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Simultaneous determination of urea herbicides in water and soil samples based on second-order photoinduced fluorescence data†

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This work presents an innovative strategy for the simultaneous determination of four widely employed urea-derivative herbicides, namely isoproturon, linuron, monuron and rimsulfuron, in interfering environments, combining second-order photoinduced fluorescence (PIF) signals, obtained upon UV irradiation in micellar aqueous solutions, and multivariate calibration. The method is simple and fast and complies with the green analytical chemistry principles because it avoids the consumption of high amounts of organic solvents. Successful results were obtained by measuring excitation–emission photoinduced fluorescence matrices processed with unfolded partial least-squares/residual bilinearization (U-PLS/RBL) algorithm. Indeed, this algorithm allowed us to achieve selectivity even in a system which shows a significant spectral overlapping among the formed photoproducts. The quality of the proposed method was evidenced on the basis of the analytical recoveries from water and soil samples spiked with analytes. After solid-phase extraction, reaching a pre-concentration factor of 250, detection limits ranging from 0.006 to 0.026 ng mL^{-1} were obtained in water samples. In soil samples, the detection limits ranged from 1.1 to 3.3 ng g^{-1} without a pre-concentration step. The relative prediction errors were lower than 7% in both cases.

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Introduction

Urea-derivative compounds are widely used as pre-emergent herbicides. They are applied as aqueous emulsions to the soil surface before target plants have emerged.[1] The two major groups of urea-derivative herbicides are phenylureas and sulfonylureas. The former are used as selective and non-selective herbicidal agents to control broadleaf and grassy weeds in cereals and other crops. Isoproturon, linuron and monuron (Fig. 1) are the most commercially important phenylurea weed-killers and represent one of the targets of the present work.[2] Sulfonylureas are a relatively new class of herbicides, applied to control broadleaf weed species, in addition to annual and perennial grasses, and are 100 times more toxic to target plants than older compounds. The sulfonylurea derivative rimsulfuron (Fig. 1) is profusely applied and is also included in our research.[3]

The studied compounds have high water solubility and persistence in soil and natural waters. Their persistence in soil is mostly influenced by the rate of chemical and microbial degradation.[4] Some herbicidal agents and their degradation products have been shown to persist in soil and leach to the surface and ground water after a normal agricultural practice.[5,6] Through the Code of Federal Regulations, the United States Environmental Protection Agency (US EPA) has set a tolerance concentration level in vegetables, grains and agricultural fields of 100.0 ng g^{-1} for pesticide residues.[7] Phenylureas and sulfonylureas have been detected in surface water at relatively higher levels[8] than the maximum permissible concentration proposed by the European Drinking Water Directive (*e.g.* 0.1 ng mL^{-1} for any individual pesticide or 0.5 ng mL^{-1} for the total content).[9] For these reasons, new sensitive methodologies for the determination of urea-derivatives at ultra-trace levels in water samples are welcome.

The most frequent methods for the analysis of herbicide residues in vegetables, soil and water samples are liquid chromatography (LC) coupled to different detection modes such as mass spectrometry,[10–15] diode arrays,[16–18] UV[19–21] and photoinduced fluorescence (PIF).[22,23] These LC methods require rigorous extraction steps, the use of significant amounts of organic solvents and large analysis times, in contrast to the green analytical chemistry (GAC) principles.[24]

Nowadays, there is particular interest in developing eco-friendly strategies for the determination of analytes of environmental concern.[25] Recently, we have developed a GAC method for the determination of emerging pharmaceutical contaminants in environmental water samples.[26] The method

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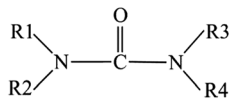


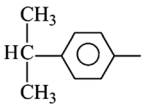
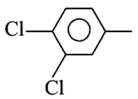
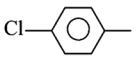
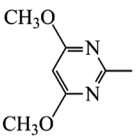
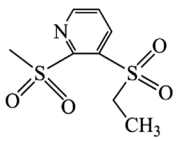
Herbicide	R1	R2	R3	R4
Phenylureas				
Isoproturon	H—		—CH_3	—CH_3
Linuron	H—		—CH_3	—O—CH3
Monuron	H—		—CH_3	—CH_3
Sulfonylureas				
Rimsulfuron	H—		—H	

Fig. 1 Chemical structures of the studied urea herbicides. R1, R2, R3 and R4 indicate the substituent groups.

was based on the detection of a PIF signal after UV irradiation; the lack of selectivity was easily overcome by second-order multivariate calibration.[27] The latter methods allow us to achieve the so-called second-order advantage, a property which is inherent to matrix instrumental data, and implies that analytes can be quantified in samples containing potential interferences.[28] Thus, the second-order advantage makes the use of clean up steps unnecessary for the removal of interfering compounds, avoiding environmentally unsafe organic solvents, and saving experimental time and operator efforts.

