Determination of Glufosinate Ammonium and Its Metabolite (AE F064619 and AE F061517) Residues in Water by Gas Chromatography with Tandem Mass Spectrometry after Ion Exchange Cleanup and Derivatization

Alain Royer,† Sylvie Beguin,† Heinz Sochor,‡ and Pierre-Yves Communal*,†

Groupement Interrégional de Recherche sur les Produits agropharmaceutiques, Angers Technopole, 8 rue H. Becquerel, 49070 Beaucouzé, France, and AgrEvo GmbH, D-65926 Frankfurt am Main, Germany

An analytical method for the determination of glufosinate ammonium and its principal metabolites, AE F064619 and AE F061517, in water of two different hardnesses (5 and 30 DH, French hardness) has been developed and validated. Samples were spiked at different levels (0.05 and 0.5 μg/L) and were purified by column chromatography on ion-exchange resins. After derivatization with glacial acetic acid and trimethylarthoacetate mixture, the derivatives were quantified by using capillary gas chromatography with an ion-trap tandem mass spectrometric detector. Analytical conditions for MS/MS detection were optimized, and the quantification was carried out on the areas of the most representative ions. The limit of quantification was validated at 0.05 μg/L for each compound. The mean recovery value and the relative standard deviation ($n = 20$) were 92.0% and 17.8% for glufosinate ammonium, 90.2% and 15.8% for AE F064619, and 89.7% and 12.7% for AE F061517.

Keywords: *Glufosinate ammonium; GC/CI/MS/MS; ion-exchange resins; derivatization; water*

1. INTRODUCTION

Glufosinate [DL-homoalanine-4-yl(methyl)phosphonic acid] is a broad-spectrum, nonselective, postemergence herbicide. It is the active ingredient in commercial herbicides (Basta F1, Final way, Final 60, ...) and is widely used in various applications for weed and vegetation control. Its herbicidal effect is to inhibit competitively the enzyme glutamine synthetase (Kataoka et al., 1996).

Glufosinate and its main metabolites, 3-methylphosphonicopropionic acid (AE F061517) and 2-methylphosphonicoacetic acid (AE F064619) are readily soluble in water (for example, 1370 and 794 g/L for glufosinate and AE F061517, respectively) and form strong complexes with Ca^{2+} and Mg^{2+} ions in water. Such complexes could cause problems for the quantitative determination of glufosinate residues.

Due to the chemical properties of glufosinate and its metabolites, classical organic solvents such as ethyl acetate or methylene chloride cannot be used for extraction. For concentration of residues from water samples and for removing cations, cleanup procedures with anion- and cation-exchange resins are necessary. In recent published methods, the determination of these types of molecules, containing phosphorus and carboxylic acid groups, was made by liquid chromatography with precolumn derivatization using 9-fluorenylmethylchloroformate (FMOC−Cl) and ultraviolet detection (Sancho et al., 1996; Hogendorn et al., 1999) or postcolumn derivatization using *o*-phthalaldehyde (OPA) and fluorescence detection (Mallat and Barcello, 1998; Lovdahk and Pietrzyk, 1999). Due to a lack of specificity of the procedure and difficult interpretation of chromatograms, it is very difficult to analyze these molecules in water at the 0.1 μg/L level (Kataoka et al., 1996; Sancho et al., 1996), the maximum allowable concentration in drinking water set by the European Community.

Recently, more sensitive and more selective liquid chromatography, electrospray ionization, and mass spectrometry (Bauer et al., 1999) and liquid chromatography electrospray ionization with tandem mass spectrometry (Vreeken et al., 1998) techniques have been developed. Results obtained by these authors showed the same difficulties of interpretation without derivatization, but good results were obtained with MS/MS detection.

The aim of this work was to develop an analytical method for the quantification of glufosinate ammonium and its metabolites in water of different hardnesses (slightly and highly mineralized) by gas chromatography, chemical ionization, and tandem mass spectrometry (GC/CI/MS/MS) after extraction and purification on ion-exchange resins and derivatization. Of the derivatization methods previously developed involving the use of diazomethane and isopropylchloroformate (Kataoka et al., 1996), heptafluorobutyric anhydride and 2-chloroethanol (Guivivan et al., 1982), *N*-methyl-*N*-(*tert*-butyldimethylsilyl)trifluoroacetamide (Moye and Deyrup, 1984), trifluoroacetic anhydride and trifluoroethanol (Roy and Konar, 1989), or trifluoroacetic anhydride and 2,2,3,3,4,4,4 heptafluoro-1-butanol (Alferness and Iwata, 1994; Deyrup et al., 1985), these experiments were performed with a derivatization method using a mixture of glacial acetic acid and trimethylorthoacetate developed by AgrEvo (*Manual of Pesticides Residues Analysis*, 1992). The chemical structures of the three

* To whom correspondence should be addressed. Phone: 33 241 48 75 70. Fax: 33 241 48 71 40. E-mail: girpa@univ-angers.fr.

