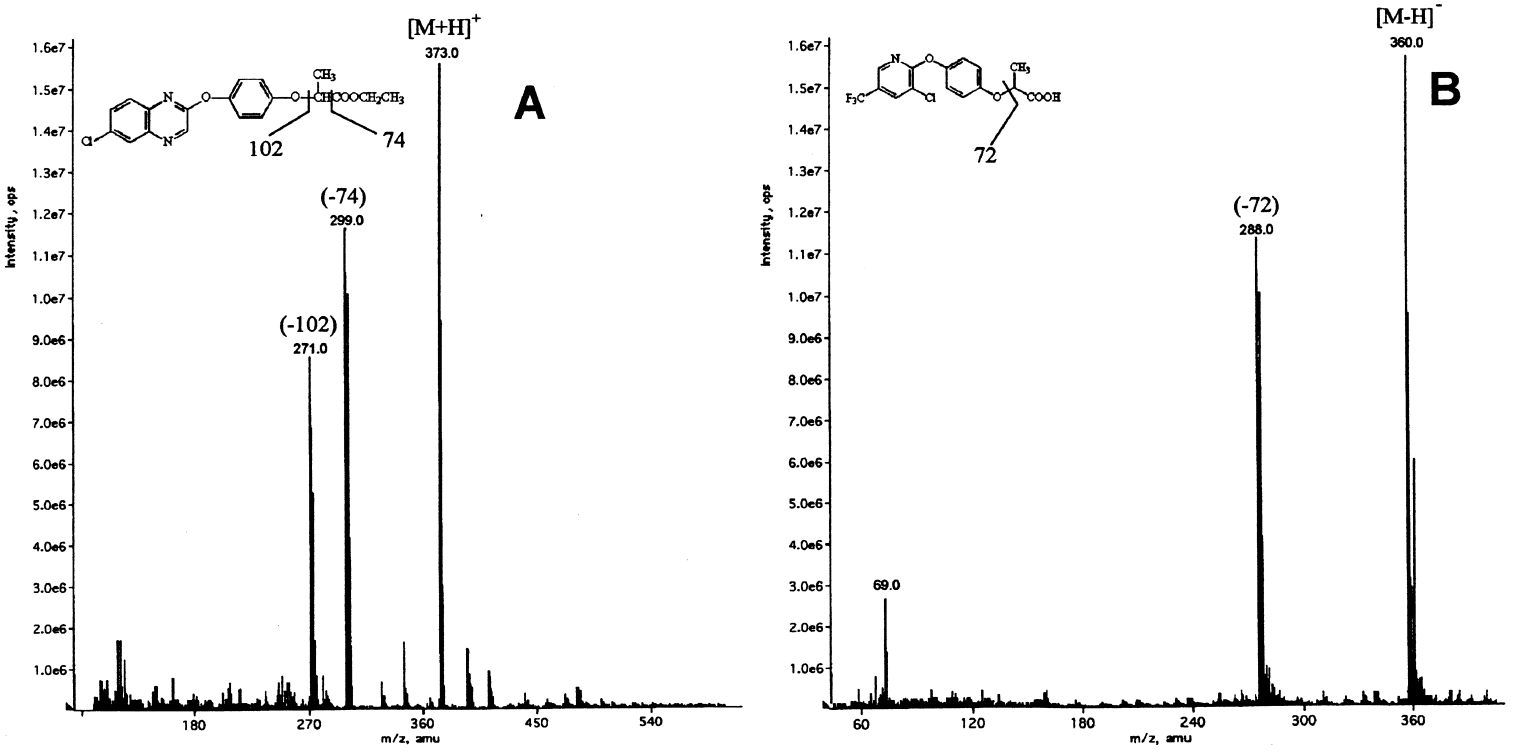

Fig. 2. Product-ion spectrum from collisionally induced dissociation of (A) Quizalofop ethyl (OR=70 V), (B) Haloxyfop free acid (OR=70 V).

