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Journal of Chromatography A, 1050 (2004) 95–101
JOURNAL OF CHROMATOGRAPHY A
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Analysis of phosphorus herbicides by ion-pairing reversed-phase liquid chromatography coupled to inductively coupled plasma mass spectrometry with octapole reaction cell

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Abstract

A reversed phase ion-pairing high performance liquid chromatographic (RPIP-HPLC) method is developed for the separation of two phosphorus herbicides, Glufosinate and Glyphosate as well as Aminomethylphosphonic acid (AMPA), the major metabolite of Glyphosate. Tetrabutylammonium hydroxide is used as the ion-pairing reagent in conjunction with an ammonium acetate/acetic acid buffering system at pH 4.7. An inductively coupled plasma mass spectrometer (ICP-MS) is coupled to the chromatographic system to detect the herbicides at $m/z = {}^{31}$P. Historically, phosphorus has been recognized as one of the elements difficult to analyze in argon plasma. This is due to its relatively high ionization potential (10.5 eV) as well as the inherent presence of the polyatomic interferences $^{14}N^{16}O^{1}H^{+}$ and $^{15}N^{16}O^{+}$ overlapping its only isotope at m/z = 31. An octapole reaction cell is utilized to minimize the isobaric polyatomic interferences and to obtain the highest signal-to-background ratio. Detection limits were found to be in the low ppt range (25–32 ng/l). The developed method is successfully applied to the analysis of water samples collected from the Ohio River and spiked with a standard compounds at a level of 20 μg/l.

Keywords: Phosphorus herbicides; Collision cell; Octapole reaction cell

1. Introduction

The superiority of ICP-MS in elemental selectivity, low level detection capability, and high sensitivity makes it an instrument of choice for elemental speciation studies. The interest in investigating the specific elemental forms for the diverse elements of the periodic table is ever increasing. Efforts to include elements usually hard to ionize under normal plasma condition and those prone to polyatomic and isobaric interferences have been given special consideration in recent years. Phosphorus is such an element. It is one of the major and active constituents in many environmental and biological samples such as insecticides, nerve agents, and phosphoproteins. Two major aspects discourage P investigation with ICP-MS and these are polyatomic interferences and the relatively high ionization potential for phosphorous. However, with the advent of collision/reaction cells, this situation has changed allowing important additional access to elemental species of nonmetals, including the very important phosphorous species varying from low to high molecular weight.

Glyphosate (*N*-phosphonomethyl glycine) and Glufosinate are used worldwide as nonselective herbicides for the control of long grasses and broadleaf weeds [1]. They interfere with a plant's ability to form amino acids in addition to negatively affecting photosynthesis and respiration. Specifically, Glyphosate inhibits 5-enolpyruvylshikimate-3-phosphate synthase, an enzyme involved in the aromatic amino acid biosynthesis pathway, and this then hinders protein production due to a lack of tyrosine, phenylalanine, and tryptophan [2]. Glufosinate inhibits glutamine synthetase, an enzyme responsible for catalyzing the reaction between ammonia and glutamate to form glutamine [3]. Aminomethylphosphonic acid (AMPA) is the major metabolite of Glyphosate [4] and as such, is usually included in analytical methodologies, since an absence of Glyphosate may be due to its conversion to AMPA. Chemical structures of

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doi:10.1016/j.chroma.2004.04.083

