Journal of Chromatographic Science, 2023, 00, 1–8
https://doi.org/10.1093/chromsci/bmad045
Article

Validation and Application of UPLC-MS/MS Method to Analysis of Glyphosate and its Metabolites in Water

Pedro de J. Bastidas-Bastidas[1], Rosina Cabrera[2], Ana I. Valenzuela-Quintanar[3], Claudia Olmeda-Rubio[1], Victor M. González-Mendoza[2], Xiomara P. Perea-Domínguez[4], Luis C. González-Márquez[4], Vilma del C. Salvatierra-Stamp[5] and José B. Leyva-Morales[6,7,*]

[1]Centro de Investigación en Alimentación y Desarrollo, A.C. Carretera a Eldorado Km. 5.5 Campo el Diez, Culiacán, C.P. 80110 Sinaloa, México
[2]Conahcyt-Centro de Investigación en Alimentación y Desarrollo, A.C., Unidad Regional Hidalgo, Distrito de Educación, Salud, Ciencia, Tecnología e Innovación de Hidalgo, Blvd. Santa Catarina,San Agustín Tlaxiaca, Hidalgo, C.P. 42163, Mexico
[3]Centro de Investigación en Alimentación y Desarrollo, A.C., Carretera Gustavo Enrique Astiazarán Rosas, No. 46 Colonia La Victoria, Hermosillo, Sonora C.P. 83304, México
[4]Doctorado en Sustentabilidad, Universidad Autónoma de Occidente, Unidad Regional Guasave, Av Universidad S/N, Fraccionamiento Villa Universidad, Guasave, Sinaloa C.P. 81048, México
[5]Facultad de Ciencias Químicas, Universidad de Colima, Carretera Colima-Coquimatlán km 9, Coquimatlán, Colima C.P. 28400, México
[6]Centro de Investigación en Recursos Naturales y Sustentabilidad (CIRENYS), Universidad Bernardo O'Higgins, Avenida Viel 1497, Santiago de C.P. 8370993, Chile
[7]Universidad Politécnica del Mar y la Sierra. Carretera a Potrerillos del Norote km.3, La Cruz, Elota, Sinaloa C.P. 82700, Mexico

*Author to whom correspondence should be addressed. Email: neo1702@gmail.com

A method was developed to determine glyphosate and their metabolites in water. The widespread use of this herbicide in agricultural activities worldwide, despite the reported adverse effects on both the environment and health, is a cause for concern and makes it necessary to monitor its presence through a method that guarantees the determination at trace levels. A direct extraction of the analytes with phosphate buffer was performed with subsequent derivatization with 9-fluorenylmethyl chloroformate. The quantification was determined by Ultra Performance Liquid Chromatography-tandem mass spectrometer. The method was validated through the following parameters: selectivity, detection and quantification limits, linearity, accuracy, precision and uncertainty. The average recoveries ranged between 94.08 and 103.31%. Additionally, detection limits from 0.396 to 0.433 μg/L, and the quantification limit was 5.0 μg/L for all the analytes evaluated. In terms of linearity and precision, the results obtained were in the ranges considered adequate ($R^2 \geq 0.99$ and CV $\leq$ 20%), the estimated expanded uncertainty was 12.95, 11.15 and 13.83% for glyphosate, aminomethylphosphonic acid and glufosinate, respectively. This method was successfully applied for the determination of the target analytes in irrigation water samples, detecting concentrations of aminomethylphosphonic acid over limit detection for some sampling sites.

Introduction

Air, soil or water pollution is an undesirable alteration process that can be derived from anthropogenic activities. Agrochemicals used in the agricultural sector can generate environmental pollution, with water being one of the main components expected to be contaminated (1). Glyphosate is the most widely used agrochemical in extensive farming systems around the world, including Mexico (2, 3). Its behavior and fate in the environment depend on the physicochemical characteristics of the formulation, the properties of the soil and the amount of product applied, being the interaction between glyphosate and the constituents of the soil of top importance in determining its mobility and potentiality contamination of aquifers and surface water bodies (4).

Glyphosate, due to its high solubility in water, it is very frequently found as a contaminant of this vital resource, which confirms that this compound has a great capacity for infiltration and groundwater contamination. As is evident, we are exposed to glyphosate through water and food for human consumption. In addition, its presence in various matrices has been associated with serious health and environmental problems (5–7).

The glyphosate molecule is relatively simple: it consists of the union of the amino acid glycine with a phosphonomethyl group. It is low molecular weight, high polarity that does not have chromophore groups, low volatility, and with low solubility in organic solvents (5).

Due to these peculiar physicochemical characteristics, it is not possible to analyze it using a multi-residue methodology, that is, simultaneously with other pesticides. The most widely used methodologies for its analysis consist of the derivatization of the glyphosate molecule, for example, with the reagent 9-Fluorenylmethyl chloroformate (FMOC-Cl), in order to increase its mass and make it more nonpolar for its subsequent determination by gas or liquid chromatography with conventional detectors and/or mass spectrometry (5, 6).

Some of the methods reported for its determination in water are as follows: Enzyme-Linked Immunosorbent Assay (ELISA) (4, 8–11), high performance liquid chromatography coupled with diode array detector (HPLC-DAD) (12) or fluorescence detector (HPLC-FLD) (13, 14), dispersive liquid–liquid extraction (DLLME) combined with ultraperformance liquid chromatography tandem mass spectrometry (UPLC-MS/MS) (15), a UV–Vis spectrophotometry (16), ion

Received: August 3, 2022. **Revised:** April 10, 2023. **Accepted:** June 5, 2023
© The Author(s) 2023. Published by Oxford University Press. All rights reserved. For Permissions, please email: journals.permissions@oup.com

Downloaded from https://academic.oup.com/chromsci/advance-article/doi/10.1093/chromsci/bmad045/7205211 by guest on 04 July 2023

chromatography with conductivity detection (17) or coupled with tandem mass spectrometry (18).