† Angers Technopole.

‡ AgrEvo GmbH.

10.1021/jf000281u CCC: $19.00
Published on Web 10/07/2000

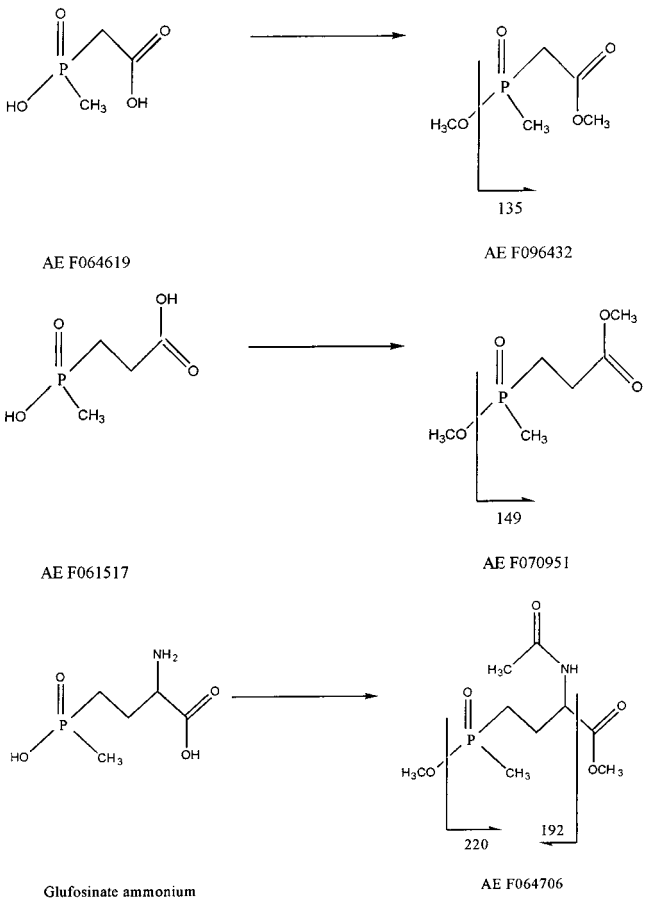

Figure 1. Structures of compounds AE F096432 (MW 166), AE F070951 (MW 180), and AE F064706 (MW 251) and principal fragmentations observed by GC/CI/MS, obtained after derivatization.

analytes and of their respective derivatives are presented in Figure 1. Glufosinate ammonium (GA) was derivatized in AE F064706 (GA-D), AE F064619 (I) was derivatized in AE F096432 (I-D), and AE F061517 (II) was derivatized in AE F070951 (II-D).

2. EXPERIMENTAL METHOD

Instrumentation. The analyses were carried out on a Varian model 3800 gas chromatograph (Walnut Creek, CA) equipped with a split/splitless injector and a 8200 autosampler. Detection was conducted with a Varian Saturn 2000 ion-trap mass spectrometer equipped with a waveboard and MS/MS software. Separation of the analytes was achieved with a 15 m × 0.25 mm i.d. AT-WAX (Alltech Associates, Inc.) fused-silica capillary column with a 0.5 μm film thickness of bonded 100% poly(ethylene glycol).

Gas Chromatographic Analysis. The optimized column oven temperature program was as follows: from 80 °C (hold 1.0 min) to 190 °C at 50 °C/min, from 190 to 230 °C at 15 °C/min, and from 230 to 280 °C at 30 °C/min (hold 5.0 min). The total run time was 12.53 min. A 2 μL sample, corresponding to a range of 0.020−0.300 ng of glufosinate-free acid-equivalent, was injected in the splitless mode with a split ratio of 25 and a purge-off time of 0.70 min, with an injector temperature program as follows: from 80 °C (hold 0.25 min) to 300 °C at 200 °C/min (hold 2 min). N55 helium was used as the carrier gas, maintained at a constant flow rate of 1 mL/min. The approximate retention times of I-D, II-D, and GA-D were 4.6, 5.3, and 9.6 min.

MS/MS Optimization Method. Due to the detection limits of pesticides in water samples (below ng/L level), all experiments were performed by GC/MS/MS in chemical ionization mode. The compounds investigated contain nitrogen and/or phosphorus atoms, which have high proton affinities. Acetonitrile was used to perform in chemical ionization mode. During the process, liquid was vaporized under a vacuum in the ion trap and was transformed into gas. It was used as a reagent gas, which often provides a strong M + 1 base peak ion (protonated molecule) (Steen et al., 1997; Fernandez-Alba et al., 1998) that could be used for molecular weight determination and trace quantification. In fact, the ionization process, which optimizes high-mass ions with minimized matrix interferences, improves the selectivity and the sensitivity of the results.