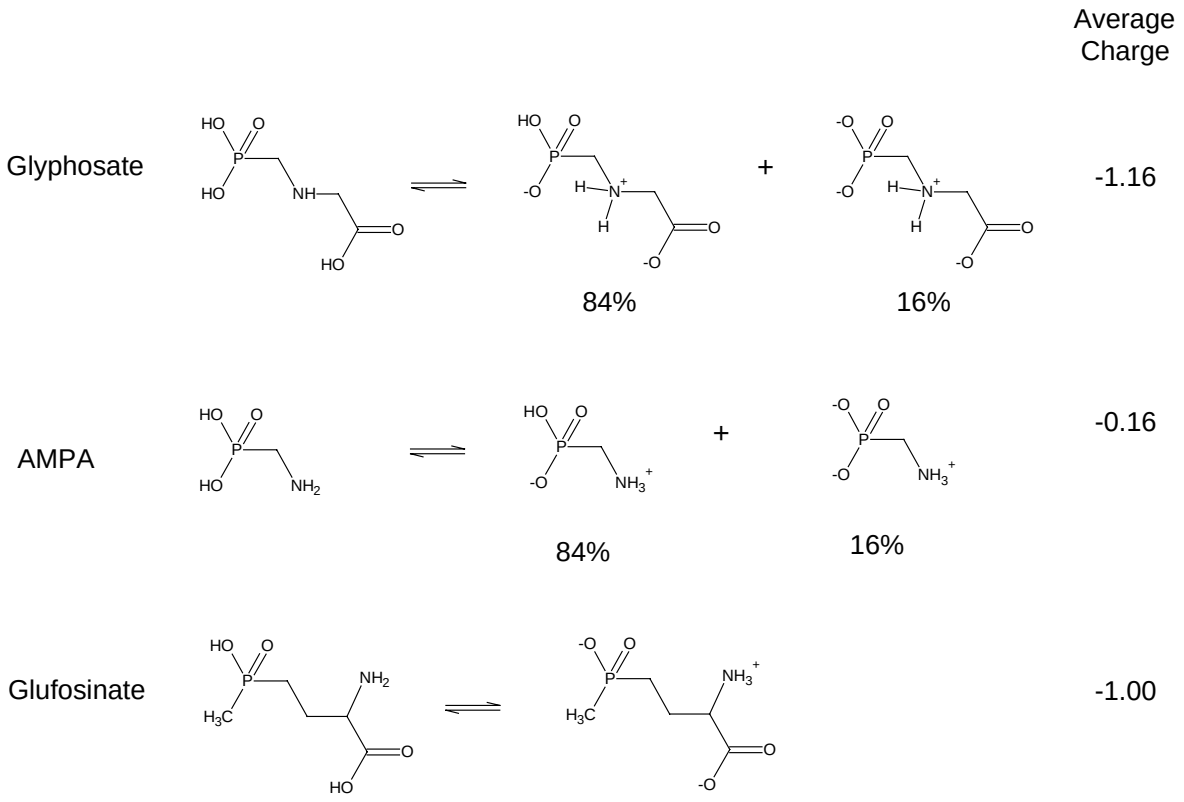

Fig. 1. Chemical structures and species distribution of Glyphosate, Glufosinate, and AMPA at pH 4.7.

these phosphorus-containing herbicides are given in Fig. 1. After the death of the plants, the herbicides may be absorbed by the soil and may enter the aquatic environment due to their high water solubility. Although these herbicides are of comparatively low toxicity to humans and animals, their overall environmental fate has not been fully evaluated and is taking on a special significance because of their extensive worldwide use [5].

Several studies report chromatographic separation of the phosphorus herbicides prior to detection. Additionally, many detection schemes have been employed in monitoring these compounds. However, their chemical properties hinder straightforward analytical schemes. They have a rather high solubility in water and are mostly insoluble in organic solvents. In order to separate these compounds by gas chromatography, derivatization must first be performed to increase volatility. Much work has been done in the investigation of an optimal method [6–8]. Kudzin et al. [9] compiled a comparison of the numerous derivatization methods employed to date in the analysis of these compounds. The use of liquid chromatography to accomplish this separation also entails prior derivatization of the analytes if conventional detection is to be used, as the compounds of interest do not possess a chromophore or a fluorophore [10–13]. Some have investigated indirect detection with HPLC [14]. Others have explored the use of mass spectrometry as a means of detection, however, in order to obtain satisfactory separations, the use of saline eluents or buffer solutions is necessary [15]. This is problematic in LC–MS coupling, since such mobile phases cause high backgrounds. Bauer et al. [16] circumvented this problem with the inclusion of a suppressor between the LC and MS. Some have investigated ion-exchange chromatography to obtain better HPLC separations [12,13]. However, work by Zhu et al. with anion-exchange chromatography showed the necessity of a mobile phase of high pH [17] so that common anions would elute early and not interfere with the later-eluting Glyphosate when utilizing conductivity detection. Others have employed alternate types of chromatography in the pursuit of separation and some researchers have utilized capillary electorphoresis (CE) [18–20]. Although CE offers high resolution and efficiency, a major drawback is its low sensitivity due the limited injection volume. Goodwin et al. [21] explored the use of isotachophoresis for increased sensitivity and reported detection limits in the low μg/l range.