In this work, we present a GAC method to quantify urea herbicides in environmental water and soil samples. The fact that the studied compounds display PIF upon UV irradiation in a micellar medium[29,30] has allowed developing a new PIF system using a laboratory-constructed reactor.[31] Second-order data were obtained as excitation–emission PIF matrices (EEPIFMs) and processed by different chemometric algorithms achieving the second-order advantage, namely parallel factor analysis (PARAFAC)[32] and unfolded partial least-squares/residual bilinearization (U-PLS/RBL).[33,34] Notable differences in the prediction capabilities of the employed algorithms were found and discussed.

To the best of our knowledge, this is the first time that a green analytical methodology is evaluated for the determination of urea herbicides employing EEPIFMs and second-order calibration. The developed method represents a new example of the power of coupling non-sophisticated analytical equipment with second-order data for the resolution of complex matrices.

Materials and methods

Instrumentation

A Perkin Elmer LS 55 luminescence spectrometer was used, equipped with a xenon discharge lamp (equivalent to 20 kW for 8 μs duration) and connected to a PC microcomputer. Excitation and emission slit widths were of 8 nm using 1.00 cm quartz cells. The photomultiplier tube sensitivity was fixed at 900 V, the scan rate at 1200 nm min^{-1} and the temperature of the cell compartment was kept constant at 6 °C by circulating water from a thermostated bath (Cole–Parmer, IL, USA). Data were saved in ASCII format and transferred to a PC for subsequent chemometric analysis.

Reagents and solutions

All solutions were prepared from high-purity grade reagents. Isoproturon [3-(4-isopropylphenyl)-1,1-dimethylurea], linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea], monuron [3-(*p*-chlorophenyl)-1,1-dimethylurea], rimsulfuron [1-(4,6-dimethoxy-2-pyrimidinyl)-3-[3-(ethylsulfonyl)-2-pyridylsulfonyl]urea] and hexadecyltrimethylammonium chloride (HTAC) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Methanol was purchased from Merck (Darmstadt, Germany). Water was obtained from a Milli-Q system (Millipore, Bedford, USA).

Stock standard solutions of individual herbicides (in the range of *ca.* 220–250 μg mL^{-1}) were prepared by dissolving an appropriate amount of each compound in methanol and stored in flasks in the dark at 4 °C. Working herbicide solutions of 1.0

and 10.0 μg mL^{-1} were prepared daily by measuring appropriate aliquots of the stock solutions, evaporating the solvent with nitrogen and completing to the mark with ultrapure water.

PIF signal optimization

A three-level central composite design of 15 experiments with five replicates at the central point was applied for investigating the influence of the three variables on the PIF intensity. These variables were the temperature, the irradiation time and the distance between the lamps, in the ranges of 5–25 °C, 5–15 minutes, and 3–9 cm, respectively. The PIF intensity was recorded for each solution using 318 and 410 nm as excitation and emission wavelengths, respectively. The runs were carried out in a randomized sequence to minimize the effect of uncontrolled variables on the response. The obtained response values of the central composite design are shown in Table S1 of the ESI† and the quadratic regression model selected to define the relationship between the response and the variables is:

$$\mathrm{PIF} = b_0 + \sum_{i=1}^{3} b_i x_i + \sum_{i=1}^{3} b_{ii} x_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{3} b_{ij} x_i x_j + e \qquad (1)$$

where PIF is the response, x_i and x_j are the studied factors, b_0, b_i, b_{ii} and b_{ij} are the intercept, linear, quadratic and interaction coefficients, and e is the model error.

Synthetic samples

Preliminary experiments indicated that, under the established working conditions, linearity is held up to 200.0 ng mL^{-1} for all analytes.

A calibration set of 12 samples was built with a semi-factorial design with two levels for each compound, two replicates of the central point and two blank samples only containing HTAC. The concentration ranges were from 30.0 to 200.0 ng mL^{-1} for isoproturon, linuron and monuron, and from 20.0 to 100.0 ng mL^{-1} for rimsulfuron (Table S2 of the ESI†). The corresponding volumes of the aqueous standard solutions of each herbicide were transferred into 2.00 mL volumetric flasks, and 0.020 mol L^{-1} HTAC solution was added to the mark. This solution was placed on a 1.0 cm quartz cell, and irradiated for 11 min in a laboratory-constructed reactor described in a previous study.[31] Finally, solutions were cooled to 6 °C and their EEPIFMs were measured in the ranges of 270–338 nm (each 2 nm, excitation) and 360–480 nm (each 0.5 nm, emission) yielding matrices of size 35 × 241.

A set of 12 validation samples was prepared employing concentrations different from those used for the calibration ones and selected from the corresponding calibration ranges.