The difference between the latter and the method developed and validated in the present work performs the direct derivatization, with a minimum extraction process and without evaporation and/or reconcentration step, for the determination at trace levels of glyphosate and its metabolites and at the same time a saving of resources invested in the reagents and supplies normally used in the extraction process as well as a shorter time in the execution of the method.

Therefore, the objective of this study was to validate a fast, sensible, and simple analytical method for the determination of glyphosate, aminomethylphosphonic acid (AMPA) and glufosinate in water that involves derivatization with FMOC-Cl and subsequent quantification by UPLC-MS/MS.

Experimental

Chemicals and reagents

Analytical standard for Glyphosate (purity 98.2%) was supplied by Accustandard Inc. (Connecticut, USA), Glufosinate (purity 98%) and AMPA (purity 99%) were purchased Sigma Aldrich (Toluca, Mexico). The solvents acetonitrile and methanol (MS Grade), acetonitrile, and water (HPLC grade) and dichloromethane (pesticide grade) were provided by Technical Control and Representations, S.A. of C.V. (Nuevo Léon, Mexico). Ammonium formate, sodium dihydrogen phosphate (NaH_2PO_4), sodium tetraborate decahydrate ($Na_2B_4O_7{*}10H_2O$), phosphoric acid, formic acid and 9-fluorenylmethyl chloroformate (FMOC-Cl), all ACS grade, was obtained from Sigma Aldrich (Toluca, Mexico).

Equipment

The equipment used are as follows: Dry bath (JR brand, Model L12), centrifuge (Hettich brand, Model EBA21), Ultra Performance Liquid Chromatograph (Waters Brand, UPLC Acquity model serie H), vortex (Thermo Brand, Model M16715), pomegranate (Mark Sartorius, Model Practum 2102-1S) and analytical balances (Brand Sartorius, Model AX224).

Instrumental details and analytical conditions

Each sample was automatically injected through a Sample-Manager system – FTN Acquity of Waters to an equipment of Ultra Performance Liquid Chromatography (UPLC Acquity serie H) equipped with a column Brand Waters Acquity UPLC BEH C18 1.7 μm, 2.1 mm × 50 mm, in a volume of 5.0 μL. Conditions employed were established by the laboratory during the development of the chromatographic method, with mobile phase A (ammonium formate 5 mM, pH 3.0) and mobile phase B (acetonitrile +0.1% formic acid), with the following gradient (Table I). With a total running time of 8.0 min, the target compounds were then detected by tandem mass spectrometry (MS/MS) using triple quadrupole mass spectrometry (Xevo TQD, Waters, Manchester, UK) with an orthogonal Z-spray-electrospray interface. The mass spectrometer was operated in positive electrospray ionization mode (ESI^+) and data were acquired and evaluated with workstation MassLynx 4.1 (Waters, Manchester, UK) using multiple reaction monitoring (MRM) for at least two transitions, which were used as quantitative and confirmation transition pairs, under the following conditions of tandem mass (Table II) (Figures 1S, 2S and 3S) (19).

Table I. Gradient of the Chromatographic Method UPLC/MS-MS

Gradient	Time (min)	Flow (mL/min)	% A	%B
0	Inicial	0.3	90	10
1	5	0.3	10	90
2	5.1	0.3	90	10
3	8	0.3	90	10

The optimized ionization source parameters were: source temperature, 150°C; ionization voltage, 3.21 kV; desolvation temperature, 400°C; desolvation gas flow, 650 L/h; cone gas flow, 300 L/h; collision gas flow, 0.15 mL/min. Nitrogen was used as desolvation gas and extracted from room air by a nitrogen generator MM32LA Model (Peak Scientific Instrument Limited, Inchinnan, Scotland, UK).

Preparation of stock solutions

Stock solution of glyphosate, AMPA and glufosinate standards were prepared using a 50:50 (v/v) water/acetonitrile mixture acidified 1% with formic acid as solvent separately at a concentration of 1.0 mg/mL, subsequently an intermediate dilution of 10 μg/mL was prepared, the latter was a mixture of the three analytes that was used for the fortification of the control samples (matrix blank) and to prepare the working solutions (5, 10, 25, 50, 250 and 500 μg/L) for a standard curve, which was carried out by derivatizing the standards diluted in 2 mL of the $KH_2PO_4/Na_2B_4O_7$ buffer (0.1 M, pH = 9).

Methods

Analysis materials

As there was no reference material or matrix blank available, water HPLC grade was used as a control material and analyzed by the method submitted for validation both in its original state (blank) and after addition (fortification) of a known mass of the analytes to the test portion. Through these preliminary tests, the probable interferences of the derivatization reagents that may interfere with the determination of the analytes of interest (selectivity) were established.

Analytical sample preparation

The control sample was diluted in a 1:1 (v/v) ratio with the $KH_2PO_4/Na_2B_4O_7$ buffer (0.1 M, pH = 9) and 2 mL were fortified at the concentration levels mentioned above with the analytes to evaluate (glyphosate, AMPA and glufosinate).

Derivatization

2.0 mL of the fortified sample were transferred into a 10 mL glass tube or vial with screw cap. Subsequently, 2 mL of FMOC-Cl reagent in acetonitrile (1 mg/mL) were added. The tube is sealed, shaken vigorously, and incubated at 60°C for 1 h. At the end of the incubation time, it is left to cool, and the reaction was stopped by adding 130 μL of 2% phosphoric acid.