In this work, a chromatographic method is developed for the separation of two phosphorus-containing herbicides in addition to one of the major metabolites. Ion-pairing chromatography is employed to accomplish this and tetrabutylammonium ion is used as the ion-pairing reagent. In addition, an acetate/acetic acid buffer is used. Detection is performed by inductively coupled plasma mass spectrometry. ICP-MS possesses the advantage of excellent selectivity in the presence of other compounds that may otherwise interfere. However, phosphorus detection may be inhibited due to the formation

of polyatomic ions and their overlap with the element of interest [22]. Helium as a collision gas is utilized to reduce such interferents; after collision, the kinetic energy of the polyatomic is preferentially reduced over that of the analyte ion, and thus, it can be removed through applying an energy barrier by adjusting the quadrupole bias of the mass spectrometer [22]. The final developed methodology is applied to spiked river water samples.

2. Experimental

2.1. Reagents and standards

Deionized water (18 MΩ cm) was prepared by passing doubly distilled water through a NanoPure treatment system (Barnstead, Boston, MA) and was used in all standards and buffer preparation. Commercial chemicals were of analytical reagent grade and were used without further purification. Aminomethylphosphonic acid (AMPA), *N*-(phosphonomethyl)glycine (Glyphosate), Glufosinate, ammonium acetate and tetrabutylammonium hydroxide were purchased from Sigma.

H_2 and He, both with a purity of 99.999%, as well as oxygen and neon, were used separately and exclusively as reaction/collision cell gases. The reactant gas flow was set and controlled by the mass flow controller provided with the instrument.

2.2. Instrumentation

2.2.1. HPLC conditions

The Agilent 1100 liquid chromatograph was equipped with the following: a binary HPLC pump, an autosampler, a vacuum degasser system, a thermostated column compartment, and a diode array detector. The HPLC system was connected through a remote cable that allowed the simultaneous start on both instruments of the chromatographic run and observing it by ICP-MS. A C_8 column (Zorbax SB-C8, 4.6 mm × 150 mm, 5 um, Agilent Technologies) was used for separation. The column temperature was maintained at 30 °C for all experiments. The details of the HPLC separation conditions are given in Table 1.

2.2.2. Inductively coupled plasma mass spectrometry

An Agilent 7500c ICP-MS (Agilent Technologies, Tokyo, Japan) was employed for detection; this instrument is equipped with an octapole ion guide operated in an rf only mode. The instrument operating conditions are shown in Table 1. ^{31}P was monitored as an element specific signal for the phosphorus herbicides. A platinum shield plate and bonnet, also known as Agilent's Shield Torch System, was used. This system is comprised of a grounded metal plate, which lies between the plasma rf load coil and the torch and has the effect of removing the capacitive coupling between them, as well as lowering the ion energy spread from the plasma so that energy discrimination may be used to reduce/eliminate polyatomic interferences.