Water samples

Herbicides were analyzed in tap water from Santa Rosa city (La Pampa, Argentina) and underground water from Funes city (Santa Fe, Argentina). They were prepared by spiking them with each studied compound at concentration levels of 0.10 and 0.12 ng mL^{-1}, respectively. The samples were sequentially filtered through paper and a 20 μm nylon membrane to remove suspended solids. A solid-phase extraction (SPE) procedure with Empore Octadecyl C18 membranes (Supelco, Bellefonte, PA, USA) was applied to improve the sensitivity of water analysis. Each membrane was previously conditioned with 0.5 mL of methanol and 1 mL of ultrapure water. For concentrations of herbicides at sub-part-per-billion levels, 500.0 mL of sample was forced through the disk under vacuum. Following the extraction, the disk was dried by forcing air through it using a 25 mL syringe. Then, the retained compounds were eluted with 0.5 mL of methanol and the liquid was collected in a 2.00 mL volumetric flask. After evaporation of the solvent with nitrogen, the residue was reconstituted to the mark with 0.020 mol L^{-1} HTAC. Thus, the pre-concentration factor was 250. Finally, the samples were subjected to the same procedure described above, and the herbicide concentrations were estimated using second-order multivariate calibration.

Soil samples

Two soil samples were taken from Santa Rosa city (La Pampa, Argentina) and San Pedro city (Buenos Aires, Argentina), and were collected from the surface (top 20 cm). They were air-dried at room temperature, pulverized and stored at −20 °C until extraction. The inner-filter effect produced by the background matrix was overcome by using the standard addition method. An aliquot of 0.5500 g of soil sample was accurately weighed into a 2 mL Teflon centrifuge tube and was spiked with each studied herbicide at concentration levels of 100.0 ng mL^{-1}. After a few minutes, 1.00 mL of methanol was added. The resultant sample was first mixed in a vortex for 5 seconds, followed by sonication for 15 minutes and subsequent centrifugation at 15.000 rpm for 30 minutes. An aliquot of 700.0 μL of the supernatant extract was transferred into a 2.00 mL volumetric flask, the solvent was evaporated with nitrogen and the residue was reconstituted to the mark with 0.020 mol L^{-1} HTAC. Afterwards, new solutions were prepared starting from the spiked samples in order to carry out three successive additions of mixtures of the four analytes. The compositions of these added mixtures are shown in Table S3 of the ESI.†

Software and chemometric algorithms

The experimental design and optimization were carried out using Design Expert 6.0 (Stat-Ease Inc.). The theory of second-order algorithms is well documented in the literature, and hence a brief description is supplied in the ESI.† All routines of employed chemometric algorithms were written in MATLAB 7.10,[35] and implemented using the graphical interface MVC2,[36] available on the Internet.[37]

Results and discussion

Preliminary studies

Urea herbicides are non-fluorescent in either aqueous or organic media, but emit fluorescence under UV irradiation in micellar media,[29,30] suggesting the formation of photoproducts (Fig. 2A). Studies have shown that photochemical degradation of phenylurea herbicides leads to direct hydrolysis to aniline

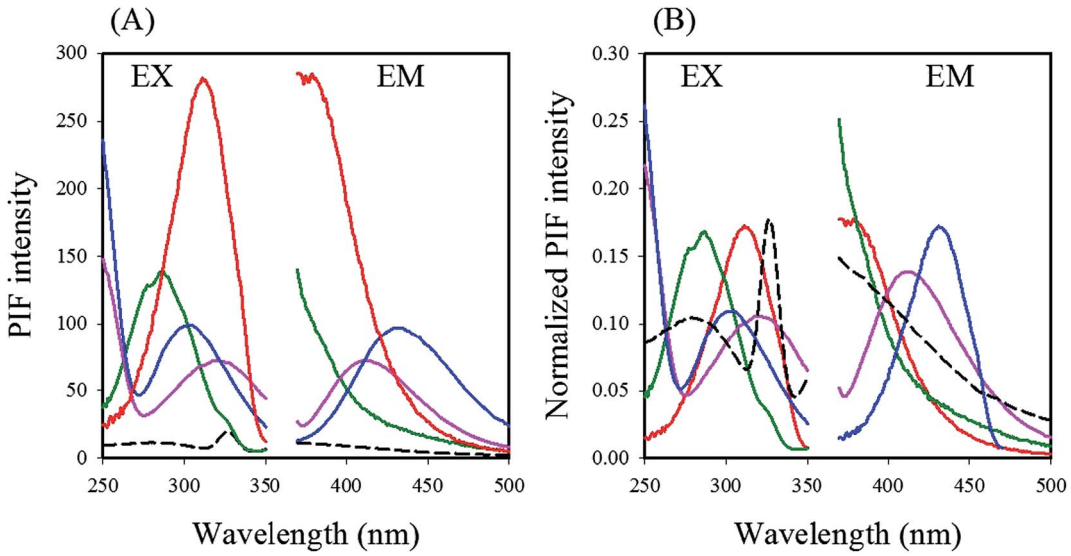


Fig. 2 Raw (A) and normalized (B) excitation and emission photoinduced fluorescence (PIF) spectra for isoproturon (blue), linuron (pink), monuron (green) and rimsulfuron (red). The dashed-black lines indicate the signals from background given by HTAC. $C_{HTAC} = 0.020$ mol L^{-1}; $C_{isoproturon} = C_{linuron} = C_{monuron} = 200.0$ ng mL^{-1}; $C_{rimsulfuron} = 50.0$ ng mL^{-1}.