The optimization of the analytical conditions for the MS/MS detection of the three analytes was performed with a three-step method (Beguin and Communal, 2000; Beguin-Georget et al., 1999), according to the conditions listed in Tables 1 and 2: (1) determination of the retention time and the main diagnostic ion of each analyte by GC/CI/MS, (2) isolation of the selected ion with a 3 amu window, a zero excitation time and a collision induction dissociation (CID) excitation voltage, and (3) determination of the optimum CID excitation voltage. After several experiments, the resonant excitation mode was selected and the parent ions were placed at a $q_z = 0.3$ stability parameter in the Paul stability diagram (set by the m/z Rf storage level).

A multisegment acquisition method was created by using the Automated Method Development (AMD) software to program the CI/MS/MS process as the analytes elute from the GC column. MS and MS/MS spectra were recorded under automatic gain control (AGC), with a fixed target of 2000 counts, by scanning a mass range from m/z 50 to m/z 650 (Table 1) and a narrow mass range ($(m/z)_{co} + 1 - (m/z)_{pi} + 2$) (Table 2), where $(m/z)_{co}$ was the low-mass cutoff of each target parent ion $(m/z)_{pi}$. The axial modulation voltage, which facilitated ion ejection and improved mass resolution, was optimized at 3.5 V. For full-scan CI and CI/MS/MS analyses, the filament emission current and the multiplier voltage were raised from 10 to 80 μA and from its software-optimized value to 300 V offset, respectively. The temperatures of the transfer line, the manifold, and the trap were set a 260, 60, and 220 °C.

Reagents and Glassware. Standard samples of glufosinate ammonium of 99.2% purity, AEF061517 of 97.9% purity, AEF064619 of 99.4% purity, AEF064706 of 99.1% purity, AEF070951 of 98.8% purity, and AEF096432 of 97.1% purity were obtained from Agrevo, F-91197 Gif-sur-Yvette, France. Methanol for HPLC, toluene for organic trace analysis, hydrochloride acid (37%), and ammonia solution (32%) were purchased from Merck, F-94736 Nogent sur Marne, France.

Table 1. MS Analysis Conditions

filament emission current	10 μA
AGC target	software optimized value (≅2000 counts)
AGC prescan ionization time	100 μs
mass range	50−650 u
scan rate	1 scan/s
multiplier delay	3.8 min
peak threshold	0
background mass	49

Table 2. MS/MS Analysis Optimization Conditions[a]

filament emission current	80 μA
AGC target	2000 counts
AGC prescan ionization time	200 μs
mass range	$(m/z)_{co} + 1 - (m/z)_{pi} + 2$
scan rate	1 scan/s
multiplier delay	3.8 min
peak threshold	0
background mass	$(m/z)_{co}$ excitation storage level
excitation mode	resonant
isolation window	3 u
excitation time	0 ms (isolation) − 20 ms (MS/MS optimization)

[a] $(m/z)_{co} = m/z$ excitation storage level of each analyte placed at a stability parameter of $q_z = 0.3$. $(m/z)_{pi} = m/z$ of the target parent ion of each analyte.