Clean-up procedure

To remove excess FMOC-Cl, a liquid–liquid extraction was performed with 5 mL of dichloromethane and centrifugation at 3500 rpm for 10 min. Finally, 1 mL of the aqueous phase was filtered through a nylon syringe filter (13 mm, 0.22 μm)

Downloaded from https://academic.oup.com/chromsci/advance-article/doi/10.1093/chromsci/bmad045/7205211 by guest on 04 July 2023

Table II. MS Tandem Conditions for the Analytes under the Scope

Analite	Parent m/z	Daughter m/z	Dwell (s)	Cone (V)	Collision (eV)
Glyphosate	392	170	0.032	20	15
		214	0.032	20	10
Glufosinate	404	136	0.032	15	15
		182	0.032	15	10
AMPA	334	111.8	0.032	20	20
		156	0.032	20	15

and 5.0 μL of the final extract was injected into the UPLC-MS/MS chromatographic system.

Quantifications

Pesticide concentrations were calculated by the external standard method (20):

$$Concentration\ (ppb\ or\ ug/L) = \frac{Rm * Cs}{Rs * Eq_v} \quad (1)$$

where

R_m = Response (area) of the sample peak.
C_s = Concentration (ng) of the injected standard.
R_s = Response (area) of the standard peak.
Eq_v = Equivalent volume (mL/μL) of injected sample of sample.

Validation study

Method validation was carried out as per the ICH guideline (21) and following the protocol previously established internally by the working group in the laboratory (22), where parameters selectivity, limit of detection (LOD), limit of quantification (LOQ), linearity, accuracy, precision and uncertainty were evaluated. All experiments were performed in triplicate and the quality criteria described in these documents were used to judge whether the validation was successful or not (21, 22).

Method application to water analysis

The validated methodology was applied to monitor the three analytes in wastewater (treated and untreated), canal and river waters from the Atotonilco de Tula Wastewater Treatment Plant (WTP) and the Irrigation District (ID) 003: Tula, located in Hidalgo, Mexico. The water samples were collected in January 2022, on a single occasion, at eight different sites distributed as follows:

1) Wastewater: before the effluent enters the Atotonilco de Tula WPT (latitude: N″9′23.21″; longitude: W 99°14′2.70″).
2) Treated water: the Atotonilco de Tula WPT effluent outlet (latitude: N 20°11′31.10″; longitude: W 99°14′35.22″).
3) Intermediate point of the Tula River: Canal Progreso, Hidalgo (latitude: N 20°14′19.14″; longitude: W 99°10′48.47″).
4) Point on the Tula River: Mixquiahuala, Hidalgo (latitude: N 20°14′8.49″; longitude: W 99°13′38.54″).
5) End point 1 of the Tula River: Ixmiquilpan, Hidalgo (latitude: N 20°28′46.37″; longitude: W 99°13′25.08″).
6) End point 2 of the Tula River: Ixmiquilpan, Hidalgo (latitude: N 20°28′58.82″; longitude: W 99°12′58.96″).
7) ID 003 Tula: Canal La Lagunilla, Hidalgo (latitude: N 20°22′2.40″: longitude: W 99°2′55.12″).
8) ID 003 Tula: Canal Ejido El Mezquital, Hidalgo (latitude: N 20°21′10.40″: longitude: W 98°55′38.91″).

The about 1-L surface water samples were transferred to amber glass bottles and kept on ice for later transport to the laboratory, where they were kept at −20°C until analysis.

Results

Analytical method validation

Selectivity

In chromatographic determination, the presence of interferents in the sample can be confirmed when injecting a matrix target using mass spectrometry as an analytical tool and applying MRM acquisition allows us to confirm the identity of the analyte with the monitoring of specific ions that are generated by fragmenting the molecule. There were no considerable chromatographic signals or interferences for the injected water blanks; this indicates that the method was specific or selective for the compounds of interest (Figures 1, 2 and 3).

Limits of detection and limits of quantification

The developed method exhibited high sensitivity, which can be clearly guaranteed from the LOD values of 0.433, 0.396 and 0.396 μg/L and LOQ values of 5.0 μg/L for all analytes evaluated (glyphosate, AMPA and glufosinate) (Table III).

Linearity

The developed method exhibited the linearity of the analytes ranging from 5 to 500 μg/L, which was confirmed by linear regression analysis of the data with a plot between the pesticide concentrations versus peak area. The data showed a coefficient of determination for the developed method as >0.99 in all cases (Table III, Supplementary Figures 4S, 5S and 6S).

Accuracy and precision

The method was accurate and precise for all compounds evaluated, with recoveries between 94.08 and 103.31% and Coefficients of Variation (CV) between 5.40 and 6.70%. In all these cases, the acceptance criteria for the recovery percentage (70–130%), and CV (≤20%) were covered (Table III, Supplementary Table IS).