derivatives, which may be responsible for the fluorescence signal.[4] In the case of sulfonylurea derivatives, an aryl sulfonamide compound should be responsible for the fluorescence emission.[38] Linear relationships between the original analyte concentrations and the obtained PIF signal were corroborated.

As can be seen in Fig. 2A, among the four studied herbicides, linuron shows the lowest fluorescence emission and, consequently, the experimental conditions for the quantitative analysis were adjusted in order to optimize this signal.

PIF signal optimization

It is known that the presence of aqueous micellar media such as those formed by HTAC and sodium dodecyl sulfate (SDS) surfactants significantly enhances the PIF intensity of urea herbicides.[29,38–40] Therefore, in order to increase the method sensitivity, HTAC and SDS at concentrations higher than their critical micellar concentrations (1.3×10^{-3} and 8.1×10^{-3} mol L^{-1}, respectively)[41] were added to the studied solutions. Since the addition of HTAC provided higher PIF signals than SDS with a lower background, the former was selected for subsequent analysis, and its concentration was optimized ranging from 5.0×10^{-3} to 3.0×10^{-2} mol L^{-1}. The optimum HTAC concentration which generated the maximum PIF signal was 0.020 mol L^{-1}.

Because pH changes in the range of 3–10 did not produce any significant modifications in the PIF signal,[40] and the analyzed solutions were approximately neutral, the pH was not adjusted.

It was found that experimental variables such as the distance between the 4 W lamps used for sample irradiation, the irradiation time and the temperature of the fluorescence cell holder have influence on the obtained PIF signal. Table S4 of the ESI† displays the ANOVA results for the selected quadratic model, where it can be appreciated that the variables explain the data and indicate that the variable effect is significant at 95% confidence level. These factors were optimized using a surface response methodology, and the optimum values obtained for the distance between the lamps, the irradiation time and the temperature were 5.6 cm, 11 minutes and 6 °C, respectively. These conditions were used for the quantitative analysis.

Quantitative analysis

Synthetic samples. Fig. 2B shows the normalized spectra for the blank (an HTAC solution) and the photoproducts obtained for the studied herbicides when the solutions were irradiated under the employed working conditions. It is evident that overlapping occurs among both the excitation and emission spectra, which hinders the direct determination of the analytes through zeroth-order calibration. The lack of selectivity becomes more severe in real samples where other matrix constituents are potentially able to produce interference. Therefore, with the objective of overcoming this problem, second-order calibration applying algorithms that achieve the already mentioned second-order advantage was proposed.[27]

Firstly, EEPIFMs under optimal working conditions were recorded for calibration and validation samples (Fig. 3A), where only the four studied herbicides are present. A set of EEPIFMs can be arranged as a three-way array, which in general complies with the trilinearity conditions[42] and, therefore, the algorithm of choice for data processing should be PARAFAC.[43] The PARAFAC algorithm was initialized using: (1) profiles derived from direct trilinear decomposition (DTLD), (2) the best results of a set of a small number of runs, including DTLD results and vectors composed of random numbers, and (3) the known analyte spectra. However, it should be noticed that the latter strategy cannot be applied in the presence of unknown interferences. Additionally, non-negativity restrictions in all three modes were applied during least-squares fit. The selection of

