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Multiresidue Method for Determination of Post-Emergence Herbicides in Water by HPLC/ESI/MS in Positive Ionization Mode

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A post-emergence (POE) herbicide can be defined as a foliage-applied product used to control weeds that have emerged in competition with the developing crop. We developed a sensitive and specific multiresidue method, based on reversed-phase liquid chromatography/mass spectrometry, with an electrospray interface (LC/ESI/MS), for determining 15 of most representative compounds of a new class of POE herbicides in water samples. The procedure used involved passing 2 L of groundwater and 4 L of drinking water samples, respectively, through a 0.5 g graphitized carbon black (GCB) extraction cartridge. A conventional 4.6 mm i.d. reversed-phase LC C-18 column, operating with a mobile phase flow rate of 1 mL/min, was used to chromatograph the analytes. A flow of 200 μL/min of the column effluent was diverted to the ESI source. The study demonstrates the sensitivity of the technique, with detection limit under 5 ng/L in drinking water samples. Performance data for the method such as recovery and precision are also reported.

Introduction

Rapid farmer acceptance of post-emergence (POE) herbicides can be ascribed to several factors including decreased use of chemicals, improved weed control efficiency, environmental and safety benefits, and soil conservation. In addition, recent advances in information systems for predicting crop damage on the basis of weed density, location, and soil type tend to favor the increasing use of such compounds.

A POE herbicide can be defined as a foliage-applied product used to control weeds that have emerged in competition with the developing crop. However, many such herbicides still retain residual activity in the soil and thus can control late-germination weeds. Their selectivity dictates the specific crop application for individual compounds. The POE herbicides that are predicted to become more widespread over the next decade are sulfonylureas (SUs), imidazolinones (IMIs), and arylphenoxypropionic acids (APPAs).

SUs are a class of herbicides introduced in the 1980s. From a chemical point of view, SUs are labile and weakly acidic compounds. Various separation techniques, such as gas chromatography−mass spectrometry of SU derivatives (*1*), supercritical fluid chromatography (*2*), capillary electrophoresis (*3*), and liquid chromatography (LC) (*4*−*6*) have been proposed for analyzing SUs in various matrixes. LC methods have become even more attractive after the introduction of robust and sensitive devices, such as thermospray (TS) and electrospray (ES) to interface LC to mass spectrometry (MS). Recently, Henion and co-workers reported that eight SUs in soil could be quantified at 50 ng/kg levels by LC-ES/MS/MS instrumentation (*7*).

On the other hand, there are relatively few methods available for the determination of APPA herbicides in environmental matrixes, and current analytical methods are targeted at single members of the group. With regard to APPAs, isolation procedures described in the literature are usually based on the 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 (*8*−*10*) or GC/ECD, after suitable derivatization (*11*−*12*), or GC/MS (*13*).

With regard to IMI analysis, Stout et al. (*14*) recently developed a method for determining all imidazolinones simultaneously in water at a level of 1 μg/L (1 ppb), without any concentration or cleanup of the sample and based on liquid chromatography/mass spectrometry with an electrospray interface (LC/ESI/MS).

This method is simple and rapid, but recent legislation enacted in many European countries (members of the European Community, EC) states that pesticides must not exceed 100 ng/L in water intended for human consumption. To judge with sufficient confidence whether a water sample complies with this EC Directive, analytical methods able to detect pesticides at levels of 20−30 ng/L are needed. In a recent paper, we developed a very sensitive and rapid LC/ESI/MS method for analyzing imidazolinone herbicides in aqueous environmental samples at the nanogram per liter-level (*15*). This method involves the use of a graphitized carbon black (GCB) reversible cartridge for extracting pesticides from water samples.

The aim of the present work was to evaluate the potentiality of coupling our sample preparation procedure with the high substantiating power of the LC/ESI/MS system in order to unambiguously monitor a selection of 15 herbicides, representative of the three classes of POE herbicides considered, in drinking and groundwater samples at the level of a few parts per trillion. The pesticides, neutral and acid compounds, were simultaneously extracted from water samples by solid-phase extraction (SPE) using a Carbograph cartridge without any sample pretreatment. 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 analyzing these compounds in an environmental matrix.

By being passed sequentially through two suitable solvent systems in the cartridge, the acidic pesticides were successfully isolated from nonacidic ones by differential elution (*16*, *17*). Class fractionation was possible because the GCB surface framework was contaminated by some positively charged adsorption sites (*18*) that allowed this material to behave as both a nonspecific sorbent and an anion exchanger (*19*). In this way, it was possible to perform extraction, preconcentration, and class fractionation of analytes using a single cartridge.

This feature of the GCB has not been exploited in the present work. To make the method as simple as possible, we collected all our analytes, the neutral ester, and the other 14 acid compounds into a single fraction.

