Talanta 160 (2016) 431–436

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Monitoring of chlorsulfuron in biological fluids and water samples by molecular fluorescence using rhodamine B as fluorophore

Magdalena Alesso [a], Luis A. Escudero [a], María Carolina Talio [b,*], Liliana P. Fernández [a,b,*]

[a] Área de Química Analítica, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, San Luis, Argentina
[b] Instituto de Química de San Luis (INQUISAL-CONICET), Chacabuco y Pedernera, San Luis, 5700 Argentina

ARTICLE INFO

Article history:
Received 25 April 2016
Received in revised form
22 July 2016
Accepted 23 July 2016
Available online 26 July 2016

Keywords:
Chlorsulfuron monitoring
Rhodamine B
Molecular fluorescence
Biological and water samples

ABSTRACT

A new simple methodology is proposed for chlorsufuron (CS) traces quantification based upon enhancement of rhodamine B (RhB) fluorescent signal. Experimental variables that influence fluorimetric sensitivity have been studied and optimized. The zeroth order regression calibration was linear from 0.866 to 35.800 μg L^{-1} CS, with a correlation coefficient of 0.99. At optimal experimental conditions, a limit of detection of 0.259 μg L^{-1} and a limit of quantification of 0.866 μg L^{-1} were obtained. The method showed good sensitivity and adequate selectivity and was applied to the determination of trace amounts of CS in plasma, serum and water samples with satisfactory results analyzed by ANOVA test. The proposed methodology represents an alternative to traditional chromatographic techniques for CS monitoring in complex samples, using an accessible instrument in control laboratories.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Pesticides are widely used in agriculture to improve productivity and, consequently, they can produce residues in crops, soils and surface water. Their persistence is an important matter of concern due to their toxicity and possible carcinogenicity. The presence of pesticides could affect ground water or disrupt water treatment plants [1].

Sulfonylurea herbicides, which were firstly introduced in the 1980s [2], are used for weed control in many crops [3,4]. Chlorsulfuron was the first commercial herbicide from the sulfonylurea group. It is mainly utilize to control a large variety of grass and broad-leaved weeds as pre-emergence application on wheat or as a post-emergence application on wheat, barley, flax, triticale and oat crops [5–7]. Therefore, their residues can be found in water sources that can be potentially used for human and animal consumption. In addition, CS can enter the body of the population consuming water and/or food with residues of this herbicide. For this reason, it is important to develop rapid and simple methods to determine sulfonylurea residues at low levels [8,9].

In order to protect water systems, U.S. and European Union (EU) have established the maximum concentration levels for herbicides. For the EU, these values are 0.1 μg L^{-1} for single compounds and 0.5 μg L^{-1} for total herbicides in drinking water [10]. The Argentine legislation only establishes a maximum concentration level for total pesticides in 100 μg L^{-1}[11].

CS determination involves the development of analytical methodologies with adequate sensitivity and selectivity because of the analyte low levels and complex matrixes [12]. Diverse analytical methods have been proposed for the determination of CS: these include high performance liquid chromatography with UV–vis detector [13–15], liquid chromatography coupled to mass spectrometry [16,17] capillary electrophoresis [18,19] and bioassays [20]. In all cases, they have certain disadvantages, mainly related to time-consuming sample pre-treatment and/or the employment of expensive instrumental.

Spectrofluorimetric methods are a combination of sensitive techniques capable of detecting changes in the local environment of the fluorophore [21,22] using inexpensive instrumental. The employ of fluorescence techniques for organic pesticide residue is limited by the fact that, relatively few compounds are strongly luminescent. If the analyte is non or weakly luminescent, it can be converted into a luminescent compound through chemical and/or photochemical reactions, representing an advantage in the selectivity [23].

Considering that it is necessary to have simple, fast, sensitive and precise methodologies for pesticides traces determination, the aim of the present work is to develop an alternative methodology to traditional techniques for CS monitoring in biological fluids and water samples, using an accessible instrument in control laboratories.

* Corresponding author.
E-mail addresses: lfernand@unsl.edu.ar (M.C. Talio), lfernand@unsl.edu.ar (L.P. Fernández).

http://dx.doi.org/10.1016/j.talanta.2016.07.053
0039-9140/© 2016 Elsevier B.V. All rights reserved.