Table 1
Instrumental operating conditions

ICP-MS parameters	
Forward power (W)	1500
Plasma gas flow rate (l/min)	15.0
Carrier gas flow rate (l/min)	1.11
Sampling depth (mm)	6
Sampling and skimmer cones	Nickel
Dwell time (s per isotope)	0.1
Isotopes monitored	^{31}P
Nebulizer	Meinhard
Spray chamber	Scott double-pass
Cell gas	He
Flow rate of cell gas (ml/min)	1.5
HPLC parameters	
Column	Zorbax SB-C8, 4.6 mm × 150 mm, 5 μm
Mobile phase	50 mM ammonium acetate/acetic acid buffer, 5 mM tetrabutylammonium as ion-pairing reagent, 1% methanol, pH 4.7
Flow rate (ml/min)	1.0
Temperature (°C)	30
Injection volume (μl)	100

2.3. Sample preparation

Water samples were collected in polypropylene bottles from the Ohio River in the downtown Cincinnati area. They were filtered with 0.45 μm pore sized polyvinylidene difluoride filters (Millipore). A 250 ml water sample was spiked with Glyphosate, AMPA, and Glufosinate to obtain a final concentration of 20 μg/l. It was extracted with 100 ml of dichloromethane to remove organic impurities. The aqueous phase was concentrated to 10 ml with rotary evaporation at 40 °C.

3. Results and discussion

Due to the potentially charged nature of the analytes of interest, ion-pairing chromatography was explored as an alternative in their chromatographic separation. The acid dissociation constants for Glyphosate are pK_{a1} 0.8 (first phosphonic), pK_{a2} 2.3 (carboxylate), pK_{a3} 5.6 (second phosphonic), and pK_{a4} 11.0 (amine). The acid dissociation constants for Glufosinate are pK_{a1} 0.8 (phosphonic), pK_{a2} 2.9 (carboxylate), and pK_{a3} 9.8 (amine). For AMPA, the acid dissociation constants are pK_{a1} 1.8 (first phosphonic), pK_{a2} 5.4 (second phosphonic), and pK_{a3} 10 (amine). Initial investigations entailed the use of a buffer system at a pH of approximately 5. As both herbicides act as zwitterions [23], at this pH, Glyphosate should contain a slightly higher average negative charge than Glufosinate. Based on the pK_a values and the pH of the mobile phase (4.7), the charge distributions among the various species of the herbicides are shown in Fig. 1. The combina-

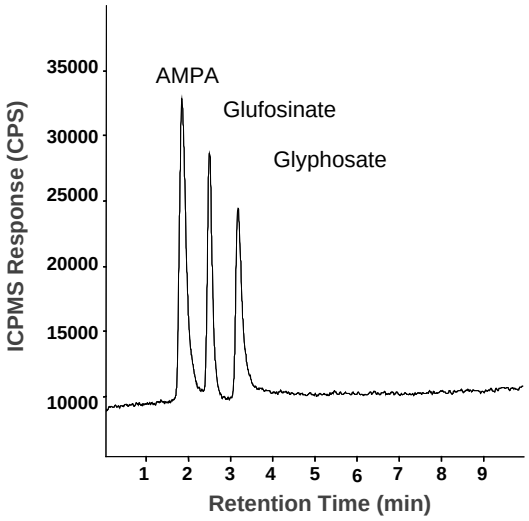

Fig. 2. Chromatogram of standard mixture (500 μg/l) of AMPA, Glufosinate, and Glyphosate.

tion of difference in average charge and hydrophobicity of the different species would serve to accomplish their separation by the proposed chromatography.

The tetraethylammonium ion was first investigated in the capacity of an ion-pairing reagent. However, baseline resolution was not achieved between the ion pairs formed with this compound. Attention was then directed at an agent with a longer alkyl chain and the tetrabutylammonium ion was explored. With the employment of an ammonium acetate/acetic acid buffer (pH 4.7) and 1% methanol for the mobile phase, the separation of both Glyphosate and Glufosinate, in addition to AMPA, was achieved in less than 4 min, as shown in Fig. 2.

3.1. Detection by inductively-coupled plasma mass spectrometry with collision cell

In general, ICP-MS is noted for its sensitivity and selectivity. Selectivity is an attractive attribute in the analysis of environmental samples. However, phosphorus has not been a popular element to monitor with this detector for several reasons. It has a rather high first ionization potential and is subject to interference by nitrogen-based polyatomic interferents. Some researchers have depended on the formation of PO^+ in an argon plasma and have subsequently measured P as $m/z = 47$ [24]. Others use a high-resolution mass spectrometer to distinguish the polyatomics from phosphorus at nominal mass of $m/z = 31$ [25–27], although this degrades the anayte throughput by virtue of achieving the necessary resolution. In this work, the chromatographic scheme entailed the use of a nitrogen-based ion-pairing reagent. A collision cell was investigated to obtain a maximum signal-to-background ratio, hence ensuring the highest sensitivity for phosphorus.