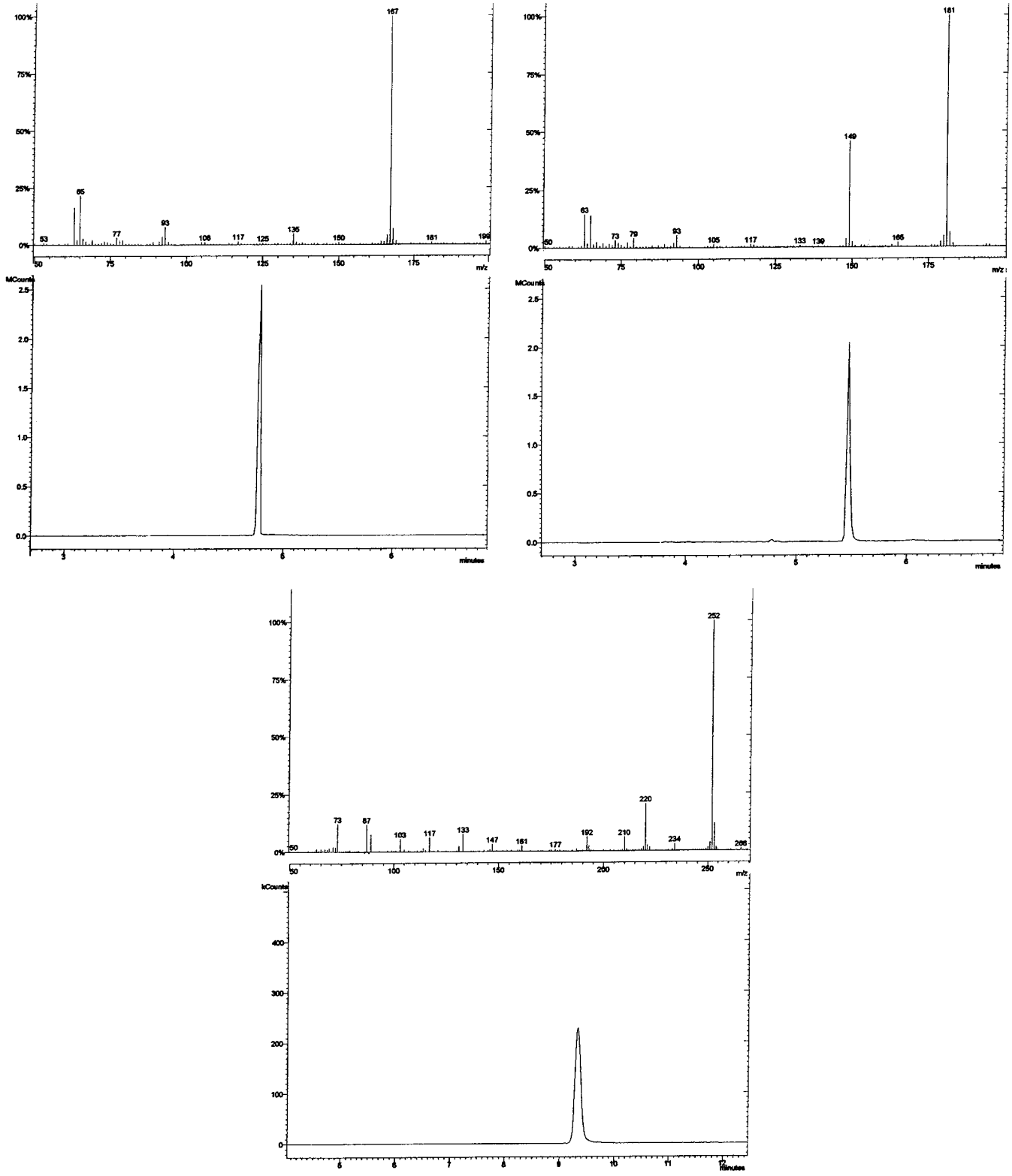

Figure 2. (A, top left) Gas chromatogram and mass spectrum of compound I-D at 10 μg/mL. (B, top right) Gas chromatogram and mass spectrum of compound II-D at 10 μg/mL. (C, bottom) Gas chromatogram and mass spectrum of compound GA-D at 10 μg/mL.

Formic acid (95−97%), trimethylorthoacetate (99%), and AG 1 × 8 anion-exchange resin (50−100 mesh) were bought from Sigma-Aldrich, F-38297 Saint Quentin Fallavier, France. Glacial acetic acid (100%) was obtained from Fischer Scientific. Sodium hydroxide was obtained from Fisons and Duolite C-467 from Prolabo, F-45250 Briare Le Canal, France. Ultrapure water was obtained by using a reverse osmosis system (Seral).

Because of the toxicity of the reagents, the sample preparation and derivatization procedure should be performed in a well-ventilated hood, and the analyst should wear protective gloves.

Spike Standard Solutions. GA (1.094 g/L), I (0.762 g/L), and II (0.839 g/L) stock solutions for spiking were separately prepared by dissolving a known amount of each analyte in 0.015 M ammonia solution to obtain a stock solution of exactly 1 g of glufosinate-free acid-equivalent/L. A 1 mL sample of each stock solution was taken with precision using a volumetric pipet and diluted in a 100 mL volumetric flask using 0.015 M

Table 3. MS/MS Conditions of Each Analyte

compd	parent ion (*m*/*z*)	excitation storage level (*m*/*z*)	resonant excitation voltage	product ion for quantification (*m*/*z*)
I-D	167	55.0	0.25	135
II-D	181	59.6	0.25	149
GA-D	252	83.2	0.30	192 + 220

Table 4. Recoveries of Glufosinate Ammonium and Its Metabolites in Water[a]

spiking level (mg/L)	hardness (DH)		GA	I	II
0.5	5		75	92	98
			82	104	90
			88	91	93
			70	90	95
			73	105	105
		mean	77.6	96.4	96.2
		RSD	8.4	6.9	5.3
	30		92	76	77
			77	101	98
			72	102	107
			82	105	69
			71	111	91
		mean	78.8	99.0	88.4
		RSD	9.7	12.1	15.6
0.05	5		94	77	85
			103	109	77
			108	104	92
			110	92	90
			91	72	85
		mean	101.2	90.8	85.8
		RSD	7.4	16.0	6.1
	30		108	76	77
			106	74	98
			102	68	107
			110	77	69
			125	78	91
		mean	110.2	74.6	88.4
		RSD	7.1	4.8	15.6
overall ($n = 20$)		mean	92.0	90.2	89.7
		RSD	17.8	15.8	12.7

[a] Mean and RSD for each water hardness and each spiking level in percent.

ammonia solution to obtain a stock solution containing both analytes at 10 μg of glufosinate-free acid-equivalent/mL. A working solution of 1 μg/mL was prepared by dilution of the stock solution (10 μg/mL in 0.015 M ammonia solution). Stock and working solutions were stored below −18 °C.