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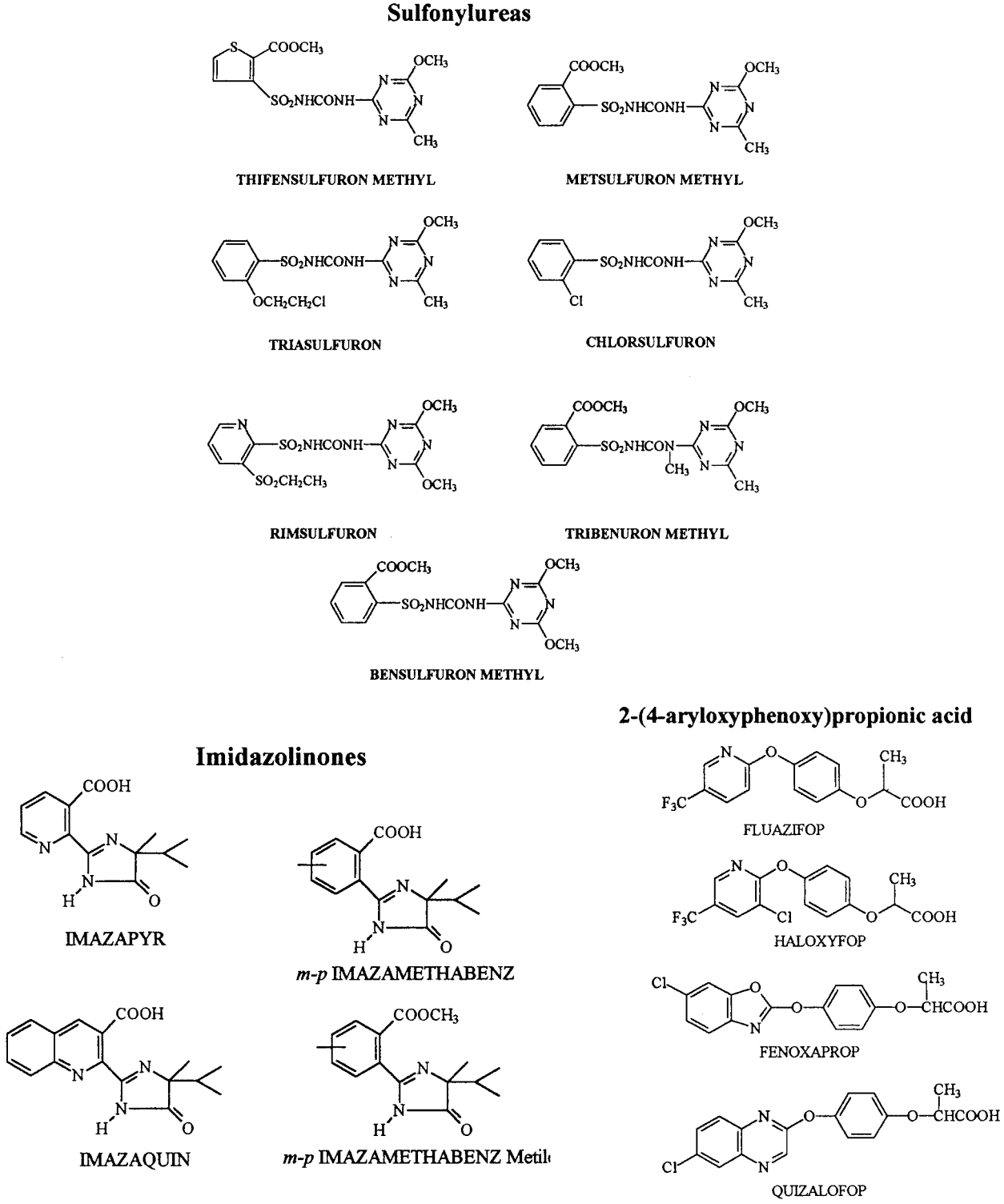

FIGURE 1. Structure and common name of POE herbicides.

Experimental Section

Reagents and Chemicals. Authentic selected SU, IMI, and APPA herbicides were purchased from LabService (Bologna, Italy) with the sole exception of quizalofop. Quizalofop free acid was obtained by hydrolysis (*20*) from quizalofop-ethyl (LabService). The structures and common names are shown in Figure 1. 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 solution and diluting to 50 mL with acetonitrile (2 ng/μL). All standard solutions were stored at 4 °C prior to use.

Formic acid and tetrabutylammonium fluoride (TBAF) were obtained from Aldrich (Milwaukee, WI).