A detailed schematic and description of specific instrumentation is given elsewhere [28]. Collision/reaction cell ICP-MS utilizes a multi-pole ion guide contained in a cell and the cell is pressurized with a gas flow. Ions sampled from the plasma undergo an interaction with the gas prior to mass spectrometric analysis [29]. Conditions are adjusted to remove interferences while allowing the analyte to remain. Subsequently, it is essential to aim for the elimination of the interference while maintaining minimal scattering of the analyte ion. Removal of an interferent can be accomplished by collisional dissociation (collision energy must be higher than bond dissociation energy), chemical reaction or energy discrimination.

Other researchers have explored various cell gases in an effort to obtain maximum sensitivity for phosphorus. Becker et al. used oxygen in the collision cell and subsequently monitored phosphorus as $m/z = 47$ [27]. Profrock et al. used helium to accomplish dissociation of the polyatomic interferents in the collision cell [30]. In this work, hydrogen and neon, in addition to helium and oxygen, were evaluated in terms of their ability to provide the highest signal-to-background ratio for phosphorus.

The background was monitored at $m/z = 31$ with the addition of increasing flow rates of each gas; the cell pressure is represented indirectly by the flow rate. The value of background equivalent concentration (BEC, μg/l) is calculated as the product of concentration of the standard (μg/l) and ratio of the count rate of the background to the background corrected signal of a standard. It is used too as an indication of optimal cell gas flow rate. The standard concentration used in this experiment was 500 μg/l of phosphorus as phosphoric acid prepared in the same buffer used as mobile phase.

Hydrogen is regarded as a reaction gas when introduced into the collision cell and may manifest itself in two ways. First, there exists the potential for an ion–molecule interaction that might result in the addition of a hydrogen atom to an ion, whether interferent or analyte. Secondly, the charge of the interferent may be transferred to a hydrogen ion. However, the addition of H_2 did not serve to enhance the phosphorus signal by reducing the background.

Oxygen is also considered a reaction gas, promoting the formation of oxides and subsequent removal of either analyte or interferent from the primary m/z. With its addition, P^+ forms PO^+ in the plasma [27] and phosphorus subsequently can be monitored at m/z 47 rather than 31 as long as the reaction is reproducible. Throughout the experimental variation of the flow rate, the background counts at m/z 47 remain constant, as shown in Fig. 3. The lowest application of oxygen flow rate (0.5 ml/min) shows the highest response for the PO^+ ion at this m/z. As shown in Fig. 3, at the optimal oxygen flow rate, BEC equaled ∼10 μg/l.

With the addition of non-reactive noble gases, increased signal-to-noise ratios are accomplished by either collisional dissociation or energy discrimination. As shown in Fig. 4, addition of neon to the collision cell showed an equal loss of both analyte and interference. This may be due to the larger collision cross-section of the gas; more frequent collisions reduced the energy of the ions to such an extent that scatter-

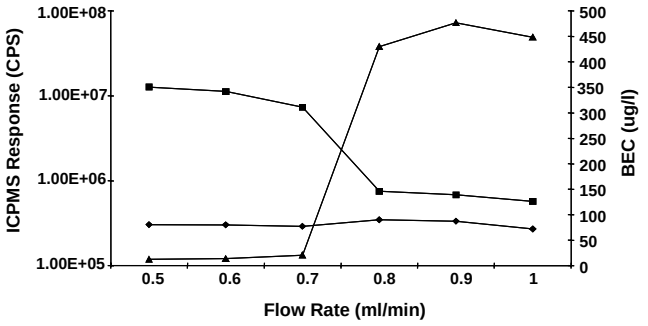

Fig. 3. Plot for reaction/collision cell experiment, oxygen as cell gas: (■) standard; (♦) blank; and (▲) BEC.