Uncertainty

The uncertainty measure was calculated at a confidence level of 95%, using the following equation:

$$U = k * RSD \quad (2)$$

Downloaded from https://academic.oup.com/chromsci/advance-article/doi/10.1093/chromsci/bmad045/7205211 by guest on 04 July 2023

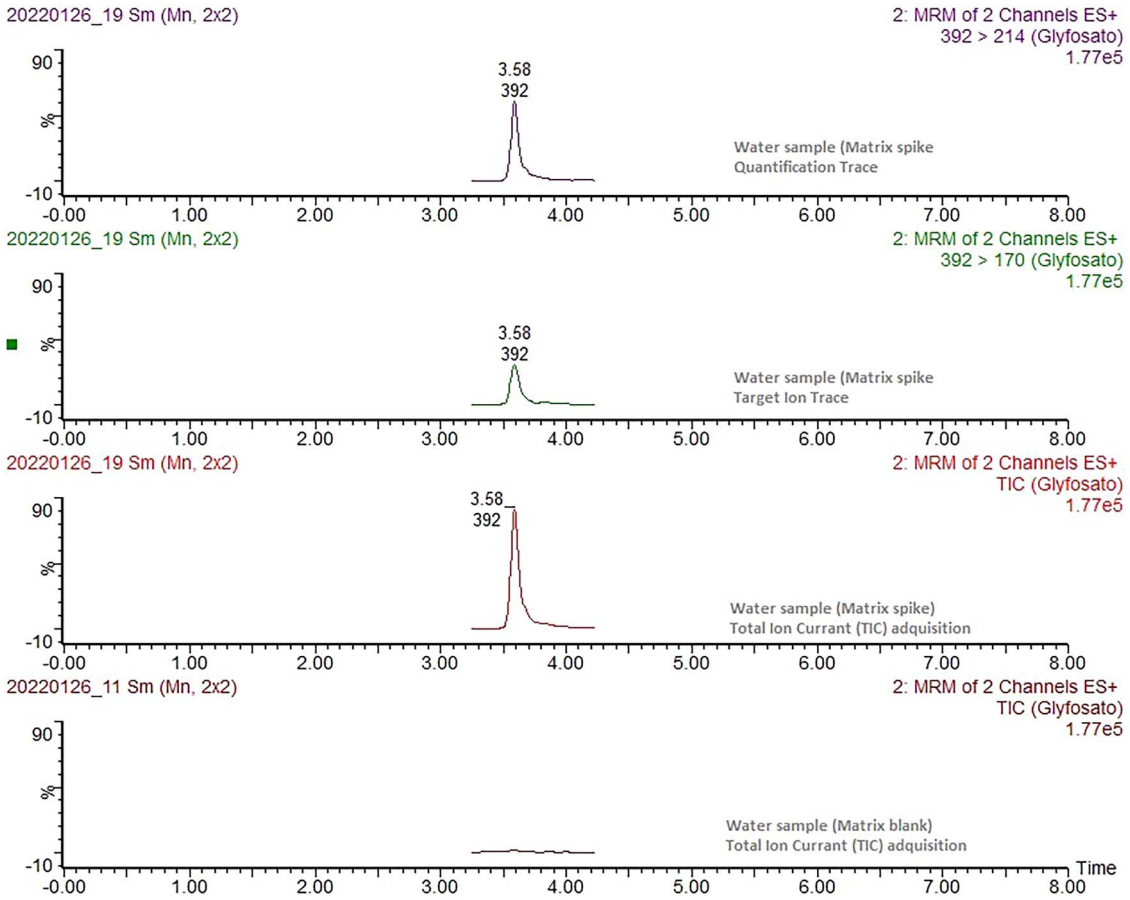

Figure 1. MRM acquisition chromatogram for glyphosate (blank reagents vs fortified samples).

Table III. Limits of Detection (LOD), Limits of Quantification (LOQ), Linearity (Criterion $R^2 \geq 0.99$), Accuracy (Criterion: Recovery Percentage between 70 and 120%), Precision (Criterion Coefficient of Variation (CV) $\leq$ 20%) and Expanded Uncertainty (%) for the Evaluated Pesticides

PESTICIDES	LOD	LOQ	Linearity (R^2)	Equation	Accuracy (average recovery %)	Precision (%CV)	Expanded uncertainty (%)
Glyphosate	0.433	5	0.9994	$y = 1.1269x - 6.2996$	103.31 ± 6.56	6.35	12.95
AMPA	0.396	5	0.9996	$y = 0.9818x - 2.2748$	96.07 ± 5.18	5.4	11.15
Glufosinate	0.396	5	0.9995	$y = 1.0307x - 4.4822$	94.08 ± 6.31	6.7	13.83

where:
U = Expanded uncertainty (expressed as a percentage).
RSD: Relative standard deviation.
k = Coverage factor (for 95% = 2).

The calculated expanded uncertainty was 12.95, 11.15 and 13.83% for glyphosate, AMPA, and glufosinate, respectively (Table III). If we want to calculate the measurement interval of the uncertainty of a real sample, the expanded uncertainty will have to be multiplied by the analyte concentration found (23). For example, if a water sample contains a glyphosate concentration of 1.1 μg/L, the interval will be equal to (12.95/100) $\times$ 1.1 = $\pm$0.14 μg/L and the result will be reported as glyphosate = 1.10 ± 0.14 μg/L.

Method application

The analysis of the water samples showed trace values, that is, below the detection limits, for the three analytes of interest. Only the sites 4 and 5 presented residues of AMPA above the LOD with 0.413 ± 0.04 and 0.472 ± 0.05 μg/L, respectively (Table IV).

Discussion

Our method's LOQ are lower than that reported by Hao et al. (24) who validated a method for direct aqueous determination of glyphosate, AMPA and glufosinate by UPLC-MS/MS establishing LOQs of 10, 20 and 9 μg/L for glyphosate, AMPA and glufosinate, respectively. Giang et al. (25) determined glyphosate, AMPA and glufosinate in drinking water by solid phase extraction (SPE) and reconcentration of the extract with nitrogen and subsequent quantification for UPLC-MS/MS reporting LODs of 2.0, 3.0 and 1.0 μg/L and LOQs of 10.0, 15.0 and 10.0 μg/L for glyphosate, AMPA and glufosinate, respectively. When compared with these direct injection methods that do not involve a derivatization step, the main advantage of the present method is its simplicity and high sensitivity.