Calibration Solutions. GA-D (1.387 g/L), I-D (0.917 g/L), and II-D (0.994 g/L) stock calibration solutions were separately prepared by dissolving a known amount of each analyte in methanol to obtain a stock solution of exactly 1 g of glufosinate-free acid-equivalent/L. A 1 mL sample of each stock solution was taken with precision using a volumetric pipet and diluted in a 100 mL volumetric flask using toluene to obtain a stock calibration solution containing both analytes at 10 μg of glufosinate-free acid-equivalent/mL. Working calibration solutions of 0.010, 0.020, 0.050, 0.075, 0.100, and 0.150 μg of glufosinate-free acid-equivalent/mL were prepared by dilution of the stock calibration containing both analytes at 10 μg of glufosinate-free acid-equivalent/mL in toluene. Stock and working calibration solutions were stored below −18 °C.

Spike. A 500 ± 0.3 g portion of water was weighed in a 500 mL flask and spiked with the appropriate spike standard solution to obtain spike levels of 0.05 and 0.5 μg/L.

Cleanup. A 10 ± 0.1 mL portion of chelating Duolite C-467 resin was transferred into a glass chromatographic column (2.0 cm diameter, 60 cm long) containing a glass wool plug (about 1 cm). A second glass wool plug (about 1 cm) was placed on the resin layer after the resin had settled. A 12 ± 0.1 mL sample of anion-exchange AG 1 × 8 resin was transferred into a glass chromatographic column (1.0 cm diameter, 100 cm long) containing a glass wool plug (about 1 cm). A second glass wool plug (about 1 cm) was placed on the resin layer after the resin had settled. Both resins were washed with 100 mL of ultrapure water before use. The chromatography tube which was filled with the chelating resin (cation exchange) was installed above the anion-exchange column. The sample was transferred to the cation-exchange column. After the sample had passed through the column, the chelating resin was rinsed with 100 mL of ultrapure water. The flow should be regulated that 1−2 drops/s pass through the resin.

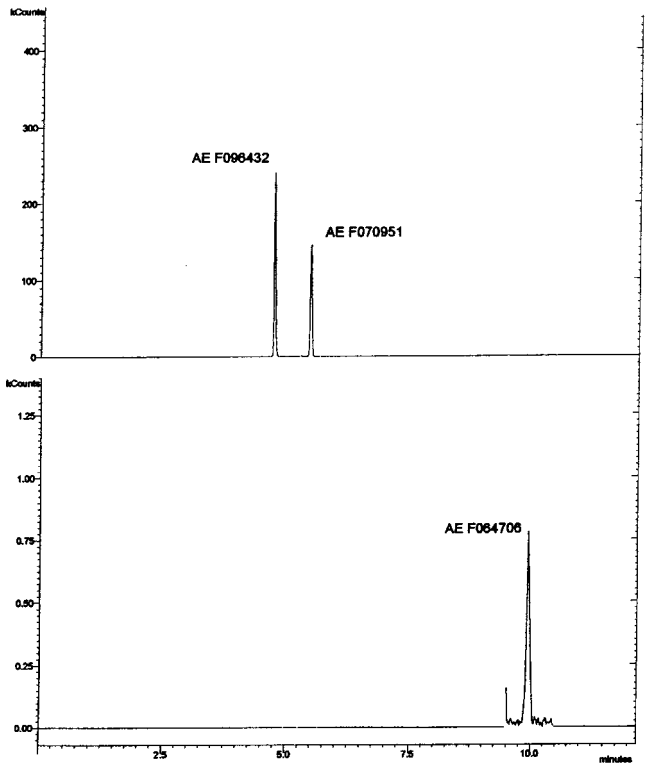

Figure 3. Gas chromatograms of I-D, II-D, and GA-D standards (100 ng/mL each analyte) obtained by chemical ionization. I-D, II-D, and GA-D were monitored using *m*/*z* 135, 149, and 220 + 192, respectively.

The total amount of liquid including the amount of water for rinsing the chelating resin was allowed to run onto the anion-exchange column. The liquid then passed through the anion-exchange column, and the retained substances from the residues were washed with 100 mL of ultrapure water.