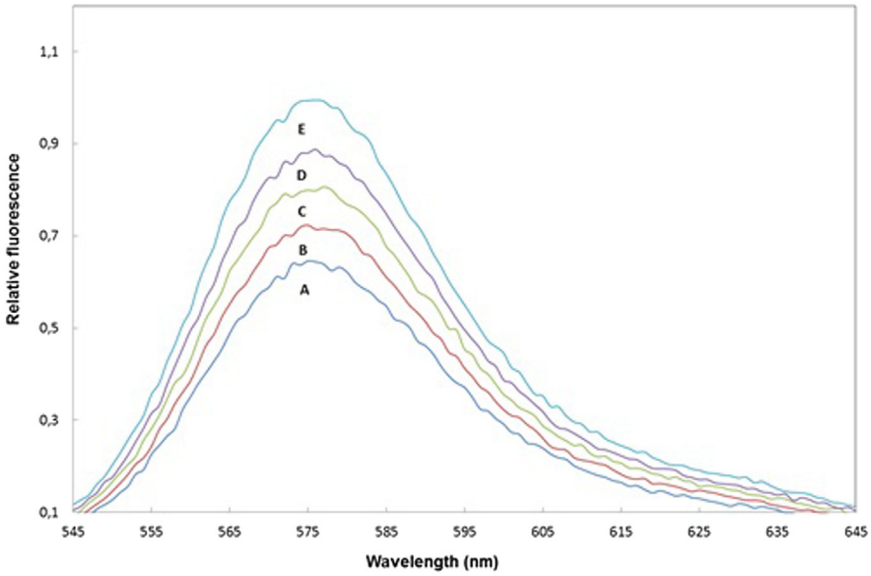

Fig. 1. Fluorescent spectra of RhB and RhB-CS systems.

2. Experimental

2.1. Reagents

Solution 1×10^{-3} mol L^{-1} of CS (Supelco, Bellefonte, P.A., USA) was prepared by dissolving in methanol. Further dilutions 1×10^{-6} mol L^{-1} in methanol were weekly prepared. All CS solutions were protected against light with aluminum foil and kept in a refrigerator at 4 °C.

Stock solution of 1×10^{-3} mol L^{-1} of RhB was prepared by dissolving RhB (Fluka AG, Chemische Fabrik, Buchs SG, Switzerland) in ultrapure water. Afterwards it was diluted obtaining working standard solution 1×10^{-6} mol L^{-1}.

Buffer Tris 1×10^{-2} mol L^{-1} (Mallinckrodt Chemical Works, NY, USA), Potassium dihydrophosphate (Biopack, Buenos Aires, Argentina) buffer solution 1×10^{-2} mol L^{-1} potasium biphthalate and sodium tetraborate (Mallinckrodt Chemical Works) were used, obtaining the desired pH by addition of dilute HCl (Merck, Darmstadt, Germany) or NaOH (Mallinckrodt Chemical Works).

All chemicals used were of analytical grade and ultrapure water was used throughout.

2.2. Apparatus

Fluorescence spectra were performed on Shimadzu RF-5301PC spectrofluorometer (Shimadzu Corporation, Analytical Instrument Division, Kyoto Japan) equipped with a 1.0 cm quartz cells and discharged Xenon lamp. The excitation and emission slits with a band pass of 5.0 nm were used for all spectral measurements.

Measurements of pH were carried out using Orion Expandable Ion Analyzer pHmeter (Orion Research, MA, USA) Model EA 940 with a combined glass electrode.

A centrifuge was used to accelerate the phase's separation process in blood samples.

Statistical analysis of data were performed by multiple analysis of variance following a simple, balanced one-way model student's test was used to compare means and the level of significance was set at 95%. Minitab® 15.1.20.0. software was used.

2.3. Collection and treatment of samples

2.3.1. Biological fluids

Blood samples from healthy subjects (each 10 mL) were obtained by vein puncture of the forearm and samples were placed in 2 polystyrene tubes with and without Li-heparin (anticoagulant). Blood tubes with anticoagulant were homogenized and centrifuged (1500*g*) during 15 min. Then the clear and transparent supernatant corresponding to plasma were extracted and reserved at 4 °C until assays. With the aim of accelerating the coagulation process to realize the serum separation, tubes containing blood without heparin were thermostated at 37 °C during 30 min. Then, systems were centrifuged (1500*g*) during 15 min and supernatant was put in polypropylene tubes with hermetic closing.