Also, the proposed method presented a higher sensitivity when compared to other analytical methods. For example, Dovidauskas et al. (17) performed the validation of a method for the determination of glyphosate and AMPA in

Downloaded from https://academic.oup.com/chromsci/advance-article/doi/10.1093/chromsci/bmad045/7205211 by guest on 04 July 2023

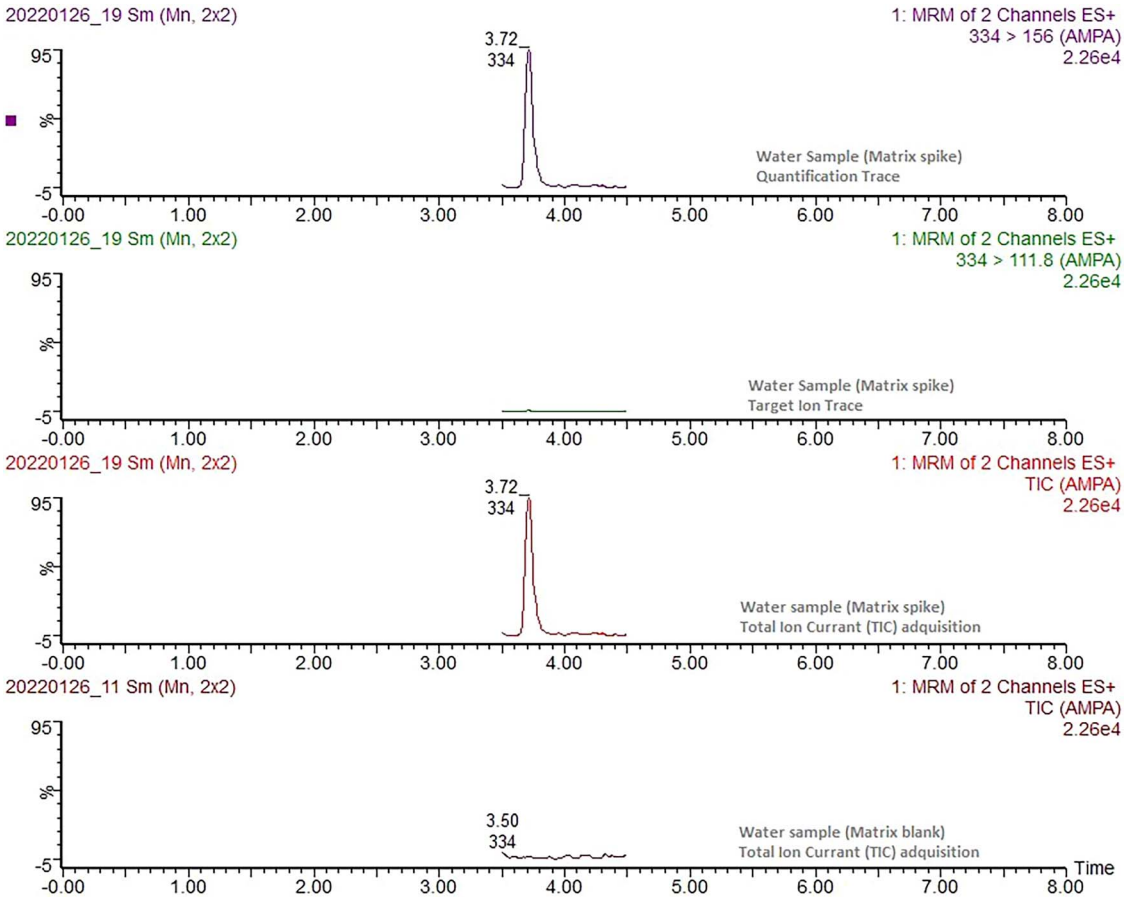

Figure 2. MRM acquisition chromatogram for AMPA (blank reagents vs fortified samples).

Table IV. Concentrations of Pesticides Detected in Water Samples from the Tula, Hidalgo, Mexico

Sample site	Identification	Pesticides	Concentration (μg/L)
Site 1	Entrance to WPT	Glyphosate	Traces < LOD
		AMPA	Traces < LOD
		Glufosinate	Not detected
Site 2	Outlet to WPT	Glyphosate	Traces < LOD
		AMPA	Traces < LOD
		Glufosinate	Not detected
Site 3	Tula River, Canal Progreso	Glyphosate	Traces < LOD
		AMPA	Traces < LOD
		Glufosinate	Not detected
Site 4	Tula River, Canal Mixquiahuala	Glyphosate	Traces < LOD
		AMPA	**0.472**
		Glufosinate	Not detected
Site 5	Tula River, end point 1	Glyphosate	Traces < LOD
		AMPA	**0.413**
		Glufosinate	Not detected
Site 6	Tula River, end point 2	Glyphosate	Traces < LOD
		AMPA	Traces < LOD
		Glufosinate	Not detected
Site 7	ID 003 Tula: Canal La Lagunilla, Hidalgo	Glyphosate	Not detected
		AMPA	Traces < LOD
		Glufosinate	Not detected
Site 8	ID 003 Tula: Canal Ejido El Mezquital, Hidalgo.	Glyphosate	Not detected
		AMPA	Traces < LOD
		Glufosinate	Not detected

water using ion chromatography with conductivity detection, obtained LODs, for glyphosate and AMPA, of 15 and 80 μg/L, respectively, which are well above those established in this work. Rubio et al. (8) established a method by ELISA for glyphosate determinations in water reporting an LOD of 0.6 μg/L, however ELISA tends to overestimate the concentration of glyphosate in water samples due to the presence of matrix interferences (10). Pimenta et al. (12) used the