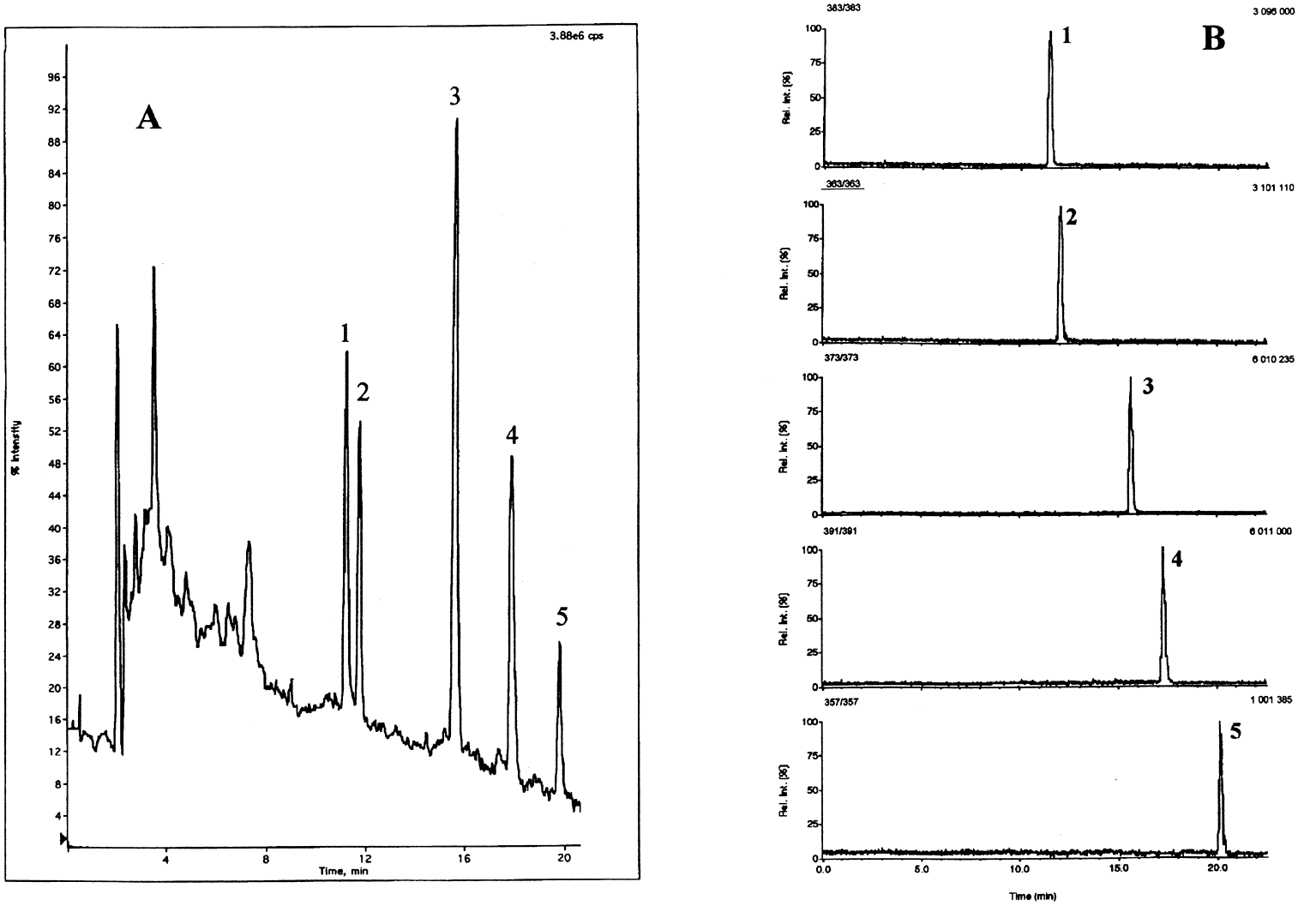

Fig. 3. TIC (A) and XICs (B) chromatogram obtained by injection 50/200 of a neutral extract relative to 2 l of drinking water spiked with the herbicides at level of 50 ng/l each: (1) Fluazifop butyl, (2) Fenoxaprop ethyl, (3) Quizalofop ethyl, (4) Haloxyfop ehtyl, (5) Diclofop methyl.