Urine sample of 24 h of healthy subject was collected in polystyrene test tubes, between 8 and 10 h AM to reduce possible variations provided by the circadian rhythms. Samples (10 mL approximately) were centrifuged 10 min at 1000*g* and processed immediately after arriving to laboratory. Supernatants (5 mL approximately) were reserved for CS quantification.

In order to skim the raw milk samples, they were centrifuged at 4000*g*, at 4 ºC, during 20 min and the solidified fat was removed using a glass spatula. The caseins were removed by centrifugation and the resulting supernatant contains whey proteins. The samples were stored at 4 ºC until analysis.

Written informed consent was obtained from all participants.

2.3.2. Water samples

2.3.2.1. Tap water. Tap water samples were allowed to run for 10 min, and approximately 1000 mL of each were collected. Tap water samples were filtered and processed once they arrived in the laboratory.

2.3.2.2. Groundwater. Water from the region surrounding the city of Vicuña Mackenna located in the Cordoba, Argentina used for irrigation and consumption by humans and animals was sampled. Samples were filtered through 80 mm Whatman filter paper to remove any sand and other possible major particles and stored in dark at 4 °C until CS determination was performed.

Please cite this article as: M. Alesso, et al., Talanta (2016), http://dx.doi.org/10.1016/j.talanta.2016.07.053

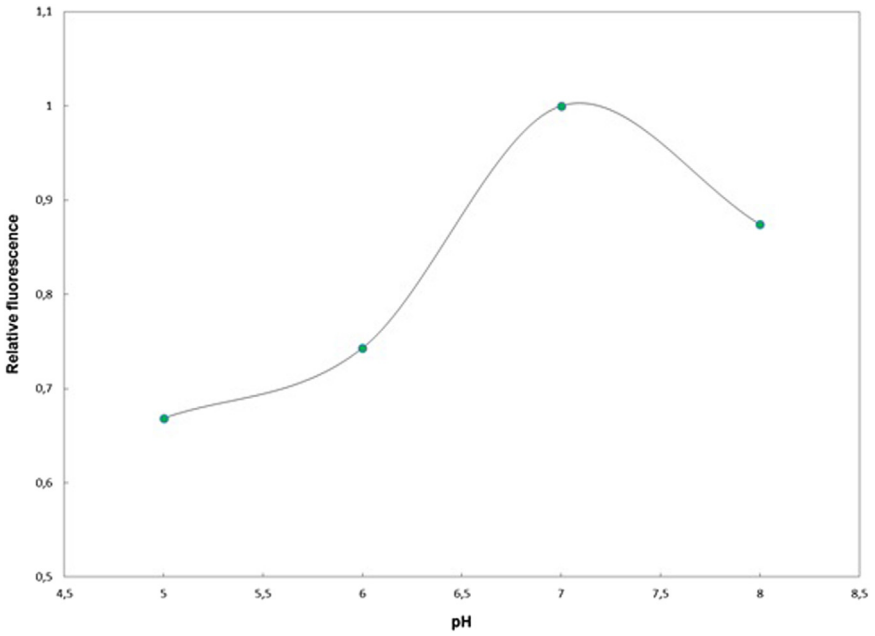

Fig. 2. Influence of pH in CS determination.