The analytes were eluated from the anion-exchange column, using 100 mL of 50% formic acid. The eluant was collected in a 250 mL round-bottom flask and concentrated to dryness until no traces of formic acid were apparent with a rotary evaporator (60 °C maximum). The rotary evaporator was operated at a moderately low speed, which avoids excessive distribution of the sample. This procedure was repeated as necessary. A 5−10 mL portion of methanol was added to the dried sample extract and concentrated as described above. This procedure was repeated once with 5−10 mL methanol.

Derivatization. A 3 mL portion of glacial acetic acid was added to the sample residue in the round-bottom flask. The solution was subjected to ultrasound at ambient temperature for approximately 1 min until all visible sample residues were dissolved or dislodged from the wall of the flask. A 12 mL sample of trimethylorthoacetate and a few pumice stones were added. The solution was then mixed by swirling during ultrasonication. The reaction mixture was refluxed at about 75 °C for 4.5 h. During this reaction, GA, I, and II were derivatized to give compounds GA-D, I-D, and II-D, respectively (Figure 1).

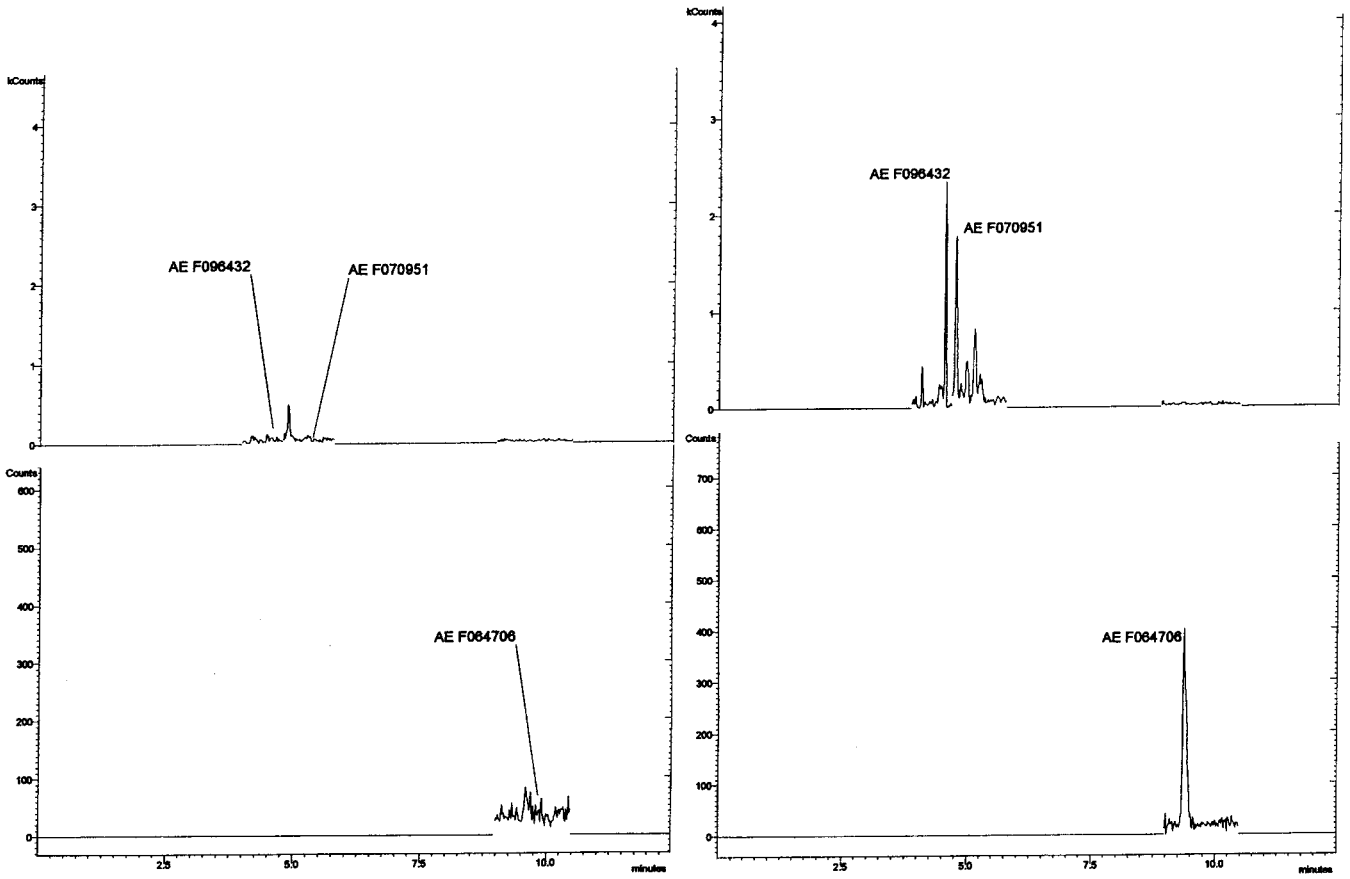

Figure 4. (A, left) Gas chromatogram of untreated water. I-D, II-D, and GA-D were monitored using *m/z* 135, 149, and 220 + 192, respectively. (B, right) Gas chromatogram of water spiked at 0.05 μg/L. I-D, II-D, and GA-D were monitored using *m/z* 135, 149, and 220 + 192, respectively.

