

Simultaneous Determination of Glyphosate, AMPA and Inorganic Anions in Water Samples by Gradient Capillary Ion Chromatography

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The herbicide glyphosate is the most widely used pesticide worldwide. Glyphosate and its major metabolite, aminomethylphosphonic acid (AMPA), have been frequently found in water samples. The widely used methods for determining these compounds are expensive and environmentally unfriendly due to reagent consumption for derivatization. Another possibility is the use of classic ion chromatography, albeit with low sensitivity and subject to interferences. Therefore, this study aimed to develop a method to directly and simultaneously determine glyphosate, AMPA, and common inorganic anions in water samples using gradient capillary ion chromatography without sample pre-treatment and derivatization. The proposed method was validated, presenting adequate linearity for glyphosate and AMPA with a determination coefficient (r^2) > 0.998. Recoveries ranged from 94 to 105% and 79 to 113% for glyphosate and AMPA, respectively, with a relative standard deviation < 10%. The practical method limits of detection and quantification for both glyphosate and AMPA were 7.5 and 25 $\mu\text{g L}^{-1}$, respectively. The method presented satisfactory results for the anions fluoride, chloride, bromide, nitrite, nitrate, phosphate, and sulfate, with limits of detection ranging from 7.5 to 200 $\mu\text{g L}^{-1}$. Application of the method in water samples proved simple, efficient, and cost-effective, enabling the monitoring of these analytes in different water matrices.

Keywords: water, polar pesticides, anions, capillary ion chromatography

Introduction

The fast development of the agricultural and forestry sectors has led to the intensive use of pesticides, especially herbicides, on genetically modified resistant crops.^{1,2} Herbicides are the group of pesticides most widely applied worldwide, especially glyphosate, the most used given its efficiency and broad application spectrum against weeds.³ The growing development of the agricultural sector in Brazil and the world has increased the demand to apply this herbicide, with emphasis on grain cultivation and introducing varieties of transgenic crops tolerant to glyphosate, such as soybeans.⁴ Another promising sector gaining prominence is forestry, which has been increasing the areas with planted forests, contributing to the increase in glyphosate application. Brazil is one of the largest pulp producers in the world, with extensive planted forests that

use large amounts of glyphosate. Despite the importance of determining pesticide residues in water samples, few studies with samples from Brazil have been published, and most studies have focused on a limited scope of pesticides.⁵

Aminomethylphosphonic acid (AMPA) is the main degradation product of glyphosate (*N*-(phosphonomethyl) glycine).⁶ There is a high possibility that glyphosate and AMPA reach the soil, water, and food through leaching, surface and groundwater runoff or volatilization.⁷

The presence of glyphosate in surface waters can be detected up to 60 days after application, indicating that it is persistent in the environment. Researchers have detected the presence of glyphosate in surface water more often than in groundwater. Monitoring glyphosate and AMPA in surface water and groundwater is focused on agricultural areas, generally reflecting their use in agriculture.⁸⁻¹² In addition, some studies¹²⁻¹⁶ have even shown that urban areas contribute to glyphosate and AMPA in surface water.

In the European Union (EU), the maximum allowable concentration in drinking water is set at 0.1 $\mu\text{g L}^{-1}$ for each individual pesticide and 0.5 $\mu\text{g L}^{-1}$ for the sum of

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Dedicated to Prof. Carol Collins, whose contribution was decisive for the development of chromatography and analytical chemistry.