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

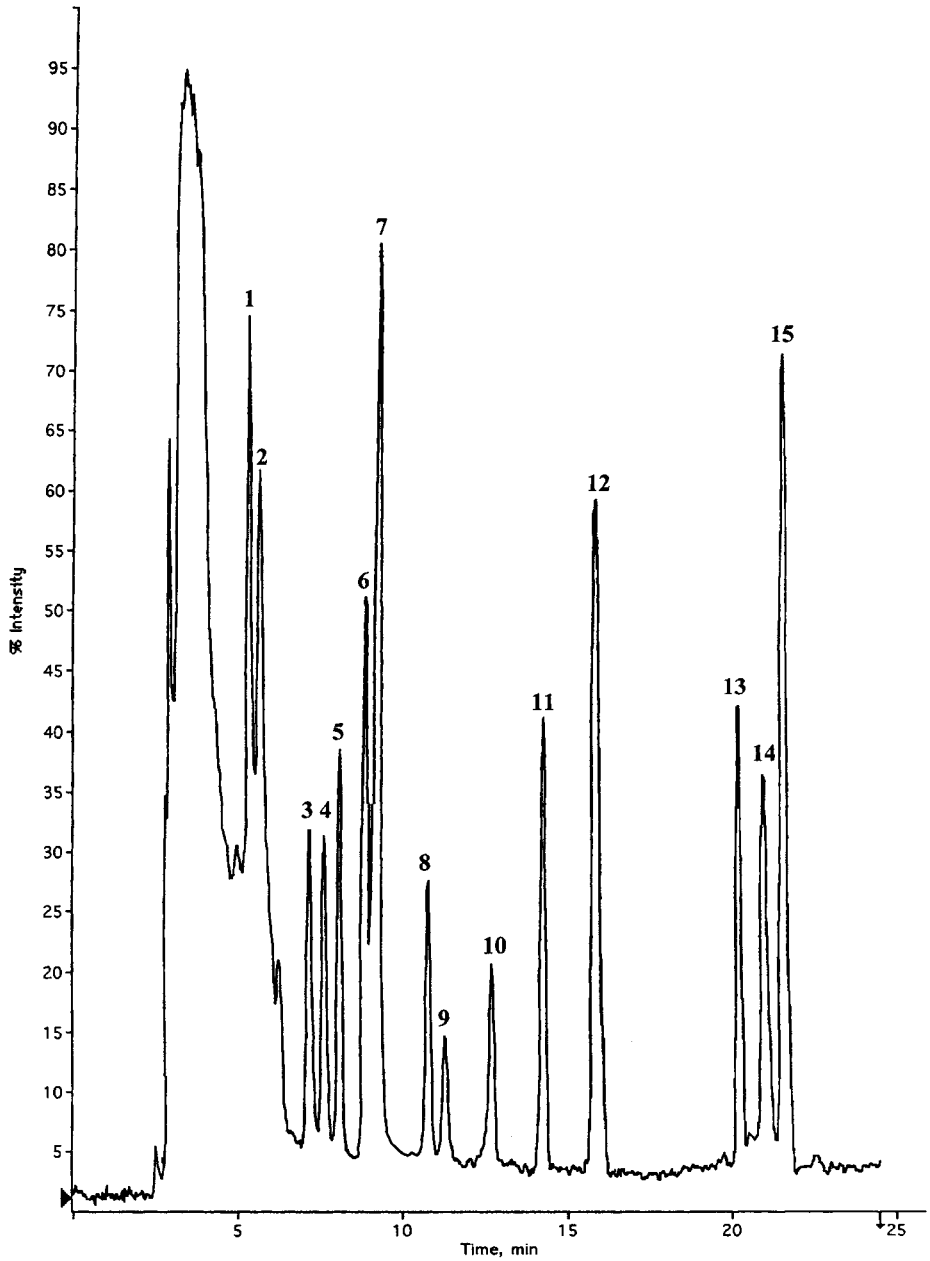

FIGURE 2. TIC chromatogram of the selected herbicides obtained by injecting 50/200 of a final extract relative to 4 L of drinking water spiked with the herbicides at a level of 100 ng/L each. Peak numbering is reported in Table 1.

Apparatus. Extraction cartridges filled with 0.5 g of Carbograph 4 (120−400 mesh size) were supplied by Carbochimica Romana (Rome, Italy) while the other materials for preparing extraction cartridges were from Supelco (Bellefonte, PA). The preparation and pretreatment of the reversible extraction cartridge were carried out as previously reported (*21, 22*). The trap was fitted into a sidearm filtering flask, and liquids were forced through the cartridge by means of the vacuum produced by a water pump.

Sampling. Grab samples of groundwater were collected in brown glass bottles and kept at 4 °C in the dark until analyzed. In any case, environmental samples were analyzed after no more than a few days' storage. Drinking water samples were collected from the tap in the laboratory. To eliminate sediments and gas pockets in the pipes, this water was collected after flushing for about 20 min. Before spiking with analytes, the hypochlorite in the drinking water samples was eliminated by addition of $Na_2S_2O_3$ (0.5 g/L).

Procedure. For recovery studies, aqueous samples were fortified with known amounts of the composite standard solution. The water samples were then stirred vigorously for about 1 min and, after an additional 2 min, poured into a glass reservoir connected to the sorbent cartridge. Water was forced through the cartridge at flow rates of ca. 150 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 allowed to pass slowly 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. Thereafter, a suitably drilled cylindrical Teflon piston with one conically indented base and a Luer tip was forced into the cartridge as far as the upper frit. The trap was turned upside down, a 1.4 cm i.d. glass vial with a conical bottom was placed below it, and the analytes were back-eluted by passing first 0.5 mL of methanol and then 10