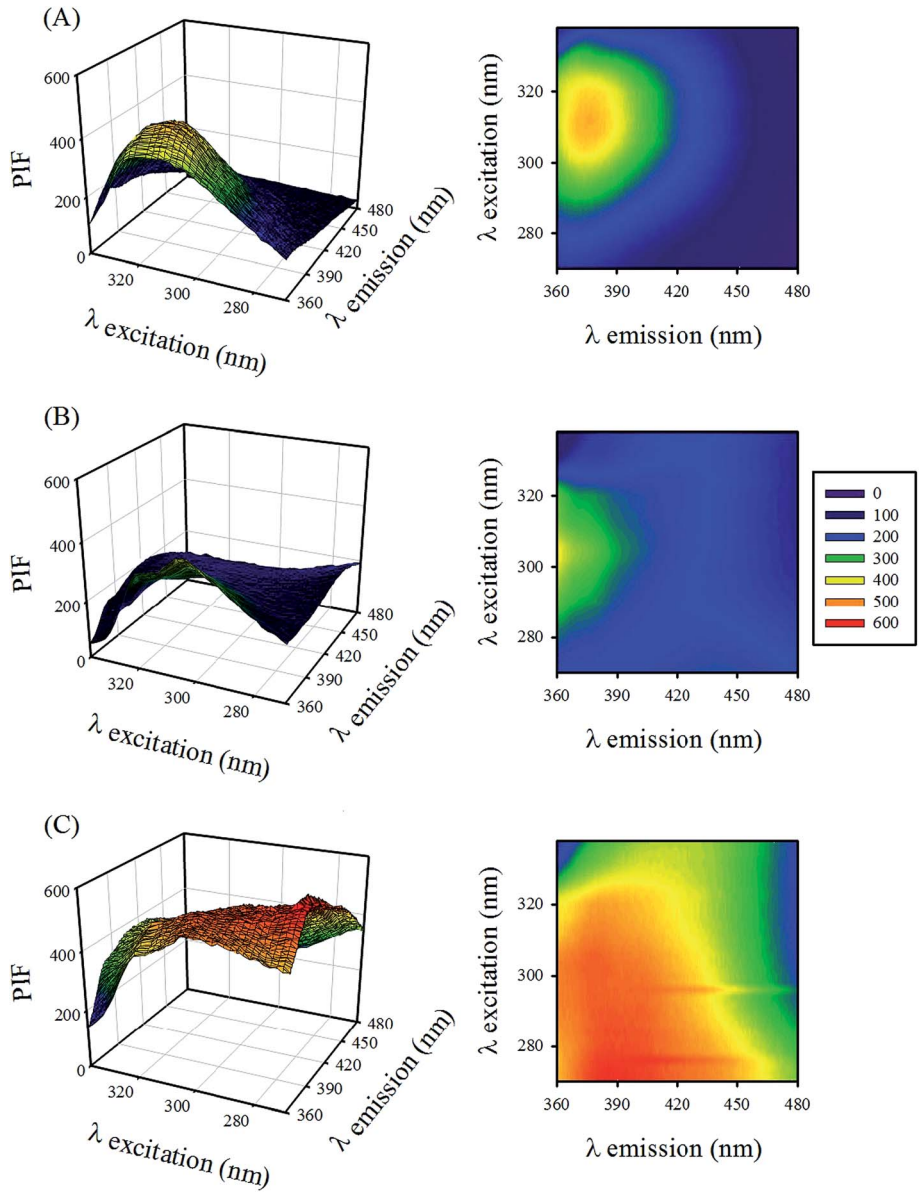


Fig. 3 Three-dimensional plots and the corresponding contour plots of excitation–emission photoinduced fluorescence (PIF) matrices for (A) a validation sample containing 62.0 ng mL^{-1} isoproturon, 188.0 ng mL^{-1} linuron, 130.0 ng mL^{-1} monuron and 63.0 ng mL^{-1} rimsulfuron; (B) a spiked underground water sample after solid-phase extraction (the original concentration for each studied herbicide is 0.12 ng mL^{-1}); (C) a spiked soil sample after the pre-treatment (the original concentration for each studied herbicide is 100.0 ng g^{-1}).

the optimum number of components was performed using the core consistency analysis.[44] The estimated number of components for validation samples was four, and could be justified by the presence of four different signals corresponding to each studied herbicide. However, as can be seen in Fig. S1 of the ESI,† the excitation and emission spectral profiles retrieved by PARAFAC were not entirely similar to the experimental ones and bad predictions were obtained, suggesting that PARAFAC is inappropriate for resolving the system under investigation. This fact may be explained considering the extreme spectral overlapping among the data.[42] Therefore, the U-PLS algorithm which is a more flexible algorithm able to cope with this type of data was applied.[43]

In U-PLS, the optimum number of factors for the calibration set applying the cross-validation method[45] was five. Apparently, this algorithm requires an additional component to model the blank signal. Fig. 4A shows the prediction results corresponding to the application of U-PLS to the complete set of validation samples for each herbicide. As can be appreciated, the predicted concentrations are in good agreement with the nominal values. With the purpose of assessing the accuracy of the predicted concentrations, the elliptical joint confidence region (EJCR) test was performed.[46] From the EJCR test (Fig. 4B), we conclude that all ellipses include the theoretically expected point (1,0), suggesting that U-PLS is appropriate for resolving the system under investigation.