Editor handled this article: Andréa R. Chaves (Associate)

pesticides,¹⁷ while the maximum level for the sum of glyphosate and AMPA is 700 $\mu\text{g L}^{-1}$ in the United States¹⁸ and 280 $\mu\text{g L}^{-1}$ in Canada.¹⁹ In Brazil, the Ministry of Health established for drinking water the maximum value allowed for the sum of glyphosate and AMPA at 500 $\mu\text{g L}^{-1}$.²⁰ For groundwater intended for human consumption, CONAMA (Brazil) resolution 396/2008 also establishes a limit of 500 $\mu\text{g L}^{-1}$ for the sum of glyphosate and AMPA, and indicates an acceptable limit of quantification of 30 $\mu\text{g L}^{-1}$.²¹ For surface freshwater, CONAMA (Brazil) resolution 357/2005 determines the quality parameters classes 1, 2 and 3, which are destined for multiple uses. Most Brazilian surface freshwater is class 2 and can be used for supplying human consumption, primary contact recreation, aquaculture and fishing.²² The limit for glyphosate in freshwater in Brazil is 60 $\mu\text{g L}^{-1}$ for class 1/2, and 280 $\mu\text{g L}^{-1}$ for class 3.²³

Glyphosate has a high ionized phosphate group, a secondary amine group and a carboxylate group. AMPA has in its structure an amine and a phosphate group.^{24,25} Both exhibit zwitterionic behavior,^{26,27} high polarity and solubility in water and are insoluble in organic solvents. These properties make very difficult the inclusion of these compounds in multiresidue methods.

Due to lack of chromophores or fluorophores groups in its structure is not possible to detect glyphosate and AMPA directly by spectrophotometry or spectrofluorimetry. Thus, in most cases, a derivatization pre- or post-column is required to optimize the chromatographic behavior and detectability of glyphosate and AMPA by liquid and gas chromatography.^{24,28} Although derivatization makes the methods most sensitive, generally presents lower accuracy and is more expensive and laborious. The most often employed method to determine glyphosate and AMPA in water involves derivatization using 9-fluorenylmethyl chloroformate (FMOC-Cl) before determination.²⁹ In the analysis without derivatization, glyphosate and AMPA are often reported as having low efficiency and poor separation which leads to study new methods according to the zwitterionic nature, polar and hydrophilic properties of these compounds, thereby leading to hydrophilic interaction chromatography (HILIC).^{30,31} Conventional packed column ion chromatography with suppression conductivity is frequently used for the determination of glyphosate and AMPA,^{24,32} although the limits of detection achieved are relatively high and the possibility of use a gradient elution is not available as done with the capillary (packed column) ion chromatography (CIC) used in this work. In comparison with the technique open tubular capillary ion chromatography (OTIC),³³ CIC uses higher injection volume achieving lower limits of detection.

The use of ion chromatography coupled to tandem mass spectrometry (IC-MS/MS) has some advantages, like high sensibility and selectivity; however, the equipment is expensive and not frequently available in routine laboratories. Limitations on direct analysis make it difficult to develop analytical methods with satisfactory limits of detection.³⁰

Michalski and Pecyna-Utylska³⁴ presented a review on the use of ion chromatography (IC) for the analysis of glyphosate and its selected metabolites in environmental, food and other samples from the last 22 years. The authors pointed out that the main advantages and benefits are easy availability, low operational cost, green chemistry aspects and adequate validation parameters. Advancements that greatly accelerated IC development include the introduction of gradient elution and high-performance suppressors, dedicated stationary phases; capillary and multidimensional IC, and IC-based hyphenated techniques. In case of difficulties in the simultaneous determination of glyphosate, AMPA and other anions, the multidimensional IC or the capillary IC can be a useful solution. Considering that multidimensional IC requires more complex and expensive systems, demanding a long analysis time,³² capillary IC, mainly using gradient elution, is a good choice for the determination of organic and inorganic ions.

Determining glyphosate, AMPA, and inorganic anions is crucial for health reasons and of environmental interest. Given the above, this study sought to develop and validate an analytical method that is rapid, simple, reliable, and economically viable to simultaneously determine glyphosate and AMPA residues together with common inorganic anions in water samples by gradient capillary ion chromatography (CIC) with better resolution and sensitivity of the analytes in comparison with the classical ion chromatography.