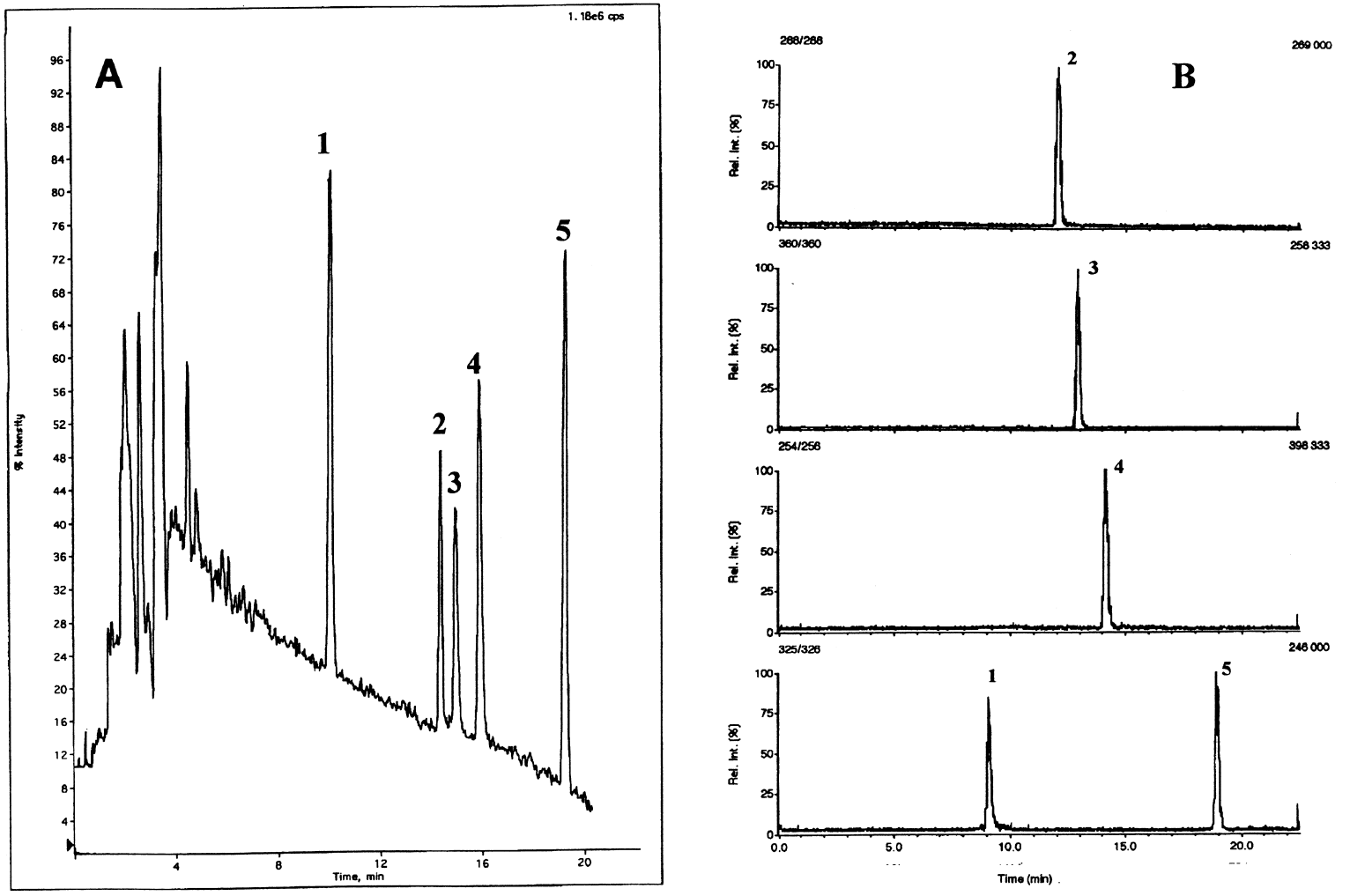

Fig. 4. TIC (A) and XICs (B) chromatogram obtained by injecting 50/200 of a acid extract relative to 2 l of drinking water spiked with the herbicides at level of 50 ng/l each: (1) Fluazifop, (2) Fenoxaprop, (3) Quizalofop, (4) haloxyfop, (5) Diclofop.