TABLE 1. Time-Scheduled SIM Condition for Monitoring Selected Herbicides in Water Samples (Orifice Plate Voltage = 100 V; Width = 1)

analyte	channel mass (*m/z*)	period	retention window (min)
1 imazapyr	202 + 217 + 262	1	0−7.0
2 imazamethabenz	162 + 229 + 275		
3 triasulfuron	141 + 167 + 402	2	7−8.5
4 thifensulfuron-methyl	141 + 167 + 388		
5 metsulfuron	167 + 199 + 382		
6 imazaquin	199 + 267 + 312	3	8.5−10
7 imazamethabenz-methyl	177 + 229 + 289		
8 chlorsulfuron	141 + 167 + 358	4	10−12
9 rimsulfuron	182 + 325 + 432		
10 tribenuron-methyl	155 + 181 + 396		
11 bensulfuron-methyl	182 + 213 + 411	5	12−16
12 fluazifop	255 + 282 + 328		
13 fenoxaprop	262 + 288 + 334	6	16−24
14 quizalofop	273 + 299 + 344		
15 haloxyfop	290 + 316 + 362		

mL of a methylene chloride/methanol (80/20, v/v) solution containing TBAF (10 mmol/L) through the trap.

The flow rate at which the eluent phase percolated through the cartridge was ca. 6 mL/min. The last few drops of this mixture were collected by further decreasing the pressure inside the flask. The eluate was dried in a water bath at 30 °C under a gentle stream of nitrogen. The residue was reconstituted with 200 μL of a water/methanol solution (75:25, v/v) acidified with 10 mM HCOOH, and 50 μL of the final extract was injected into the LC column.

LC/ESI/MS Analysis. Liquid chromatography was carried out using a Perkin-Elmer series 200 binary pump (Perkin-Elmer, Norwalk, CT) 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 of C-18 reversed-phase packing (Alltech, Deerfield, IL). For the purpose of fractionating the analytes, methanol was selected as phase A and water was selected as phase B. Both solvents contained 10 mmol/L HCOOH. Gradient elution was performed by linearly increasing the percentage of organic modifier from 40 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. Electrospray mass spectrometry was performed on a Perkin-Elmer/Sciex API I single-stage quadruple instrument equipped with an TurboIonspray interface (Sciex, Thornton, Canada). 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 100 V, and the interface temperature was 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 40 psi. Mass spectra collected in full-scan mode were obtained by scanning over the range 140−440 m/z in 2 s. 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 given analyte, the XIC was selected 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 described above. The peak area ratio for selected ions was determined using the PE Sciex package Multiview 1.3.

Time-scheduled selected ion monitoring (SIM) LC/MS was performed by following the procedure reported in Table 1.

TABLE 2. Recovery and Relative Standard Deviation (RSD) of POE Herbicides Added to 4 L of Drinking Water and 2 L of Groundwater

herbicides	recovery[a] (%) ± RSD: drinking water (100 ng/L)[b]	recovery[a] (%) ± RSD: groundwater (200 ng/L)[b]
imazapyr	85 ± 4	90 ± 6
imazamethabenz	88 ± 4	86 ± 5
triasulfuron	88 ± 4	91 ± 8
thifensulfuron-methyl	92 ± 7	90 ± 6
metsulfuron	98 ± 4	89 ± 6
imazaquin	103 ± 4	92 ± 5
imazamethabenz-methyl	104 ± 5	108 ± 4
chlorsulfuron	92 ± 7	91 ± 5
rimsulfuron	88 ± 5	93 ± 6
tribenuron-methyl	92 ± 5	92 ± 8
bensulfuron-methyl	96 ± 4	93 ± 9
fluazifop	93 ± 5	92 ± 4
fenoxaprop	92 ± 5	92 ± 7
quizalofop	95 ± 4	107 ± 8
haloxyfop	95 ± 4	96 ± 5

[a] Mean values from 10 determinations. [b] Spike level for each pesticide.

Results and Discussion

Recovery Studies. The ability of the Carbograph 4 extraction cartridge to retain quantitatively even very highly water-soluble pesticides was evaluated. This experiment consisted of passing through the cartridge 4 L of drinking water (Figure 2) and 2 L of groundwater, respectively. Results are shown in Table 2.

These figures were the result of averaging recovery data obtained by analyzing each water sample 10 times. Recovery exceeded 85% for all analytes investigated, with relative standard deviations ranging from 4 to 9%.

Collision-Induced Dissociation Spectra. The correspondence between retention time and molecular weight ascertained using the LC/ESI/MS technique could provide sufficient specificity for identifying a target compound in a complex matrix, yet legal criteria for testing the presence of contaminants in various matrixes usually accept spectra displaying the molecular ion species plus characteristic ion fragments. The ESI/MS system entails fragment ions being obtained by collision ion-induced (CID) reactions (*23*). With our instrumentation, molecular ion decomposition can be achieved by increasing the voltage between interface plate and orifice plate in the desolvation chamber. The effects of varying the orifice plate (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 70 (minimum value for fragmentation of all analytes) to 100 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 all the OR voltages 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 obtained from the total ion current (TIC) chromatograms. Results are reported in Table 3. For the sake of conciseness, in this table only the relative abundance of the molecular ions plus those of the two strongest related fragments have been reported.

In terms of specificity, abundant fragmentation of the $[M + H]^+$ ion of the analyte was obtained in the 90−100 V range. OR = 100 V was selected as the operating condition.