Experimental

Chemicals and apparatus

Solid standards of glyphosate and AMPA were purchased from LGC Standards (Augsburg, Germany) with a purity of 97.0 and 98.0%, respectively. Purity was considered to prepare individual stock solutions of glyphosate and AMPA at 1000 mg L^{-1} in ultrapure water. From these stock solutions, 10 mL of a mixture containing glyphosate and AMPA at 10 mg L^{-1} in ultrapure water was prepared. This solution was used for analytical curves and for validation. The standard analytical solutions containing the mixture of 20 mg L^{-1} of F^{-} , 100 mg L^{-1} of Cl^{-} , Br^{-} , NO_3^{-} , PO_4^{3-} and SO_4^{2-} , and 200 mg L^{-1} of NO_2^{-} , respectively, was purchased from Dionex (Sunnyvale, USA).

Ultrapure water (resistivity of 18.2 M Ω cm) obtained from a Milli-Q Direct UV3[®] system from Millipore (Bedford, USA) was used for the production of the eluent, to prepare the stock solutions and for dilution of analytical solutions. Polytetrafluoroethylene (PTFE) syringe filters (13 mm) with porosity of 0.22 μ m from Millipore (Bedford, USA), autosampler polypropylene (PP) vials with 2 mL capacity from Dionex (Sunnyvale, USA), PP conical tubes, with screw caps and capacity of 15 and 50 mL from Sarstedt (Nümbrecht, Germany) were used for sampling and dilution of the analytical solutions and samples.

The determination of the analytes was performed in a CIC system model ICS-4000 from Dionex (Sunnyvale, USA), equipped with autosampler AS-DV, continuously regenerated anion trap column (CR-ATC), carbonate remover device (CRD 200 capillary), eluent generator capillary system for potassium hydroxide (EGC-KOH), conductivity detector (CD) and software for data acquisition Chromeleon[™] 6.8.

Instrumentation conditions

The CIC system used a capillary anion exchange column IonPac[™] AS19 (250 \times 0.4 mm, 7.5 μ m) with guard column IonPac[™] AG19 (50 \times 0.4 mm, 11 μ m), both maintained at 35 $^{\circ}$ C; anion capillary electrolytic suppressor (ACES 300) in the mode recirculation and conductivity detection cell maintained at 35 $^{\circ}$ C.

For separation of glyphosate, AMPA and the 7 inorganic anions, the gradient elution parameters have been optimized using the eluent generator cartridge with KOH concentrations between 10 and 90 mmol L⁻¹ and flow-rate of 10 μ L min⁻¹. The injection volume was 0.4 μ L. Sample and standard solutions were filtered through a PTFE syringe filter (13 mm) with porosity of 0.2 μ m before injection.

Method validation

The validation of the proposed method was performed evaluating the parameters linearity, analytical curve, matrix effect, limits of detection (LOD) and of quantification (LOQ), accuracy, in terms of recovery, and precision, by repeatability and intermediate precision assay. Linearity was assessed by the determination coefficient (r^2) of the analytical curves prepared at 25, 50, 100, 250 and 500 μ g L⁻¹ for glyphosate and AMPA, at 20, 100, 500, 1,000 and 2,000 μ g L⁻¹ for F⁻, and at 100, 200, 500, 1,000 and 2,000 μ g L⁻¹ for Cl⁻, Br⁻, NO₂⁻, NO₃⁻, SO₄²⁻ and PO₄³⁻ in ultrapure, treated and surface water free of glyphosate and AMPA. The matrix effect for glyphosate and AMPA were estimated comparing the slopes of the

analytical curves prepared in ultrapure and in blank matrix water.³⁵ Matrix effect is considered significant for pesticides when above 20%.³⁶ The components of the aqueous matrices that can influence the analysis of these compounds can involve suspended solids, organic matter, as well as humic and fulvic acids generally present in water samples. LOD and LOQ values were established using the signal/noise (S/R) ratio, where LOD and LOQ are defined as the analyte concentration which results in S/N > 3 and > 10, respectively. Accuracy was determined from the recovery results and the intra-day precision was evaluated by the repeatability assay on the same day and same operator at the concentrations of 25, 50, 250 and 500 μ g L⁻¹, with 6 replicates for each level. Recovery and intermediate precision (inter day assay) were evaluated at the concentration of 250 μ g L⁻¹, considering the relative standard deviation (RSD in percentage) of 6 replicates.