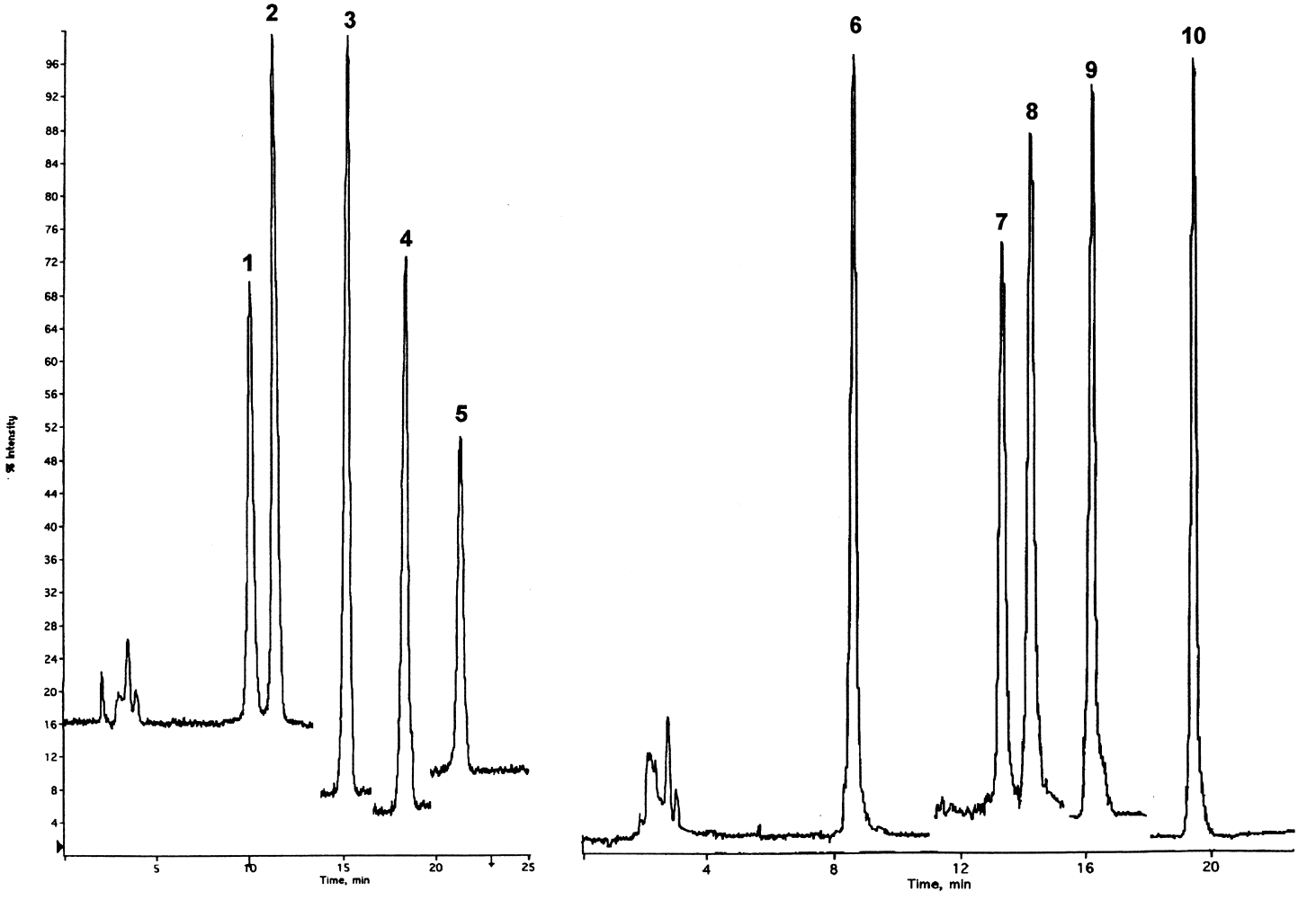

Fig. 5. Time-scheduled SIM chromatogram obtained by injecting 50/200 of a neutral and acid extract relative to 2 l of drinking water spiked with the herbicides at level of 50 ng/l each: (1) Fluazifop butyl, (2) Fenoxaprop ethyl, (3) Quizalofop ethyl, (4) Haloxyfop ethyl, (5) Diclofop methyl, (6) Fluazifop, (7) Fenoxaprop, (8) Quizalofop, (9) Haloxyfop, (10) Diclofop.

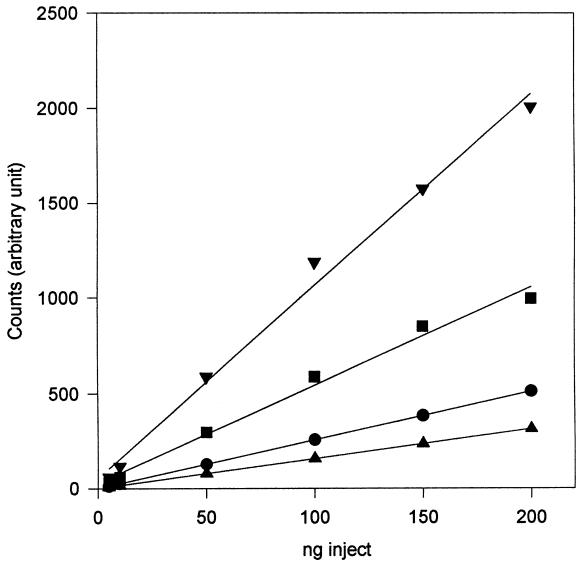

Fig. 6. Ion signal vs. amount of selected analytes injected into the LC column:

	Analytes	Regression analysis	R^2	R.S.D.
●	Fluazifop	$Y=0.14+2.47X$	0.999	7.4
△	Haloxyfop	$Y=0.29+1.56X$	0.999	6.3
■	Diclofop methyl	$Y=29.1+5.1X$	0.988	5.2
▽	Quizalofop ethyl	$Y=10.1+10.1X$	0.992	3.8

that both ion signals and the CID process are stable enough to allow reliable analysis of APPs herbicides to be performed using this method.

4. Conclusion

Use of the Carbograph-1 cartridge allows efficient extraction of APPs from water. Acid and neutral pesticides in the low ng/l range can be efficiently concentrated from large water samples, without pretreatment, with SPE by Carbograph 1. Recoveries from water are in the range of 91% to 97%.

We have shown that the combination of a Carbograph 1 SPE cartridge with LC–ESI-MS can be advantageously used for rapid, unequivocal, and accurate determination of pesticide traces in aqueous matrices. Our investigation involved only one class of herbicides. Nevertheless, this method can be extended to the analysis of a much larger number of base–neutral and acid pesticides by operating the ESI source in both positive- and negative-ion mode.

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