Downloaded from https://academic.oup.com/chromsci/advance-article/doi/10.1093/chromsci/bmad045/7205211 by guest on 04 July 2023

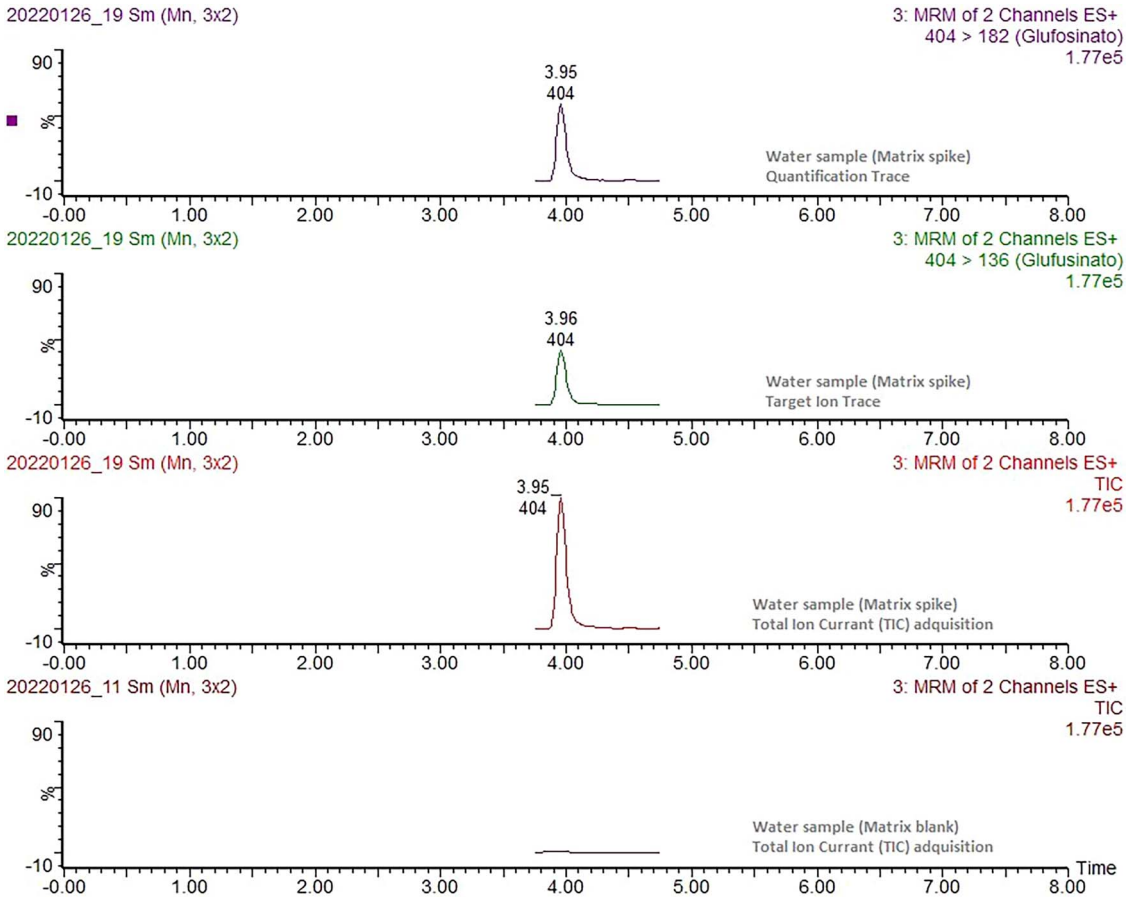

Figure 3. MRM acquisition chromatogram for glufosinate (blank reagents vs fortified samples).

HPLC-DAD method for the determination of glyphosate and AMPA in water with LODs of 8.2 and 300 μg/L, respectively; and Abdullah et al. (26) developed a method for the determination of glyphosate and AMPA that involves SPE in an anion exchange cartridge and subsequent elution with citrate buffer and determination by HPLC-FL reporting LODs of 2.0 μg/L, for both analytes.

On the other hand, some authors have reported LOQs similar to those of the present study. For example, Pinto et al. (15) reported a LOQ of 1.0 μg/L for glyphosate, AMPA and glufosinate in water by in-situ derivatization and dispersive liquid–liquid extraction (DLLME) combined with UPLC-MS/MS.

Although there are methods that have been reported for the determination of the analytes evaluated here with lower LODs than those of the proposed method. These imply a greater effort since to increase sensitivity they subject the sample to lyophilization and reconcentrate the extract using nitrogen (14) or sample acidification with increased derivatization time (27) or with limitation in the maximum detectable concentration (9–11). For example, Vu et al. (28) implemented a method for the determination of glyphosate, AMPA and glufosinate in water without derivatization employing SPE followed by UPLC-MS/MS fixing LOQs of 0.5 μg/L for glyphosate and AMPA, and 1.0 μg/L for glufosinate.

Furthermore, even though in Mexico there are no regulations that establish the maximum limits allowed for glyphosate and its metabolites in water (3), the developed method could be proposed as an alternative for its determination since the LODs and LOQs are lower than those established in the regulations of countries such as United States of America (700 μg/L), Canada (280 μg/L), Australia (1000 μg/L), New Zealand (1000 μg/L), Brazil (500 μg/L) and China (700 μg/L) (29).