Method applicability

Samples of drinking water, groundwater, and river water samples from the Rio Grande do Sul State, Brazil, were collected to apply the method for the determination of glyphosate and AMPA as well the inorganic common anions. Twelve samples of each type were collected in Falcon tubes of polypropylene of 50 mL. After filtration in PTFE syringe filters (0.22 μ m) samples were injected in the CIC system.

Results and Discussion

Establishment of the capillary ion chromatography (CIC) conditions

The *in situ* generation of high purity hydroxide ion as eluent enables a more efficient suppression of the conductivity of the mobile phase than using carbonate or hydrogen carbonate ions, resulting in a more stable base line and higher sensitivity. An initial multi-step elution gradient obtained increasing the concentration of potassium hydroxide, resulted in a good resolution of glyphosate, AMPA and the inorganic anions. Glyphosate eluted after phosphate, well separated from the others analytes, in the linear increasing section of OH⁻ gradient, but separation of the metabolite AMPA from nitrate and sulfate, requires a rapid change in OH⁻ concentration from 25 to 30 mmol L⁻¹, to reduce peak tailing. It was observed an enlargement in the AMPA peak with lower intensity in comparison with glyphosate at the same concentration levels. Similar behavior was observed by Dimitrakopoulos *et al.*²⁴

The chromatographic peaks shown in Figure 1 for AMPA and glyphosate for concentrations ranging from 25 to 500 $\mu\text{g L}^{-1}$ in presence of F^- , Cl^- , Br^- , NO_2^- , NO_3^- , SO_4^{2-} and PO_4^{3-} corroborate the absence of interferences, despite the disparity in signal response of glyphosate and AMPA in comparison to inorganic anions of up to 40 times.

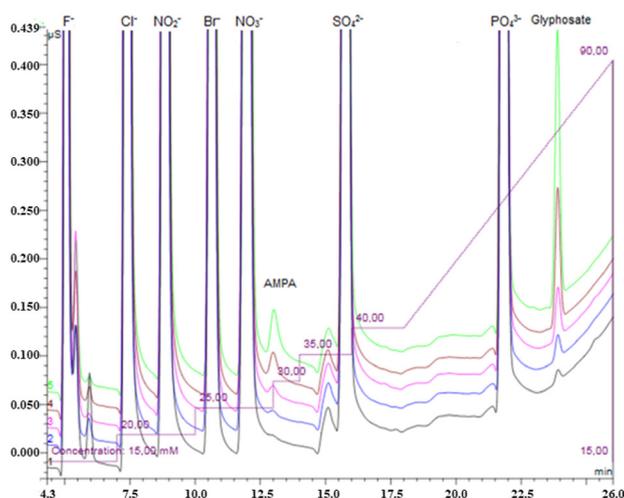


Figure 1. Chromatographic peaks of the compounds AMPA and glyphosate obtained by gradient CIC for the concentrations 25, 50, 100, 250 and 500 $\mu\text{g L}^{-1}$, in the presence of inorganic anions in fixed concentration of 0.5 mg L^{-1} F^- , 2.5 mg L^{-1} Cl^- , Br^- , NO_2^- , NO_3^- and SO_4^{2-} , and 5.0 mg L^{-1} PO_4^{3-} .

Method validation

The selectivity of the method was ensured since the determination by gradient CIC of blank samples did not detect the presence of any background interference at the peak retention times of glyphosate and AMPA (Figure 1). Results presented in Table 1 show that glyphosate and AMPA have linear response in the range of 25 to 500 $\mu\text{g L}^{-1}$ with $r^2 > 0.999$. The inorganic anions showed a linear response from the LOQ to 2000 $\mu\text{g L}^{-1}$, with $r^2 > 0.994$.