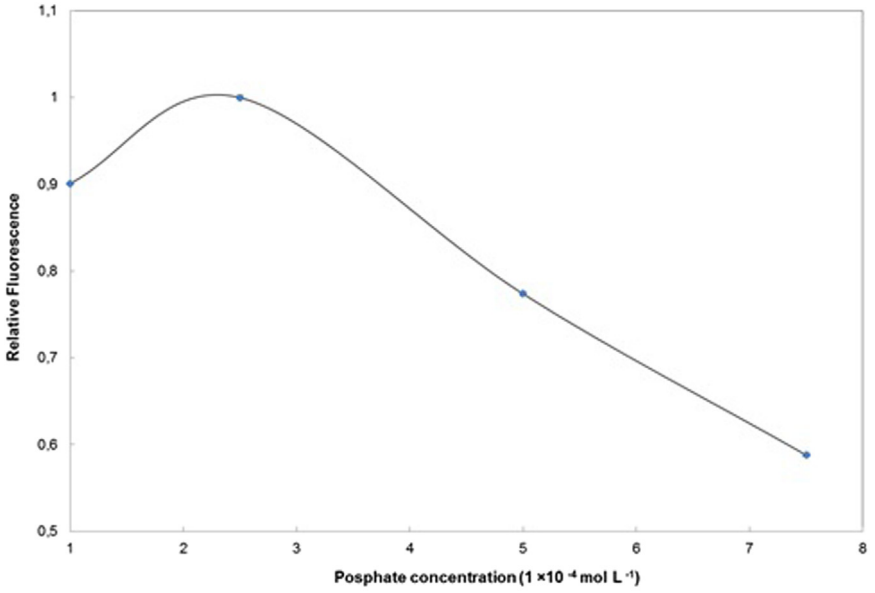

Fig. 3. Influence of phosphate buffer concentration in CS determination.

2.4. General procedure

Adequate aliquot of CS standard solution 1×10^{-6} mol L^{-1}, 0.5 mL of Rhodamine B 1×10^{-6} and 0.250 mL of phosphate buffer solution (pH 7.0), were placed in a 10 mL graduated volumetric flask. The whole mixture was diluted to 10 mL with ultrapure water. The system was kept at room temperature for 5 min. Fluorescent emission was determined at 576 nm (λ_{ex}=540 nm). Emission spectra of CS-RhB systems at optimal experimental conditions are shown in Fig. 1.

2.5. Accuracy study

Adequate volumes of samples were spiked with increasing CS amounts 0.00, 8.98, 17.9 μg L^{-1}. CS contents were determined by the proposed method applying General procedure.

2.6. Precision study

The precision of the method was evaluated in terms of repeatability and intermediate precision (inter day precision). Individual repeatabilities were calculated from the assay values of independent samples spiked at two concentration levels of chlorsulfuron standards (5.37 and 21.47 μg L^{-1}). Each one was analyzed by triplicate on the same day. The number of values (n) was six per level and sample. The repeatability (expressed as relative standard deviations (RSD%)) were found to be 2.684 and 3.039; 3.256 and 2.114; 3.282 and 1.917 for water, urine and serum samples, respectively.

3. Results and discussion

As with all of the sulfonylureas, CS molecule consists of three distinct parts: an aryl group, the sulfonylurea bridge, and a

Please cite this article as: M. Alesso, et al., Talanta (2016), http://dx.doi.org/10.1016/j.talanta.2016.07.053

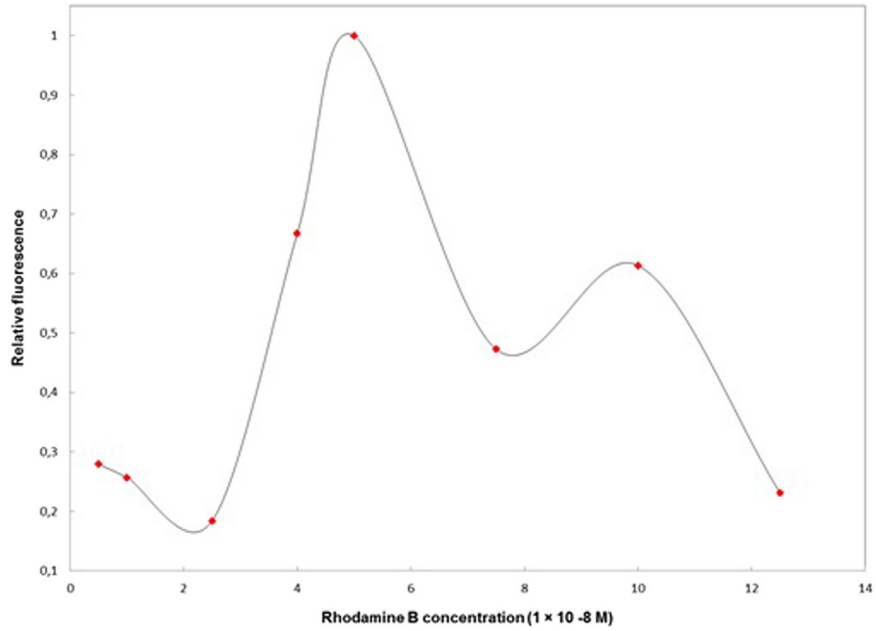

Fig. 4. Optimization of RhB concentration.