In accordance with our preceding work (*15*), as the collision energy was increased by increasing the OR plate

TABLE 3. Effects of Increasing Orifice Plate Voltage on Both Signal Intensities and Production of Fragments Ions for POE Herbicides[a]

herbicides	70 V	80 V	90 V	100 V
imazapyr	**7851**[a] 202(15), 217(40) **262**(100)	**8510** 202(17), 217(41) **262**(100)	**9287** 202(34), 217(80) **262**(100)	**10084** 202(57), 217(100) **262**(98)
imazamethabenz	**5558** 162(16), 229(19) **275**(100)	**6001** 162(37), 229(22) **275**(100)	**6151** 162(50), 229(39) **275**(100)	**6321** 162(76), 229(59) **275**(100)
triasulfuron	**3581** 141(25), 167(−) **402**(100)	**4368** 141(38), 167(28) **402**(100)	**5289** 141(61), 167(45) **402**(100)	**6561** 141(80), 167(65) **402**(100)
thifensulfuron-methyl	**3947** 141(−), 167(31) **388**(100)	**4258** 141(−), 167(42) **388**(100)	**5684** 141(20), 167(80) **388**(100)	**6809** 141(30), 167(98) **388**(100)
metsulfuron	**3581** 167(31), 199(−) **382**(100)	**4287** 167(54), 199(−) **382**(100)	**5541** 167(90), 199(20) **382**(100)	**7161** 167(100), 199(40) **382**(90)
imazaquin	**11258** 199(23), 267(31) **312**(100)	**12369** 199(31), 267(46) **312**(100)	**13525** 199(33), 267(55) **312**(100)	**14369** 199(43), 267(70) **312**(100)
imazamethabenz-methyl	**15001** 177(21), 229(20) **289**(100)	**16025** 177(30), 229(34) **289**(100)	**16658** 177(41), 229(48) **289**(100)	**17314** 177(48), 229(58) **289**(100)
chlorsulfuron	**2554** 141(40), 167(42) **358**(95)	**4058** 141(61), 167(52) **358**(95)	**4804** 141(98), 167(64) **358**(95)	**5709** 141(100), 167(76) **358**(95)
rimsulfuron	**1845** 182(25), 325(−) **432**(100)	**2154** 182(61), 325(25) **432**(100)	**3520** 182(100), 325(47) **432**(90)	**4002** 182(100), 325(60) **432**(65)
tribenuron-methyl	**3244** 155(81), 181(−) **396**(100)	**3784** 155(100), 181(15) **396**(100)	**4258** 155(100), 181(22) **396**(100)	**5046** 155(100), 181(41) **396**(30)
bensulfuron-methyl	**6852** 182(35), 213(19) **411**(100)	**7125** 182(56), 213(26) **411**(100)	**7598** 182(70), 213(31) **411**(100)	**8318** 182(80), 213(59) **411**(100)
fluazifop	**7852** 255(−), 282(26) **328**(100)	**7958** 255(15), 282(38) **328**(100)	**8051** 255(25), 282(58) **328**(100)	**8269** 255(38), 282(70) **328**(100)
fenoxaprop	**7774** 262(18), 288(15) **334**(100)	**7850** 262(26), 288(21) **334**(100)	**8025** 262(38), 288(41) **334**(100)	**8417** 262(65), 288(60) **334**(100)
quizalofop	**6142** 273(−), 299(21) **344**(100)	**6358** 273(−), 299(34) **344**(100)	**6778** 273(15), 299(48) **344**(100)	**7096** 273(25), 299(74) **344**(100)
haloxyfop	**8952** 290(−), 316(38) **362**(100)	**9312** 290(15), 316(46) **362**(100)	**9758** 290(28), 316(61) **362**(100)	**10625** 290(38), 316(82) **362**(100)

[a] The signal (arbitrary units) is given in the first line. The relative abundance of ions (%) is given in the second line. Protonated molecular ions are reported in bold. Fragment ions having relative abundance less than 10% were not considered.

voltage, the production of fragment ions for the analytes considered was steadily accompanied by an enhancement of the ion signal intensity. This positive effect has been already observed with several other compounds (*24*) and can perhaps be traced to a more efficient adduct ion sampling performed in the sample cone region.

Ion Signal Optimization. Ion spectra for selected herbicides displayed major peaks for MNa^+, MK^+, and MH^+ ions, the latter being generally more abundant than the former ones. These 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 can 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 that 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. (*25*), the addition of HCOOH to the LC mobile phase suppressed production of Na^+ and K^+ adduct ions.

A general enhancement of the ion signal was achieved by increasing the HCOOH concentration from 1 to 10 mmol/L. Further additions of HCOOH resulted in a gradual weakening of the ion signal. Our results agree sufficiently well with previous work by Zhou (*26*), who observed a steady increase in the $[M + H]^+$ ion signal for quercetin on increasing formic acid concentration up to 25 mmol/L.