The LOD and LOQ values obtained for glyphosate and AMPA were considered satisfactory as meet the maximum allowed value (500 $\mu\text{g L}^{-1}$) in Brazil for drinking water and for groundwater intended for human consumption, as well the limit for freshwater of class1/2 (60 $\mu\text{g L}^{-1}$), and for class 3 (280 $\mu\text{g L}^{-1}$). The levels also meet the acceptable limit of quantification of 30 $\mu\text{g L}^{-1}$ recommended for groundwater by CONAMA (Brazil).²¹ LOD and LOQ values achieved also meet the limit of 700 and 280 $\mu\text{g L}^{-1}$ established for drinking water by the United States and Canada, respectively.^{18,19} The achieved limits are below the limits obtained by classical ion chromatography³⁷ or by anion-exchange chromatography with coulometric detection.³⁸ Determinations using high performance liquid

chromatography with fluorescence detection can achieve lower limits of detection although requires a derivatization step. The analysis by liquid chromatography with tandem mass spectrometry can be done by direct injection or after a derivatization step²⁹ achieving lower limits of detection, but demand expensive instrumentation.

Table 1. Linear range, analytical curves equations, r^2 , LOD and LOQ for glyphosate and AMPA, as well for the inorganic anions

Analyte	Analytical curve	r^2	LOD / ($\mu\text{g L}^{-1}$)	LOQ / ($\mu\text{g L}^{-1}$)
Linear range: 25-500 $\mu\text{g L}^{-1}$				
Glyphosate	$y = 0.00012x - 0.0004$	0.999	7.5	25
AMPA	$y = 0.00004x - 0.0009$	0.999	7.5	25
Linear range: 20-2,000 $\mu\text{g L}^{-1}$				
F^-	$y = 0.0005x - 0.008$	0.999	6.1	20
Linear range: 100-2,000 $\mu\text{g L}^{-1}$				
Cl^-	$y = 0.0016x - 0.0199$	0.998	30	100
Br^-	$y = 0.0006x - 0.0137$	0.998	30	100
NO_2^-	$y = 0.0011x - 0.0179$	0.999	30	100
NO_3^-	$y = 0.0010x - 0.0141$	0.998	30	100
SO_4^{2-}	$y = 0.0014x - 0.0631$	0.994	30	100
PO_4^{3-}	$y = 0.0014x - 0.0495$	0.998	60	200

AMPA: aminomethylphosphonic acid; r^2 : determination coefficient; LOD: limit of detection; LOQ: limit of quantification.

Results for recovery and precision presented in Table 2, obtained by gradient CIC from blank samples spiked with glyphosate and AMPA. As the analysis is performed by direct injection of the sample, the LOD and LOQ of the instrument are the same as the limits of the method. The use of CIC allows reaching adequate LOD and LOQ for the evaluated analytes.

Table 2. Recovery and precision (RSD) results at different spike levels of glyphosate and AMPA analyzed by CIC in the presence of inorganic anions

Compound	Spike levels / ($\mu\text{g L}^{-1}$)				
	25	50	250	500	250
	Rec \pm RSD, repeatability / %				Rec \pm RSD, ip / %
Glyphosate	96 \pm 6	94 \pm 6	105 \pm 2	103 \pm 1	89 \pm 8
AMPA	113 \pm 4	79 \pm 5	101 \pm 1	93 \pm 6	74 \pm 7

AMPA: aminomethylphosphonic acid; Rec: recovery; RSD: relative standard deviation; ip: intermediate precision.

In the accuracy assay, the method provides satisfactory recoveries in the range of 94 to 105% and from 79 to 113% for glyphosate and AMPA, respectively, accordingly the range from 70 to 120% stated by the SANTE guideline.³⁹ The RSD values for glyphosate and AMPA in intra-day

repeatability conditions were both < 6%, indicating good precision. Inter-day intermediate precisions for glyphosate and AMPA, as shown in Table 2, were lower than 8% with recoveries values ranging from 74 to 89% which are acceptable.