Table 1
Experimental conditions and analytical quality parameters for chlorsulfuron determination by proposed methodology.

Parameter	Studied range	Optimal condition
pH	2–9.22	7
Phosphate buffer concentration	$1–7.5 \times 10^{-4}$ mol L^{-1}	2.5×10^{-4} mol L^{-1}
RhB concentration	$0.5–12.5 \times 10^{-8}$ mol L^{-1}	5×10^{-8} mol L^{-1}
LOD	0.259 μg L^{-1}	
LOQ	0.866 μg L^{-1}	
Linearity range	0.860–35.800 μg L^{-1}	

Table 2
Chlorsufuron determination in biological fluids and water samples. Recovery study (n =3; α=0.05).

Sample	CS added (μg L^{-1})	CS found ± CI (μg L^{-1})	Recovery (%)[a]
Plasma	–	0.00 ± 0.15	–
	8.98	9.21 ± 0.17	102.50
	17.90	17.6 ± 0.05	99.30
Serum	–	0.00 ± 0.27	–
	8.98	9.56 ± 0.42	106.50
	17.90	17.69 ± 0.42	98.80
Water	–	0.00 ± 0.15	–
	8.98	9.40 ± 0.05	104.60
	17.90	17.70 ± 0.25	98.90
Urine (24 h)	–	0.00 ± 0.07	–
	8.98	9.42 ± 0.20	104.90
	17.90	17.81 ± 0.12	99.50
Breast milk	–	0.00 ± 0.10	–
	8.98	8.96 ± 0.12	99.77
	17.90	18.01 ± 0.22	100.61
Ground water	–	0.00 ± 0.05	–
	8.98	8.99 ± 0.02	100.11
	17.90	17.82 ± 0.25	99.55

[a] Recovery (%)=[(found-base)/added] x100.

nitrogen-containing heterocycle with different substituents in the ortho position in the phenyl or aryl group. CS is a weak acid with dissociation constant of $pK_a=3.6$ [24].

Conventionally, sulfonylureas have been analyzed by separative methodologies as HPLC and capillar electrophoresis in different samples [25,26]. CS molecule does not show native fluorescence, so that, to perform fluorescence detection, a previous step of photochemical degradation has been necessary [27,28]. In this work, the fluorosphore Rhodamine B (RhB) has been chosen for CS determination by fluorescence.

The effect of CS on RhB fluorescent signal was studied preparing a system with dye solution in the presence of CS. Simultaneously, RhB blank was also prepared. In the presence of CS, an increase of fluorescent signal of RhB was observed (Fig. 1).

It is well known that RhB has different structures pH-dependent. So that, the pH of system has a direct influence in RhB molecule and their capability to complex formation with CS. Also, self-aggregation of protonated RhB causes a diminution of fluorescence signal [29]. As a result of the interaction of the sulfonylurea with RhB, the carboxylic group of RhB becomes more basic once the positive charge of the dye has been neutralized. At pH below 5, the sulfonylurea induces the association/protonation of RhB and its spectral characteristics change [30].

The pH value of the aqueous systems containing a constant concentration of both CS and RhB was adjusted between 3.6 and 9.22 by addition of biphthalate (pH 4), acetic acid (pH 3.6 and 4.2), Tris (pH 6), phosphate (pH 6, 7, 7.2, 8) and tetraborate (pH 9.22) buffers. The best emission signal was achieved when phosphate buffer pH 7 was used (Fig. 2). Buffer concentration was optimized in the range from 1 to 7.5×10^{-4} mol L^{-1}. As exhibits in Fig. 3, a concentration of 2.5×10^{-4} mol L^{-1} produced the best results and it was chosen as optimal.

Other important parameter is the dye RhB concentration; this parameter must be maintained constant in order to assure the same contribution to the fluorescence signal in all samples/standards systems. Additionally, the RhB concentration must be sufficiently high to guarantee the CS/RhB association, assuring a quantitative complex formation. However, this molecule self-aggregates in concentrations over 1×10^{-4} mol L^{-1} by means of π-π interactions [30]. The aggregation induces spectroscopic changes and affects dye efficiency and photostability [31,32]. Concentration of RhB solution was optimized, varying from 0 to 1.25×10^{-7} mol L^{-1}. As shown in Fig. 4, the best result was obtained by employing a RhB concentration of 5×10^{-8} mol L^{-1}.