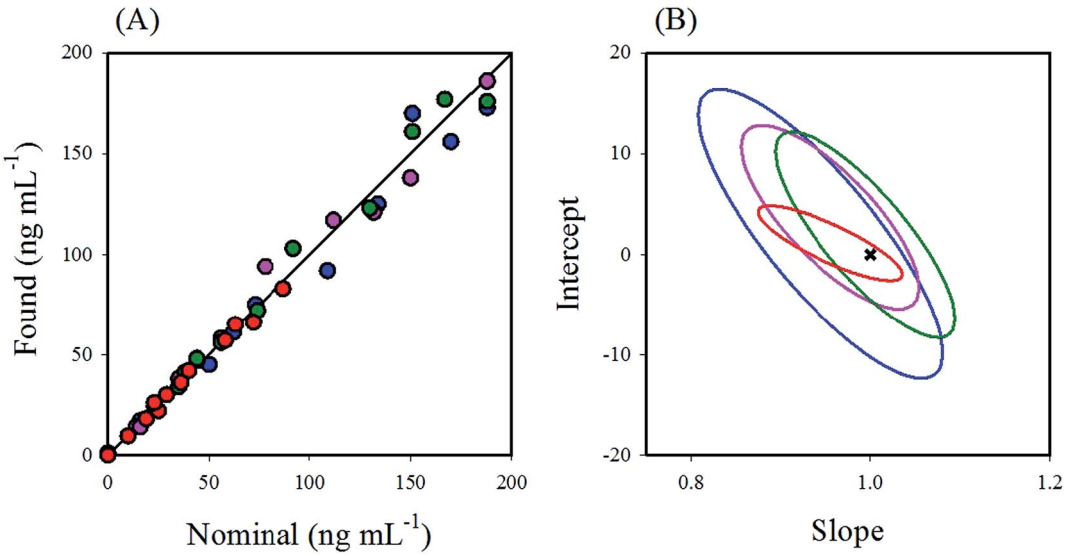


Fig. 4 (A) Plot for isoproturon (blue), linuron (pink), monuron (green) and rimsulfuron (red) predicted concentrations by U-PLS in validation samples, as a function of the nominal values (the black line is the perfect fit). (B) Elliptical join regions (at 95% confidence level) for the slope and the intercept of the regression of the corresponding data. The black cross marks the theoretical (intercept = 0, slope = 1) point.

The analytical performance for the U-PLS algorithm applied to the validation samples can be evaluated from the statistical results shown in Table 1. The relative error of prediction (REP) equal to or less than 7% for all herbicides indicates acceptable precision and supports the conclusion obtained with the EJCR test.

It is important to mention that the limits of detection (LODs) were calculated according to a novel IUPAC-consistent estimator,[47,48] adopting the form of a detection interval, as shown in Table 1. These values are acceptable taking into account that the simultaneous and successful quantification of the four compounds is rapidly achieved.

According to these results, U-PLS was the algorithm selected for the analysis of real samples. Note that when this algorithm was applied to samples containing interferents, it required the introduction of the RBL procedure with an additional number of components corresponding to the unexpected sample constituents. This number is estimated by suitable consideration of RBL residues.[49]

Water samples. The proposed method was employed in the quantification of the four studied herbicides in real water samples of different kinds and origins. Because the analyzed water samples did not contain the studied herbicides at levels

Table 1 Statistical results for herbicides in validation samples and real water samples applying the proposed classical calibration methodology and U-PLS/RBL

	Isoproturon	Linuron	Monuron	Rimsulfuron
Validation samples[a]				
LOD range (min–max) (ng mL^{-1})	3.4–6.4	5.2–10.0	4.1–8.2	1.1–2.2
LOQ range (min–max) (ng mL^{-1})	10.3–19.4	15.6–30.3	12.4–24.8	3.3–6.7
RMSEP (ng mL^{-1})	8	8	7	3
REP (%)	7	7	6	4
Tap water[b,d]				
LOD range (min–max) (ng mL^{-1})	0.024–0.029	0.023–0.028	0.026–0.033	0.007–0.010
LOQ range (min–max) (ng mL^{-1})	0.073–0.088	0.070–0.085	0.079–0.100	0.021–0.030
RMSEP (ng mL^{-1})	4	5	2	4
REP (%)	4	4	2	7
Underground water[c,d]				
LOD range (min–max) (ng mL^{-1})	0.021–0.026	0.022–0.027	0.024–0.030	0.006–0.010
LOQ range (min–max) (ng mL^{-1})	0.064–0.079	0.067–0.082	0.073–0.091	0.018–0.030
RMSEP (ng mL^{-1})	3	4	3	4
REP (%)	3	4	3	7

[a] Twelve samples. [b] From Santa Rosa City (La Pampa, Argentina). [c] From Funes City (Santa Fe, Argentina). [d] Pre-concentration factor = 250. LOD, limit of detection; LOQ, limit of quantification; RMSEP, root-mean-square error of prediction and REP, relative error of prediction, were calculated according to ref. 47 and 48.

higher than the attained detection limits, a recovery study was carried out. In general, herbicide residues are detected in water sources in the order of part- and sub-part-per-billon levels.[8] Hence, the sensitivity of the present method was increased using a pre-concentration SPE procedure with a C18 membrane. It is important to point out that the selection of C18 membranes was based on the good experience with this solid-support as an eco-friendly extractor of low-polarity compounds, such as the studied analytes.[24,26,39] Before the SPE procedure, the samples were spiked with the four compounds, in duplicate, following the treatment indicated in the Experimental section.