The results of the matrix effect evaluation for glyphosate and AMPA in surface and treated water in comparison with ultrapure water, shown in Figure 2, were low. As in CIC with conductivity detection there is no ionization step, satisfactory matrix effect results (< 4.1 and < 1.9% for surface and treated water, respectively) were obtained. Therefore, there is no need to use matrix-matched calibration, contrary to what is commonly used in chromatographic techniques coupled to mass spectrometry where the matrix generally affects the ionization efficiency of the analytes.⁴⁰ Thus, the preparation of analytical curves is faster and simpler.

Method application

The proposed method was applied in samples of drinking water, groundwater, and river water samples from the Rio Grande do Sul State, Brazil (Table 3). In most of the treated drinking water samples glyphosate and AMPA concentrations were below the LOQ. Groundwater samples presented similar concentration levels as drinking water. These values are above the limit established by the Brazilian legislation and others agencies such as US EPA and European Union.¹⁸ Despite the fact that the main activity in central region of Rio Grande do Sul (Brazil) is the agriculture, in two water samples collected out of cultivation time, from the rivers Jacuí and Vacacaí Mirim, glyphosate and AMPA were not detected. From the same places, samples collected during summer time presented residues higher than the method LOQ for both compounds.

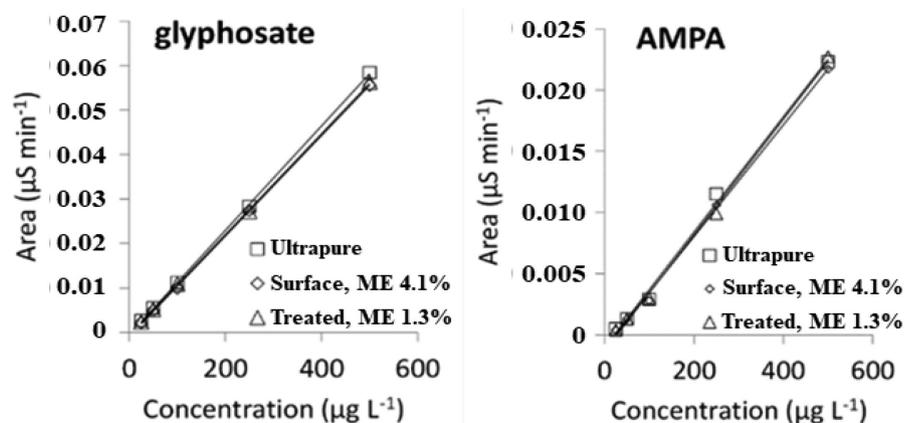


Figure 2. Results of the evaluation of the matrix effect (ME in percentage) for spiked samples of ultrapure, surface and treated water.

Table 3. Results from method application to 34 water samples of different types

Sample type	Total samples	nd	< LOQ	> LOQ	Range / ($\mu\text{g L}^{-1}$)
Glyphosate					
Drinking water	10	3	4	3	29-57
Groundwater	12	2	5	5	27-79
River water	12	2	1	9	28-371
AMPA					
Drinking water	10	2	5	3	30-77
Groundwater	12	2	7	3	31-43
River water	12	2	3	7	26-234

AMPA: aminomethylphosphonic acid; nd: not detected; LOQ: limit of quantification = $25 \mu\text{g L}^{-1}$.

Conclusions

The gradient CIC proved to be adequate for determining glyphosate and AMPA residues since it allows one to separate compounds by ion exchange with subsequent detection by conductivity, with good sensitivity and selectivity, allowing the principal inorganic anions of interest to be simultaneously determined. The use of a gradient allows an adequate separation and determination of glyphosate, AMPA and common inorganic anions in 26 min.

The results for the parameters evaluated in method validation were satisfactory. When applied in water samples, the method performed well, leading us to conclude that determination by gradient CIC of glyphosate and AMPA residues in water samples simultaneously with inorganic anions is effective, fast, and inexpensive. Given these findings, the proposed method can be applied in routine analysis and presents the advantages of enabling direct injection of the sample without requiring exhaustive extraction and derivatization steps.

Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001 and from CNPq.

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Submitted: April 3, 2023

Published online: July 6, 2023