Please cite this article as: M. Alesso, et al., Talanta (2016), http://dx.doi.org/10.1016/j.talanta.2016.07.053

Table 3
Precision study (repeatability and intermediate precision) of chlorsulfuron determination in water, urine and serum samples (α=0.05).

		Level 1				Level 2			
	Sample	**Recovery (%)[a]**	**Average CS (μ L^{-1})[b]**	**RSD (%)**	**n**	**Recovery (%)[a]**	**Average CS (μ L^{-1})[b]**	**RSD (%)**	**n**
Day 1	Water	99.776	5.358 ± 0.146	2.612	6	100.670	21.614 ± 0.463	2.045	6
Day 2		102.569	5.508 ± 0.471	2.541	6	97.028	20.832 ± 0.952	4.356	6
Day 3		101.080	5.428 ± 0.146	2.578	6	100.256	21.525 ± 0.515	2.279	6
Intra-Day RSD		101.446	5.431 ± 0.186	2.728	18	99.319	21.324 ± 1.063	2.500	18
Day 1	Urine	100.893	5.418 ± 0.165	2.903	6	99.170	21.292 ± 0.505	2.262	6
Day 2		101.694	5.461 ± 0.177	3.100	6	100.582	21.595 ± 0.311	1.373	6
Day 3		98.417	5.285 ± 0.207	3.703	6	97.987	21.038 ± 0.567	2.553	6
Intra-Day RSD		100.334	5.388 ± 0.228	3.428	18	99.245	21.308 ± 0.692	1.158	
Day 1	Serum	99.459	5.341 ± 0.220	3.942	6	98.495	21.147 ± 0.365	1.647	6
Day 2		102.588	5.509 ± 0.211	3.664	6	100.493	21.576 ± 0.311	1.376	6
Day 3		99.236	5.329 ± 0.099	1.773	6	97.931	21.026 ± 0.563	2.554	6
Intra-Day RSD		100.427	5.393 ± 0.250	0.672	18	98.973	21.250 ± 0.717	1.044	18

Level 1 and 2: 5.37 and 21.47 μg L^{-1}, respectively.
[a] Recovery (%)=[(found-base)/added] x100.
[b] Confidence interval, *t* test.

3.1. Analytical figures of merit

Calibration plot for crescents CS concentration levels from 0.866 to 35.8 μg L^{-1} was assayed applying the developed methodology. Table 1 summarizes the main characteristics of the calibration plot and optimized experimental conditions, which sustain the proposed procedure for quantification of CS traces. The limits of detection (LOD) and quantification (LOQ) were calculated in accordance to the formulas given by the official compendia methods [33], using the relation k (SD)/m where k=3.3 for LOD and 10 for LOQ. SD represents the standard deviation from 15 replicate blank responses and *m* is the slope of the calibration curve.

3.2. Interference study

In trade, CS is available in mixtures together with metsulfuron-methyl. Therefore, in order to evaluate the possible interferences caused by other sulfonylureas, metsulfuron-methyl spectral analysis was carried on in the same CS determination conditions. It was not observed chemical interferences and spectral overlaps.

3.3. Validation and applications

In order to evaluate the versatility of the developed methodology, recovery studied was conducted on 25 μL of biological samples and 100 μL water dopped with 0.00, 8.98 and 17.9 μg L^{-1} CS; prepared system were analyzed applying General procedure. Levels of added CS were chosen in accordance of the range of linearity of the proposed methodology and current legislation.

The repeatability of the method was evaluated by repeating the proposed approach 3 times for each addition in a total of three levels of spiked CS for each sample (serum R^2=0.999; plasma R^2=0.978; water sample R^2=0.987). The recoveries of CS are illustrated in Table 2. The results obtained showed a satisfactory agreement with good precision.

Considering a statistically non-significant decrease in the content of the analyte, intermediate precisions are calculated by means of an analysis of variances (ANOVA). This precision level includes the method variability and the variance contribution between days. The samples were analyzed on three non-consecutive days to determine the precision or repeatability. Table 3 reported the study of precision on three samples of water, urine and serum. Results showed a good intermediate precision for CS determination and acceptable recovery in all studied cases.