The sample was then allowed to cool to room temperature. After derivatization, the flask was removed from the reflux condenser and 15 mL of toluene was added. The sample was evaporated to a final volume of approximately 1−2 mL using a rotary evaporator (bath temperature does not exceed 40 °C). Two portions of 15 mL of toluene were added successively, and the evaporation procedure was repeated. The mixture was evaporated each time to an approximate volume of 0.5−1 mL to remove all traces of the derivatization solution. Finally, the mixture was dissolved in 1 mL of toluene.

3. RESULTS AND DISCUSSION

Full-Scan and MS/MS Optimization of I-D, II-D, and GA-D. The full-scan CI mass spectrum of a standard mixture of the three analytes at 1 mg of glufosinate-free acid equivalent/L (Figure 2) allowed determination of their retention times and verification of their identities by the target and/or the daughter ions. The retention times of I-D, II-D, and GA-D were approximately 4.6, 5.3, and 9.6 min, respectively. The protonated molecule ion was observed as the base peak for glufosinate and the two metabolites, and the CI spectra showed only low fragmentation with respect to the EI process (Fernandez-Alba et al., 1998). For all analytes, the M + 1 peak was selected as the parent ion for CI/MS/MS experiments to increase the sensitivity as a consequence of a lower background and a better signal-to-noise ratio. In electron impact mode, a quantification level of 0.010 mg/L could not be reached. To avoid absorption effects of the analytes in the injection system and the column, the system was conditioned by injections (three times) of a matrix (untreated sample).

The isolation step was performed according to the conditions listed in Tables 2 and 3 to ensure that the target ion was correctly isolated in the ion trap without interference in the isolation window and so that the daughter ions which formed could be detected. Optimization of the MS/MS conditions of the analytes was done using the AMD software. After the evolution of the daughter ions' intensity as a function of the resonant CID excitation voltage was examined, the excitation voltage which produced the most intensive daughter ions and achieved maximum sensitivity was chosen for quantification of the analytes. The highest intensity of daughter ions occurred at an excitation voltage of 0.25 V for I-D and II-D, and 0.30 V for GA-D. A fragmentation mechanism of the target ion of compounds for the determination of the structure of the quantification ions is proposed in Figure 2.

Recovery of Glufosinate Ammonium and Its Metabolites. For quantification of the analytes, the following ions were used: the *m/z* 135 ion for I-D, the *m/z* 149 ion for II-D, and the *m/z* 220 and 192 ions for GA-D. Spiked water samples were quantified using an external standard method. The external standard method was performed using calibration curves for each compound, which were linear in the range of 0.010−0.100 μg/mL, and the square correlation coefficients, r^2, which were 0.9962 (RSD = 0.2%), 0.9959 (RSD = 0.2%), and 0.9946 (RSD = 0.3%) for I-D, II-D, and GA-D, respectively (n = 5).

Two different mineralized waters (5 and 30 DH) were analyzed. These waters were spiked with the mixture of GA, I, and II at two different levels (0.5 and

0.05 μg/L). As shown in Table 4, the recoveries of these compounds in water, expressed in glufosinate-free acid, were in the range of 71−125% for GA, 72−111% for I, and 69−107% for II. The overall recoveries ($n = 20$) were 92.0% (RSD = 17.8%), 90.2% (RSD = 15.8%), and 89.7% (RSD = 12.7%) for GA, I, and II. The detection limit of derivatized compounds, defined as a signal-to-noise ratio better than 5, was 0.010 μg/L for each compound (Figure 3). For each type of water, untreated samples were analyzed and no residues were observed (Figure 4).

4. CONCLUSION

This study shows a new approach for the determination of glufosinate ammonium and its metabolites in water. The cleanup on ion-exchange resins has permitted a high purification of the residues. Analysis by GC/CI/MS/MS after derivatization of compounds has demonstrated a very good selectivity and a high sensitivity. We have demonstrated the utility of MS/MS to obtain specific mass spectra, excluding false positives that could be observed by other methods. This method was validated by spiking levels of 0.05 and 0.5 μg/L in water of 5 and 30 DH, covering the European Community requirement for drinking water. The limit of detection was 0.010 μg/L, and the limit of determination was 0.05 μg/L (Figure 4).