Finally, in Mexico, there are few reports of the presence of glyphosate in water. Ruiz-Toledo et al. (9) evaluated the presence of glyphosate in different water bodies (surface and underground) from Chiapas, Mexico reporting a maximum concentration of 36.71 and 1.33 μg/L for the dry and rainy seasons, respectively.

Rendón-Von Osten and Dzul-Caamal (10) analyzed samples of groundwater and bottled drinking water from Campeche, Mexico, to determine glyphosate residues, the maximum concentrations observed were 1.41 and 0.65 μg/L for groundwater and bottled drinking water, respectively.

Reynoso et al. (11) quantified the presence of glyphosate in different water bodies (groundwater, surface and drinking water) from the Tenampulco, Puebla, Mexico the maximum concentrations observed corresponded to 0.81, 4.36, 3.11 and 4.33 μg/L for sampling seasons spring, summer, winter and autumn, respectively.

In all cases, the concentrations observed in the aforementioned studies were higher than those found in the irrigation water of Tula, Hidalgo sampled in the present study (Table IV).

Downloaded from https://academic.oup.com/chromsci/advance-article/doi/10.1093/chromsci/bmad045/7205211 by guest on 04 July 2023

Conclusions

This study presents an analytical method to determinate glyphosate, AMPA and glufosinate in water by derivatization with FMOC-Cl and UPLC-MS/MS quantification. The performance parameters obtained in the validation of the analysis method guarantee that it is suitable for the proposed purpose because the parameters are among the recommended values for an analytical method.

In addition, the method proposed here involves fewer sample processing steps, which reduces the possibility of errors due to loss of analyte or sample contamination. This method is also cheaper, which is an important factor in routine work.

Finally, the method to irrigation water samples showed that it can be a good option for the quantification of the analytes evaluated in this type of samples.

Supplementary data

Supplementary data are available at *Journal of Chromatographic Science* online.

Acknowledgments

The authors thank Juan Pablo Pérez Carrillo, Héctor García López and Jorge Manuel Pineda Landeros for their technical assistance to carry out this research. Mayra de la Torre is acknowledged for providing laboratory facilities, particularly at CIAD-Unidad Regional Hidalgo. Researchers for Mexico Conahcyt Program.

Funding

This work was supported by Conahcyt (grant no. 316145) to Rosina Cabrera.