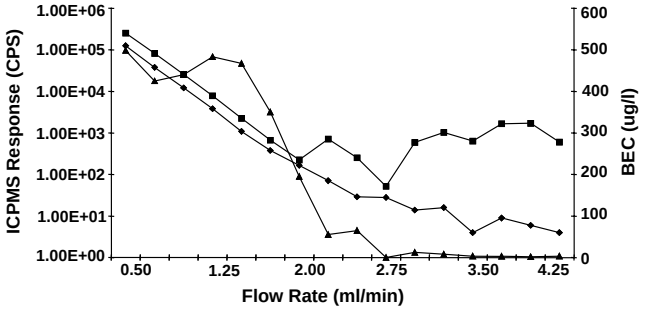

Fig. 4. Plot for reaction/collision cell experiment, neon as cell: (■) standard; (♦) blank; and (▲) BEC.

ing losses of analyte and interferent were equivalently high. However, the addition of a lighter noble gas, helium, resulted in an enhancement in P analyte detection. Again, the flow rate of helium was varied and the background signal plotted against these values. Results for this can be found in Fig. 5. As can be seen, the background is substantially reduced, yet the analyte signal is relatively unaffected with a flow rate of 1.5 ml/min of He. The BEC in case of both oxygen and helium were approximately equal. However, in this work, helium was chosen over oxygen since it may be easily argued that a non-reactive environment within the pressurized cell is preferred.

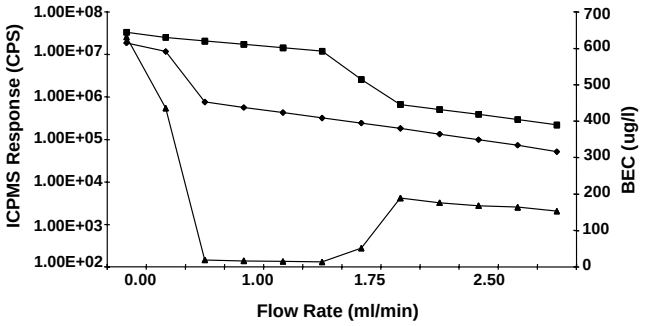

Fig. 5. Plot for reaction/collision cell experiment, helium as cell gas: (■) standard; (♦) blank; and (▲) BEC.

Elimination of the $^{14}N^{16}OH^+$ and the $^{15}N^{16}O^+$ interferents must be accomplished by either collisional dissociation or energy discrimination. In order for fragmentation to be successful in a single collision, the nitrogen–oxygen bond energy must be lower than the collision energy (oxygen–hydrogen bond energy is irrelevant due to the presence of $^{15}N^{16}O^+$) [25]. However, the $N–O^+$ bond energy (7.7 eV) exceeds the collision energy (2.0 eV) under normal cell conditions by a factor of about four. Decrease of background at m/z = 31, therefore, is more likely to be accomplished by energy discrimination. This phenomenon relies on the fact that, for a given analyte and interference of equal mass and kinetic energy, the polyatomic interferent may suffer more collisions due to its larger collision cross-section [31,32]. If all the ions start with equal energy (via the shield torch system), collisions will selectively reduce the energy of the interfering species. By imposing a stopping potential difference between the octapole and the quadrupole (this amounts to changing the quad bias), interferent ions have insufficient energy to enter the quad, but analyte ions retain enough energy and make it into the analyzer [33]. After pressurizing the collision cell, an octapole bias of −10 V and a quadrupole bias of −9 V were set to allow the selective transmission of the analyte ions. Additionally, a platinum shield plate and bonnet were employed, which reduce ion energies to <2 eV with a minimal spread of <0.5 eV [34]. By comparison, a typical balanced load coil ICP produces ions with energies just below 5 eV. Further, this approach does not overly complicate the gas phase chemistry in the cell since no reactive gases are required.