Fig. 3B shows both the three-dimensional plot of the EEPIFM and the corresponding contour plot for a real underground water sample spiked with the herbicides and treated with the C18 membrane. The strong matrix interference is evident, but it does not represent a problem when using second-order analysis.

When U-PLS is applied to the real water samples, in addition to the five latent variables estimated for the calibration set, these samples required the introduction of the RBL procedure with four unexpected components in most cases.

Table 2 shows the recovery results obtained, suggesting that the methodology can overcome the problem of the unexpected compounds present in real samples. The good figures of merit obtained for tap and underground water samples using U-PLS/RBL can be appreciated from the statistical results shown in Table 1. Besides, very low LODs in the range of 0.006–0.026 ng mL^{-1} (part-per-trillion levels) reflect the benefits of the pre-concentration procedure.

In comparison with the performances of selected methods for the determination of urea herbicides in water samples (Table 3), LODs from 0.004 to 130 ng mL^{-1} have been found using different strategies, all employing pre-concentration procedures and most of them applying chromatographic approaches. In the present work, low LODs are achieved in real samples applying a non-sophisticated second order method. A relevant feature of the proposed method that distinguishes it from those currently used is that measurements are developed without the use of organic solvents. Finally, a sampling rate of about 7 samples per hour (including the EEPIFM measurement) makes the proposed strategy an appropriate alternative to improve the greenness of chromatographic techniques, which in general involve longer analysis times.

Soil samples. As was stated, post-emergent urea herbicide residues can exhibit activity in the soil for more than a year and, consequently, it is important to quantify their levels in soils.[4] Since the evaluated samples obtained from different regions did not contain the studied herbicides at levels higher than the attained detection limits, a recovery study was performed by spiking them with standard solutions of analytes at tolerance concentration levels established by the EPA.[7] These samples were prepared in duplicate. The signals of the four analytes were highly overlapped with the fluorescent matrix constituents (Fig. 3C), which could be ascribed to the presence of fulvic and humic acids,[50] and the inner filter effect was verified in these systems. This effect was corroborated through a significant change in the slopes of the univariate calibration curves for each analyte in water solution and in the presence of the soil matrix. The results of the slopes and intercepts are shown in Table S5 of the ESI.†

Table 2 Recovery study of herbicides for spiked real water samples using U-PLS/RBL

		Isoproturon		Linuron		Monuron		Rimsulfuron	
Sample	Taken (ng mL^{-1})	Found[a] (ng mL^{-1})	Rec (%)	Found[a] (ng mL^{-1})	Rec (%)	Found[a] (ng mL^{-1})	Rec (%)	Found[a] (ng mL^{-1})	Rec (%)
Tap water[b]	0.10	0.09 (2)	90	0.119 (2)	119	0.093 (5)	93	0.11 (2)	110
Underground water[c]	0.12	0.132 (3)	110	0.109 (8)	91	0.13 (1)	108	0.137 (3)	114

[a] Mean of duplicates. The corresponding standard deviations in the last significant figure are given between parentheses. [b] From Santa Rosa City (La Pampa, Argentina). [c] From Funes City (Santa Fe, Argentina). Rec, recovery.

Table 3 Analytical performance of selected methods reported for urea herbicides in natural water samples[a]

Compounds	Method	Medium	Calibration data order	LOD (ng mL^{-1})	RSD, REP, Rec (%)	Ref.
Isoproturon, monuron, linuron, others	ES-QIT-LC-MS	30–80% MeOH	Zeroth-	0.01–0.025	Rec = 39–76	10
Isoproturon, monuron, linuron, others	LC-DAD	10–70% ACN	Zeroth-	0.004–0.04	RSD = 3–8, Rec = 74–104	17
Isoproturon, monuron, rimsulfuron	PIF-LC	55% ACN	Second-	1.7–2.9	REP = 2.7–4.8, Rec = 79–110	39
Linuron	FIA-PIF-SPF	40% MeOH	Zeroth-	130	RSD = 0.8, Rec = 91–107	40
Isoproturon, monuron, linuron, rimsulfuron	PIF	Water	Second-	0.006–0.026	REP = 3–7, Rec = 90–110	This work

[a] ACN, acetonitrile; DAD, diode array detection; ES, electrospray; FIA, flow-injection analysis; LC, liquid chromatography; MeOH, methanol; MS, mass spectrometry; PIF, photoinduced fluorescence; QIT, quadrupole ion trap; SPF, solid-phase-spectroscopy. LOD, limit of detection; RSD, relative standard deviation; REP, relative error of prediction and Rec, recovery.