Precision. For the selected pesticides, the repeatability and reproducibility of the signal intensities were assessed, together with those of the CID spectra. The intraday precision was estimated by injecting 10 ng of each pesticide drawn from a standard solution into the LC column six times during one working day. The interday precision was evaluated by analyzing daily the standard solution four times over one working week. The instrumental conditions were the same as those reported in the Experimental Section. For each analyte, the ion signal intensity was assessed by measuring the peak area from the XIC of the most abundant ion. The variation of the abundance of the ion in the CID process at an OR of 100 V ranged from 4 to 10%. The intra- and the interday variations of the signal intensities for the analytes lay within the ranges of 4−6% and 8−10%, respectively. These data show that both ion signals and the CID process are stable enough to allow reliable analysis of selected POE herbicides to be performed using this method.

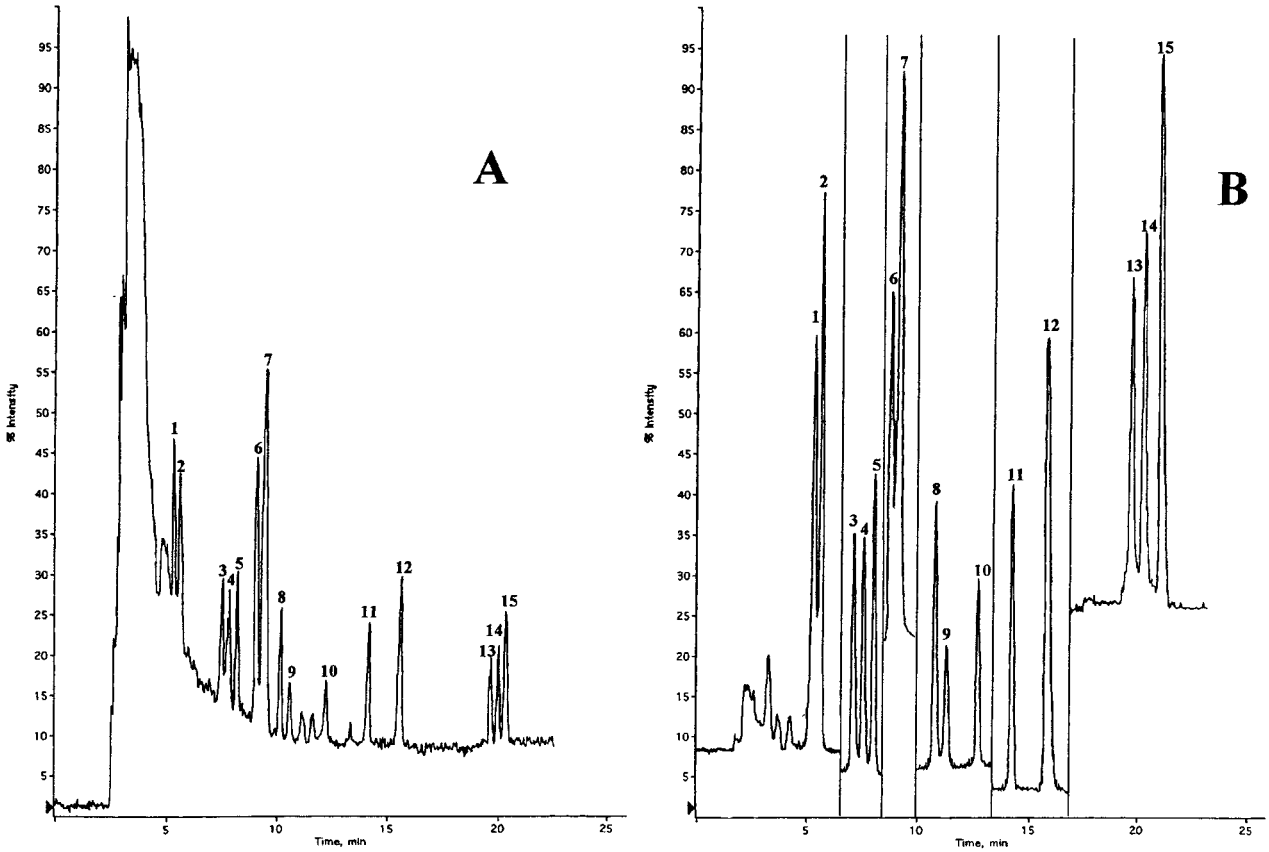

FIGURE 3. (A) TIC and (B) time-scheduled SIM chromatogram of the selected herbicides obtained by injecting 50/200 of a final extract relative to 4 L of drinking water spiked with the herbicides at a level of 25 ng/L each. Peak numbering is reported in Table 1.