3.2. Forward power

The incident rf power of the plasma is another common parameter that is optimized when utilizing ICP-MS. The results obtained by the application of various forward powers in conjunction with previously described chromatographic parameters show 1500 W as most favorable.

3.3. Analytical figures of merit and real samples

Calibration curves were prepared with standards that ranged from 10 μg/l to 250 μg/l. All regression coefficients (r^2) were acceptable, with the lowest value being 0.998. The detection limits were 25 ng/l, 27 ng/l, and 32 ng/l for AMPA, Glufosinate, and Glyphosate, respectively. Detection limits were calculated based on the three times standard deviation of seven replicates of the blank (IUPAC). The analytical figures of merit are summarized in Table 2. Percent recovery was calculated to evaluate the extraction efficiency for the sample preparation and separation technique. A standard mixture of all the three analytes at a final concentration of 20 μg/l prepared in 250 ml deionized water was subjected to the same sample treatment and preconcentration procedure. The percent recovery ranges between 80% and 89%.

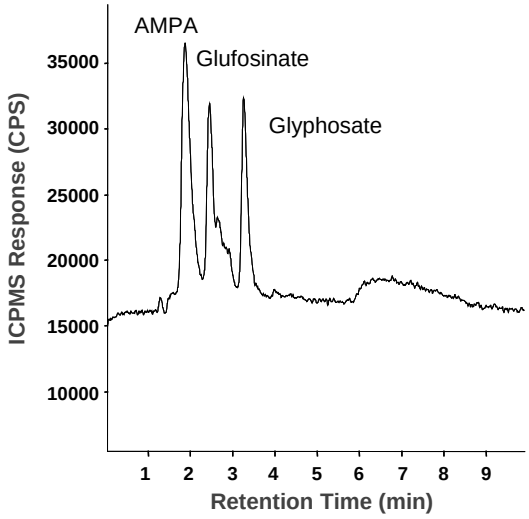

Fig. 6. Chromatogram of AMPA, Glufosinate, and Glyphosate in river water (original sample fortified at 20 μg/l).

To ascertain the potential effect of an actual water matrix, samples were collected from the Ohio River near the downtown Cincinnati area. Samples were treated with the sample preparation procedure described in the Experimental section. Fig. 6 shows a chromatogram obtained from the analysis of river water fortified at a final concentration of 20 μg/l of the herbicides mixture. Although no detectable amounts of any of the herbicides were found in the raw river water sample, the presence of other phosphorus-containing compounds can be viewed as eluting near Glufosinate as well as later in the chromatographic run. No measures were taken to identify these unknown compounds by other mass spectrometric techniques. Also worthy of note is the slightly elevated baseline in the chromatogram of the river water sample (Fig. 6) as compared to that of an analytical standard (Fig. 2) suggesting a background presence of an *m*/*z* 31 species.

4. Conclusions

Coupling of an ion-pairing reversed phase HPLC system to ICP-MS equipped with a collision/reaction cell enabled the separation and detection of several phosphorus-containing herbicides. As hypothesized, the dynamic retention mechanism via ion-pairing reversed phase chromatography offers the best separation (in terms of interaction for the analytes between the stationary and the mobile phase) and subtle charge differentials among the analytes result in a fast separation. Moreover, the mobile phase used for the chromatographic separation is readily compatible with ICP-MS operation. The use of a collision/reaction cell pressurized with helium yielded detection limits in the low ng/l range for all analytes investigated.

Table 2
Analytical figures of merit

	AMPA	Glufosinate	Glyphosate
Regression coefficient (r^2)	0.999	0.998	0.999
LOD (concentration, ng/l)	25	27	32
LOD (amount, pg)	2.5	2.7	3.2
R.S.D. (%) (retentions time, n = 8)	1.1	0.8	1.2
R.S.D. (%) (signal, n = 8)	3.1	2.6	3.4

Acknowledgements

The authors would like to thank Agilent Technologies for their ongoing support of our work. We would also like to acknowledge NIEHS grant #ES04908 for partial funding of this research.

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