LITERATURE CITED

Alferness, P. L.; Iwata, Y. Determination of glyphosate and (aminomethyl)phosphonic acid in soil, plant and animal matrices, and water by capillary gas chromatography with mass-selective detection. *J. Agric. Food Chem.* **1994**, *42*, 2751−2759.

Bauer, K.-H.; Knepper, T. P.; Maes, A.; Schatz, V.; Voihsel, M. Analysis of polar organic micropolluants in water with ion chromatography-electrospray mass spectrometry. *J. Chromatogr., A* **1999**, *837*, 117−128.

Beguin, S.; Communal, P. Y.; Tabet, J. C. Manuscript in preparation.

Beguin-Georget, S.; Communal, P. Y.; Rosati, D.; Tabet, J. C. 44th ASMS Conference on Mass Spectrometry, Allied Topics, Dallas, 1999.

Deyrup, C. L.; Chang, S.; Weintraub, R. A.; Moye H. A. Simultaneous esterification and acylation of pesticides for analysis by gas chromatography. 1. Derivatization of glyphosate and (aminomethyl)phosphonic with fluorinated alcohols-perfluorinated anhydrides. *J. Agric. Food Chem.* **1985**, *33*, 944−947.

Fernandez-Alba, A. R.; Aguera, A.; Contreras, M.; Penuela, G.; Ferrer, I.; Barcelo, D. Comparison of various sample handling and analytical procedures for the monitoring of pesticides and metabolites in ground waters. *J. Chromatogr., A* **1998**, *823*, 35−47.

Guivivan, R. A.; Thompson, N. P.; Wheeler, W. B. Derivatization and cleanup improvements in determination of residues of glyphosate and aminomethylphosphonic acid in blueberries. *J. Assoc. Off. Anal. Chem.* **1982**, *65* (1), 35−39.

Hogendorn, E. A.; Ossendrijver, F. M.; Dijkman, E.; Baumann, R. A. Rapid determination of glyphosate in cereal samples by means of pre-column derivatisation with 9-fluorenylmethyl chloroformate and coupled-column liquid chromatography with fluorescence detection. *J. Chromatogr., A* **1999**, *833*, 67−73.

Kataoka, H.; Ryu, S.; Sakiyama, N.; Makita, M. Simple and rapid determination of the herbicides glyphosate and glufosinate in river water, soil and carrot samples by gas chromatography with flame detection. *J. Chromatogr., A* **1996**, *726*, 253−258.

Lovdahl, M. J.; Pietrzyk, D. J. Anion-exchange separation and determination of bisphosphonates and related analytes by post-column indirect fluorescence detection. *J. Chromatogr., A* **1999**, *850*, 143−152.

Mallat, E.; Barcelo, D. Analysis and degradation study of glyphosate and of aminomethylphosphonic acid in natural waters by means of polymeric and ion-exchange solid phase extraction columns followed by ion chromatography-post-column derivatization with fluorescence detection. *J. Chromatogr., A* **1998**, *823*, 129−136.

Manual of Pesticides Residues Analysis; Thier, H. P., Kirchhoff, J., Eds.; Deutsche Forschungsgemeinschaft, Pesticides Commission, 1992; Vol. II, pp 217−227.

Moye, H. A.; Deyrup, C. L. A single-step derivatization method for the gas chromatographic analysis of the herbicide glyphosate and its metabolite. *J. Agric. Food Chem.* **1984**, *32*, 192−195.

Roy, D. N.; Konar, S. K. Development of an analytical method for the determination of glyphosate and (aminomethyl)-phosphonic acid residues in soil by nitrogen-selective gas chromatography. *J. Agric. Food Chem.* **1989**, *37*, 441−443.

Sancho, J. V.; Hernandez, F.; Lopez, F. J.; Hogendoorn, E. A.; Dijkman, E.; Van Zoonen, P. Rapid determination of glufosinate, glyphosate and aminomethylphosphonic acid in environmental water samples using precolumn fluorogenic labeling and coupled-column liquid chromatography. *J. Chromatogr., A* **1996**, *737*, 75−83.

Steen, R. J. C. A.; Freriks, I. L.; Cofino, W. P.; Brinkman, U. A. Th. Large-volume injection in gas chromatography-ion trap tandem mass spectrometry for the determination of pesticides in the marine environment at the low ng/L level. *Anal. Chim. Acta* **1997**, *353* 153−163.

Vreeken, R. J.; Speksnijder, P.; Bobeldijk-Pastorova, I.; Noij, Th. H. M. Selective analysis of the herbicides glyphosate and aminomethylphosphonic acid in water by on-line solid-phase extraction-high-performance liquid chromatography-electrospray ionization mass spectrometry. *J. Chromatogr., A* **1998**, *794*, 187−199.

Received for review March 1, 2000. Accepted July 28, 2000.

JF000281U