TABLE 4. Limits of Detection (LODs) for Herbicides Extracted from 4 L of Drinking Water (Spike Level 25 ng/L)

	LOD (ng/L)	
herbicides	TIC	time-scheduled SIM
imazapyr	3.8	0.8
imazamethabenz	4.5	0.7
triasulfuron	6.2	1.8
thifensulfuron-methyl	6.0	2.1
metsulfuron	5.7	2.4
imazaquin	2.8	1.0
imazamethabenz-methyl	2.3	0.5
chlorsulfuron	7.1	2.1
rimsulfuron	9.9	4.5
tribenuron-methyl	8.0	3.3
bensulfuron-methyl	5.1	1.2
fluazifop	5.0	0.6
fenoxaprop	4.8	1.3
quizalofop	5.8	1.1
haloxyfop	3.8	0.5

TABLE 5. Recovery of Selected POE Herbicides Added to 1 L of Groundwater by Extracting with the GCB and C-18 Cartridge

	recovery[a] (%)	
herbicides	GCB (1000 ng/L)[b]	C-18 (1000 ng/L)[b]
imazapyr	89	77
imazamethabenz	90	80
triasulfuron	87	74
thifensulfuron-methyl	95	74
metsulfuron	92	78
imazaquin	100	82
imazamethabenz-methyl	94	80
chlorsulfuron	102	85
rimsulfuron	92	39
tribenuron-methyl	95	48
bensulfuron-methyl	96	73
fluazifop	91	80
fenoxaprop	90	23
quizalofop	93	18
haloxyfop	101	76

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

Limits of Detection (LODs) and Linear Dynamic Range. As mentioned above, a limit of 0.1 μg/L for individual pesticides in drinking water has been set by a EC Directive, which means that methods used to monitor drinking water should preferably display detection limits of about one-tenth of this limit or less.

The LODs given in Table 4 were calculated using a signal-to-noise ratio of 3 (the ratio of the peak intensity and the intensity of the noise was used). These data were obtained by measuring peak heights for any analyte against the averaged background noise from the TIC chromatogram referring to analysis of 4 L of a drinking water sample spiked with analytes at the individual level of 25 ng/L. In the same table, LODs calculated time-scheduled SIM are also presented. Figure 3 shows the TIC and time-scheduled SIM chromatogram for analytes. By using the time-scheduled SIM, we achieved two goals simultaneously: the best sensitivity of the method and the identification of the compounds by means of the selection of the characteristic ions of the analytes to their retention time. The experimental condition for time-scheduled SIM was reported in Table 1.

The LODs calculated in time-scheduled SIM for drinking water were in the range of 0.5−4.5 ng/L. Examination of

TABLE 6. Concentration Levels of Analytes in Three Samples of Groundwater Collected Every 2 Weeks between June and September 1997

	concentration (ng/L)[a]						
	Cese 1			Cese 2		Luco dei Marsi 1	
sample	imazamethabenz	imazamethabenz-methyl	haloxyfop	imazamethabenz	fluazifop	chlorsulfuron	haloxyfop
June A	64	nd[b]	15	68	108	35	67
June B	55	24	35	84	88	48	121
July A	58	67	38	67	25	25	68
July B	87	68	89	32	48	nd	26
August A	31	68	66	nd	58	nd	nd
August B	37	45	nd	nd	51	nd	nd
September A	37	31	nd	nd	26	nd	nd
September B	23	44	nd	nd	18	nd	nd

[a] Mean values obtained from duplicate measurements. [b] nd, not detected.

Table 5 shows that this method can potentially be used for analyzing pesticides present in drinking water at a few nanograms per liter in the selected ion-monitoring acquisition mode.

The linear dynamic range of the ESI/MS detector for selected herbicides was estimated under the conditions reported in the Experimental Section. 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 results indicate that a good linear response can be obtained from 5 to 250 ng for all analytes.

Method Comparison. Octadecyl-bonded silica (C-18) has frequently been proposed as a sorbent material for extracting pesticides from aqueous samples (*27*−*30*). This method was compared to that involving the use of a C-18 SPE cartridge. Aliquots (1 L) of a groundwater sample were spiked with 1 μg/L of the selected herbicides and analyzed by extracting with Carbograph 4 and with a disposable 0.5 g C-18 cartridge (Supelco Inc., Bellefonte, PA). Before extraction, the C-18 cartridge was conditioned with 5 mL of methanol followed by 5 mL of water (*27*). In addition, the water was acidified to pH 2 with HCl in order to suppress analyte dissociation (*28*). After the passage of the sample, the C-18 cartridge was washed with 10 mL of water. Interstitial water was partly eliminated by forcing room air through the cartridge for 5 min. Analytes were then eluted with 5 mL of methanol. Solvent removal and residue reconstitution were carried out according to our procedure. Experiments were performed in triplicate. The results in Table 5 indicate a severe loss of APPAs and two SUs: rimsulfuron and tribenuron-methyl.

The necessity to acidify the sample in order to be able to keep acid pesticides on C-18, like imazethapyr ($pK_a = 2.2$) or haloxyfop ($pK_a = 2.6$), leads to loss of compounds that are barely stable in an acidic environment. Especially quizalofop and fenoxaprop (*31*) are quickly degraded by the presence of dilute mineral acid. In this situation, the capacity of Carbograph to extract acid analytes from water without any sample pretreatment is a substantial advantage over the C-18 cartridge.

Environmental Samples Analysis. The described method was applied, as a random test, to the determination of herbicides in real groundwater samples from the Valle del Fucino, a paleolacustrine basin situated in the Abruzzi Region (central Italy). The original environmental conditions were not defined a priori. The groundwater samples were related to the sites of origin only after the determination of the analytes.

Samples of deep groundwater were collected every 15 days, from June to September 1997, in six different sites: two in the northern part of the basin (near Celano), two in the southwestern part (near Luco dei Marsi), and two in the western part (Cese).