Table 4 Recovery study and statistical results of herbicides for spiked soil samples applying the proposed standard addition methodology and U-PLS/RBL

		Isoproturon		Linuron		Monuron		Rimsulfuron	
Sample	Taken (ng g^{-1})	Found[a] (ng g^{-1})	Rec (%)	Found[a] (ng g^{-1})	Rec (%)	Found[a] (ng g^{-1})	Rec (%)	Found[a] (ng g^{-1})	Rec (%)
Soil #1[b]	100.0	106 (3)	106	84 (4)	84	100 (3)	100	116 (1)	116
Soil #2[c]	100.0	110 (1)	110	115 (2)	115	87 (3)	87	100 (2)	100
LOD range (min–max) (ng g^{-1})		2.7–3.6		2.4–3.2		3.3–4.2		1.1–1.5	
LOQ range (min–max) (ng g^{-1})		8.2–10.9		7.3–9.7		10.0–12.7		3.3–4.5	
RMSEP (ng g^{-1})		1		3		1		1	
REP (%)		1		3		1		2	

[a] Mean of duplicates. The corresponding standard deviations in the last significant figure are given between parentheses. [b] From Santa Rosa City (La Pampa, Argentina). [c] From San Pedro City (Buenos Aires, Argentina). LOD, limit of detection; LOQ, limit of quantification; RMSEP, root-mean-square error of prediction and REP, relative error of prediction, were calculated according to ref. 47 and 48. Rec, recovery.

Table 5 Analytical performance of selected methods reported for urea herbicides in soil samples[a]

Compounds	Method	Medium	Calibration data order	LOD, LOQ (ng g^{-1})	RSD, REP, Rec (%)	Ref.
Rimsulfuron, others	LC-MS	10–100% ACN	Zeroth-	LOQ = 2.4	RSD = 3–13 Rec = 83–110	13
Isoproturon, monuron, linuron, others	LC-MS-MS	10–100% ACN	Zeroth-	LOD = 0.1–9.0	RSD = 2–6 Rec = 76–108	15
Rimsulfuron, others	LC-UV	37–57% ACN	Zeroth-	LOD = 0.15–0.35	RSD = 4–11 Rec = 61–121	19
Isoproturon, monuron, linuron, others	LC-UV	ACN–MeOH	Zeroth-	LOQ = 10	RSD = 1–35 Rec = 41–113	20
Isoproturon, monuron, linuron, rimsulfuron	PIF	Water	Second-	LOD = 1.1–3.3	REP = 1–3 Rec = 84–116	This work

[a] ACN, acetonitrile; LC, liquid chromatography; MeOH, methanol; MS, mass spectrometry; PIF, photoinduced fluorescence; UV, ultraviolet. LOD, limit of detection; LOQ, limit of quantification; RSD, relative standard deviation; REP, relative error of prediction and Rec, recovery.

In principle, U-PLS/RBL could not be employed with standard addition data, because the model requires the nominal analyte concentration of the calibration samples.[43] Nevertheless, there is a way in which U-PLS/RBL can be applied,[51] where the soil sample matrix data are subtracted digitally from the three standard addition matrices, so three new virtual samples are created. These virtual samples contain the analyte at three known concentrations, the three added concentrations, and the quantification is processed by a classical external calibration procedure.

Since soil samples contain the calibrated compounds and also potential interferences from the background, the calibration step was performed using five latent variables, and three additional components were included in the RBL procedure.

Table 4 displays the satisfactory prediction results obtained for these spiked soil samples, suggesting that the proposed methodology using the U-PLS/RBL algorithm can overcome the problem of the inner filter effect.

The statistical results shown in Table 4 support this conclusion with values for REP equal to or less than 3% for all compounds. In addition, the LODs indicate that the sensitivity of the present method is appropriate, taking into account that simultaneous determination of four herbicides is carried out using a very simple and green methodology.

In Table 5, a comparison with selected methods for the determination of urea herbicides in soil samples is performed. In the studied method, measurements are carried out in aqueous solution and involving short analysis time (sample throughput of about 4 samples per hour). As in the case of the analysis of water samples, this represents a significant green advantage in relation to usual chromatographic analysis. It should be noted that this is the first time that a second-order method is described for the quantification of these herbicides in soil samples.

Conclusions

This work shows that photoinduced fluorescence (PIF) combined with unfolded partial least-squares/residual bilinearization (U-PLS/RBL) algorithm can be applied to the simultaneous quantification of four urea-derivative herbicides. The method is simple and fast and complies with the principles of green analytical chemistry, avoiding the use of significant amounts of organic solvents. Successful results were obtained when the methodology was applied to real samples such as underground and tap water, and soil samples. We can conclude that the new technique favorably compares with more sophisticated ones.

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