References

1. Leyva Morales, J.B., Valdez-Torres, J.B., Bastidas-Bastidas, P.J., Angulo-Escalante, M.A., Sarmiento-Sánchez, J.I., Barraza-Lobo, A.L., *et al.*; Monitoring of pesticides residues in northwestern Mexico rivers; *Acta Universitaria*, (2017); **27**: 45–54.
2. García-Hernández, J., Leyva-Morales, J.B., Martínez-Rodríguez, I.E., Hernández-Ochoa, M.I., Aldana-Madrid, M.L., Rojas-García, A.E., *et al.*; Estado actual de la investigación sobre plaguicidas en México; *Revista Internacional de Contaminación Ambiental*, (2018); **34**: 29–60.
3. Alcántara-de la Cruz, R., Cruz-Hipolito, H.E., Domínguez-Valenzuela, J.A., De Prado, R.; Glyphosate ban in Mexico: potential impacts on agriculture and weed management; *Pest Management Science*, (2021); **77**(9): 3820–3831.
4. Paravani, E.V., Sasal, M.C., Sione, S.M., Gabioud, E.A., Oszust, J.D., Wilson, M.G., *et al.*; Determinación de la concentración de glifosato en agua mediante la técnica de inmunoabsorción ligada a enzimas (ELISA); *Revista Internacional de Contaminación Ambiental*, (2016); **32**: 399–406.
5. Huhn, C.; More and enhanced glyphosate analysis is needed; *Analytical and Bioanalytical Chemistry*, (2018); **410**: 3041–3045.
6. Valle, A.L., Mello, F.C.C., Alves-Balvedi, R.P., Rodrigues, L.P., Goulart, L.R.; Glyphosate detection: methods, needs and challenges; *Environmental Chemistry Letters*, (2019); **17**: 291–317.
7. Rivas-García, T., Espinosa-Calderón, A., Hernández-Vázquez, B., Schwentesius-Rindermann, R.; Overview of environmental and health effects related to glyphosate usage; *Sustainability*, (2022); **14**: 6868.
8. Rubio, F., Veldhuis, L.J., Clegg, B.S., Fleeker, J.R., Hall, J.C.; Comparison of a direct ELISA and an HPLC method for glyphosate determinations in water; *Journal of Agricultural and Food Chemistry*, (2003); **51**: 691–696.
9. Ruiz-Toledo, J., Castro, R., Rivero-Pérez, N., Bello-Mendoza, R., Sánchez, D.; Occurrence of glyphosate in water bodies derived from intensive agriculture in a tropical region of southern Mexico; *Bulletin of Environmental Contamination and Toxicology*, (2014); **93**: 289–293.
10. Rendón-von Osten, J., Dzul-Caamal, R.; Glyphosate residues in groundwater, drinking water and urine of subsistence farmers from intensive agriculture localities: a survey in Hopelchén, Campeche, Mexico; *International Journal of Environmental Research and Public Health*, (2017); **14**: 595.
11. Reynoso, E.C., Peña, R.D., Reyes, D., Chavarin-Pineda, Y., Palchetti, I., Torres, E.; Determination of glyphosate in water from a rural locality in México and its implications for the population based on water consumption and use habits; *International Journal of Environmental Research and Public Health*, (2020); **17**: 7102.
12. Pimenta, E.M., Silva, F.F.D., Barbosa, É.S., Cacique, A.P., Cassimiro, D.L., Pinho, G.P.D., *et al.*; Quantification of glyphosate and AMPA by HPLC-ICP-MS/MS and HPLC-DAD: a comparative study; *Journal of the Brazilian Chemical Society*, (2020); **31**: 298–304.
13. Nedelkoska, T.V., Low, G.C.; High-performance liquid chromatographic determination of glyphosate in water and plant material after pre-column derivatisation with 9-fluorenylmethyl chloroformate; *Analytica Chimica Acta*, (2004); **511**: 145–153.
14. Pires, N.L., Passos, C.J.S., Morgado, M.G., Mello, D.C., Infante, C.M.C., Caldas, E.D.; Determination of glyphosate, AMPA and glufosinate by high performance liquid chromatography with fluorescence detection in waters of the Santarém Plateau, Brazilian Amazon; *Journal of Environmental Science and Health, Part B*, (2020); **55**: 794–802.
15. Pinto, E., Soares, A.G., Ferreira, I.M.; Quantitative analysis of glyphosate, glufosinate and AMPA in irrigation water by in situ derivatization–dispersive liquid–liquid microextraction combined with UPLC-MS/MS; *Analytical Methods*, (2018); **10**: 554–561.
16. Catrinck, T.C.P.G., Dias, A., Aguiar, M.C.S., Silvério, F.O., Fidêncio, P.H., Pinho, G.P.; A simple and efficient method for derivatization of glyphosate and AMPA using 9-fluorenylmethyl chloroformate and spectrophotometric analysis; *Journal of the Brazilian Chemical Society*, (2014); **25**: 1194–1199.
17. Dovidauskas, S., Okada Akemi, I., Rodrigues Dos Santos, F.; Validation of a simple ion chromatography method for simultaneous determination of glyphosate, aminomethylphosphonic acid and ions of public health concern in water intended for human consumption; *Journal of Chromatography A*, (2020); **1632**: 461603.
18. Feltracco, M., Barbaro, E., Morabito, E., Zangrando, R., Piazza, R., Barbante, C., *et al.*; Assessing glyphosate in water, marine particulate matter, and sediments in the lagoon of Venice; *Environmental Science and Pollution Research*, (2022); **29**: 16383–16391.
19. Bastidas-Bastidas, P.D.J., Leyva-Morales, J.B., Olmeda-Rubio, C., Pineda-Landeros, J.M., Martínez-Rodríguez, I.E.; Comparison of two methods for multi-residue analysis of organophosphorus pesticides in agricultural products with high and low moisture content; *Revista Bio Ciencias*, (2019); **6 (SPE)**: e654.
20. McMahon, N.F., Hardin, B.M. (eds); *Pesticide Analytical Manual (PAM)*, Vol **1**, 3rd ed. Food and Drug Administration (FDA), Washington, DC, (1998), pp. 504-1–504-2.
21. Guideline, I.H.T.; *Validation of analytical procedures: text and methodology Q2 (R1)*. International Conference on Harmonization, Geneva, Switzerland, (2005).
22. Leyva-Morales, J.B., Valdez-Torres, J.B., Bastidas-Bastidas, P.J., Betancourt-Lozano, M.; Validation and application of a multiresidue method, using accelerated solvent extraction followed by gas chromatography, for pesticides quantification in soil; *Journal of Chromatographic Science*, (2015); **53**: 1623–1630.
23. Instituto Mexicano de Normalización y Certificación. (IMNC); *Norma Mexicana. NMX-CH-140-IMNC-2002: Guía para la expresión de incertidumbre en las mediciones*. Instituto Mexicano

Downloaded from https://academic.oup.com/chromsci/advance-article/doi/10.1093/chromsci/bmad045/7205211 by guest on 04 July 2023

de Normalización y Certificación, Ciudad de México, MX, (2002), pp. 20–35.
24. Hao, C., Morse, D., Morra, F., Zhao, X., Yang, P., Nunn, B.; Direct aqueous determination of glyphosate and related compounds by liquid chromatography/tandem mass spectrometry using reversed-phase and weak anion-exchange mixed-mode column; *Journal of Chromatography A*, (2011); **1218**: 5638–5643.
25. Giang, L.T., Thien, T.L.T., Yen, D.H.; Studying method of underivatized determination glyphosate, glufosinate and their metabolites in drinking water; *Vietnam Journal of Chemistry*, (2020); **58**: 74–79.
26. Abdullah, M.P., Daud, J., Hong, K.S., Yew, C.H.; Improved method for the determination of glyphosate in water; *Journal of Chromatography A*, (1995); **697**: 363–369.
27. Demonte, L.D., Michlig, N., Gaggiotti, M., Adam, C.G., Beldoménico, H.R., Repetti, M.R.; Determination of glyphosate, AMPA and glufosinate in dairy farm water from Argentina using a simplified UHPLC-MS/MS method; *Science of the Total Environment*, (2018); **645**: 34–43.
28. Vu, C.T., Le, P.T., Chu, D.B., Phung, T.L.A., Le, H.Y.N., Labanowski, J., *et al.*; One-step purification/extraction method to access glyphosate, glufosinate, and their metabolites in natural waters; *Journal of Chromatography A*, (2021); **1649**: 462188.
29. Li, Z., Jennings, A.; Worldwide regulations of standard values of pesticides for human health risk control: a review; *International Journal of Environmental Research and Public Health*, (2017); **14**: 826.

Downloaded from https://academic.oup.com/chromsci/advance-article/doi/10.1093/chromsci/bmad045/7205211 by guest on 04 July 2023