Only in three of the sites were any of the selected analytes found (Table 6). Indeed, the use of this kind of herbicide is limited to these sites in the areas where samples were collected. However, to provide a more exhaustive environmental evaluation, herbicides other than those specifically involved in this study were found in the other sites considered. A correct interpretation of the presence of the selected herbicides during the summer, i.e., at some distance in time from the direct use of substances (*32*), will be the object of further research involving the characteristics of the terrain, possible interactions, and relative mobility.

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Literature Cited

(1) Klaffenbach, P.; Holland, P. T. *J. Agric. Food. Chem.* **1993**, *41*, 388−395.
(2) Berger, A. *Chromatographia* **1995**, *41*, 133−140.
(3) Dinelli, G.; Vicari, A.; Bonetti, A. *J. Chromatogr.* **1995**, *700*, 19−200.
(4) Raiser, R. W.; Barefoot, A. C.; Dietrich, R. F.; Fogiel, A. J.; Johnson, W. R.; Scott, M. T. *J. Chromatogr.* **1991**, *554*, 91−101.
(5) Nilve, G.; Knutsson, M.; Joansson, J. A. *J. Chromatogr.* **1994**, *688*, 75−82.
(6) Cambon, J. P.; Bastide, J. *J Agric. Food Chem.* **1996**, *41*, 333−337.
(7) Li, L. Y. T.; Campbell, D. A.; Bennet, P. K.; Henion, J. *Anal. Chem.* **1996**, *68*, 3397−3404.
(8) Negre, M.; Gennari, M.; Cignetti, A. *J. Chromatogr.* **1987**, *387*, 541−545.
(9) Zanco, M.; Pfister, G.; Kettrup, A. *Fresenius J. Anal. Chem.* **1992**, *344*, 39−41.
(10) Wokobey, B. C.; Shield, J. B. *J. AOAC Int.* **1989**, *72*, 368−371.
(11) Clegg, B. S. *J. Agric. Food Chem.* **1987**, *35*, 269−273.
(12) Hajslova, J.; Pudil, F.; Jehlickova, Z.; Viden, I.; Davidek, J. *J. Chromatogr.* **1988**, *438*, 55−60.
(13) Hajslova, J.; Pudil, F.; Jehlickova, Z.; Viden, I.; Davidek, J. *Z. Lebensm-Unters.-Forsch* **1990**, *190*, 435−440.
(14) Stout, S. J.; daCunha, A. R.; Picard, G. L.; Safarpour, M. M. *J. Agric. Food Chem.* **1996**, *44*, 2182−2186.
(15) D'Ascenzo, G.; Gentili, A.; Marchese, S.; Perret, D. *J. Chromatogr.* In press.
(16) Di Corcia, A.; Marchetti, M. *Environ. Sci. Technol.* **1992**, *26*, 68−74.
(17) Di Corcia, A.; Marcomini, A.; Samperi, R. *Environ. Sci. Technol.* **1994**, *28*, 850−857.
(18) Campanella, L.; Di Corcia, A.; Gambacorta, A.; Samperi, R. *Mater. Chem.* **1982**, *7*, 425−427.
(19) Di Corcia, A.; Marchese, S.; Samperi, R. *J. Chromatogr.* **1993**, *642*, 163−169.

(20) Padiglioni, P.; Polcaro, C. M.; Marchese, S.; Sinibaldi, M.; Flieger, M. *J. Chromatogr.* **1996**, *756*, 119−127.
(21) Crescenzi, C.; Di Corcia, A.; Passariello, G. M.; Samperi, R.; Turnes, Carou, M. I. *J. Chromatogr.* **1996**, *733*, 41−55.
(22) Di Corcia, A.; Bellioni, A.; Magdy Diab, M.; Marchese, S. *J. Chromatogr.* **1996**, *733*, 383−389.
(23) Voyksner, R. D. *Environ. Sci. Technol.* **1994**, *28*, 118−126.
(24) Crescenzi, C.; Di Corcia, A.; Guerriero, E.; Samperi, R. *Environ. Sci. Technol.* **1997**, *31*, 479−488.
(25) Pleasance, S.; Anacleto, J. F.; Bailey, R. M.; Marth, T. H. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 378−392.
(26) Zhou, S.; Hamburger, D. *Rapid Commun. Mass Spectrom.* **1995**, 1516−1521.
(27) Galletti, G. C.; Bonetti, A.; Dinelli, G. *J. Chromatogr.* **1995**, *692*, 27−37.
(28) Volmer, D.; Wilkes, J. G.; Levsen, K. *Rapid Commun. Mass Spectrom.* **1995**, *9*, 767−771.
(29) Zahnow, E. W. L. *J. Agric. Food Chem.* **1982**, *30*, 854−859.
(30) Redondo, M. J.; Ruiz, M. J.; Boluda, R.; Font, G. *J. Chromatogr.* **1996**, *719*, 69−76.
(31) Smith, A. E. *J. Agric. Food Chem.* **1985**, *33*, 483−488.
(32) *Herbicide Handbook*; Weed Science Society of America: Champaign, IL, 1997.

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