4. Conclusions

The methodology proposed represents an alternative to conventional methods to CS monitoring with a lower operational cost and a suitable limit of detection. Among the experimental parameters, nature and concentration of fluorescent complexing, buffer pH and most favorable buffer concentration were studied and optimized. The developed technique was validated using the standard addition method and applied to diverse biological and water samples with successfully results, showing ample applicability. Samples spiked with a known quantity of CS were analyzed to demonstrate the absence of interferences and to provide a check of recovery efficiency near 100 ± 2%. Furthermore, no interferences with other sulfonylurea herbicides are demarcated. Precision and accuracy were tested through an analysis of variances (ANOVA) with adequate results. Taking into account the generation of low amounts of waste, the care of the analyst and the environment, the present proposal represent a contribution to green analytical chemistry.

Acknowledgments

Authors gratefully acknowledge at Instituto de Química de San Luis–Consejo Nacional de Investigaciones Científicas y Tecnológicas (INQUISAL-CONICET Project PIP 112 201301 00605 CO) and Universidad Nacional de San Luis (Project 22/Q228) for financial support.

References

[1] P.A. Diaw, A. Maroto, O.M.A. Mbaye, M.D. Gaye-Seye, L. Stephan, A. Coly, L. Deschamps, A. Tine, J.J. Aaron, P. Giamarchi, Determination of phenyl urea pesticides by direct laser photo-induced fluorescence, Talanta 116 (2013) 569–574.
[2] H.M. Brown, Mode of action, crop selectivity and soil relations of the sulfonylurea herbicides, Pestic. Sci. 29 (1990) 263–281.
[3] S.E. Baker, A.O. Olsson, L.L. Needham, D.B. Barr, High performance liquid chromatography–tandem mass spectrometry method for quantifying sulfonylurea herbicides in human urine: reconsidering the validation process, Anal. Bioanal. Chem. 383 (2005) 963–976.
[4] P. Degelmann, S. Egger, H. Jürling, J. Müller, R. Niessner, D. Knopp, Determination of sulfonylurea herbicides in water and food samples using sol–gel

glass-based immunoaffinity extraction and liquid chromatography-ultraviolet/diode array detection or liquid chromatography-tandem mass spectrometry, J. Agric. Food Chem. 54 (2006) 2003–2011.
[5] V.H. Springer, A.G. Lista, A simple and fast method for chlorsulfuron and metsulfuron methyl determination in water samples using multi walled carbon nanotubes (MWCNTs) and capillary electrophoresis, Talanta 83 (2010) 126–129.
[6] S. Kaczmerek, K. Matysiak, Application of reduced doses of chlorsulfuron in semi-dwarf and full-height cultivars of winter triticale, J. Plant Res. 55 (2015) 8–15.
[7] J. Mankowski, K. Pudelko, Effect of herbicides on yield and quality of straw and homomorphic fibre in flax (Linum usitatissimum L), Ind. Crop. Prod. 70 (2015) 185–189.
[8] W.A. Battaglin, E.T. Furlong, M.R. Burkhardt, C.J. Peter, Occurrence of sulfonylurea, sulfonamide, imidazolinone, and other herbicides in rivers, reservoirs and ground water in the Midwestern United States, Sci. Total Environ. 1998 (2000) 248, 123.
[9] M.P. Azcarate, J. Montoya, W. Koskinen, Sorption, desorption and leaching potential of sulfonylurea herbicides in Argentinean soils, J. Environ. Sci. Health B 50 (2015) 229–237.
[10] Official Journal of European Communities Council Directive 98/83/EC.
[11] Ley 24051, decreto 831, Régimen de desechos peligrosos, Anexo II, Tabla I. ⟨http://www2.medioambiente.gov.ar/mlegal/residuos/dec831/dec831_anxII_t1.htm⟩.
[12] H. Niu, Y. Shi, Y. Cai, F. Wei, G. Jiang, Solid-phase extraction of sulfonylurea herbicides from water samples with single-walled carbon nanotubes disk, Microchim. Acta 164 (2009) 431–438.
[13] P. Liang, J. Wang, G. Liu, Determination of sulfonylurea herbicides in food crops by matrix solid-phase dispersion extraction coupled with high-performance liquid chromatography, Food Anal. Methods 7 (2014) 1530–1535.
[14] J.B. Chao, J.F. Liu, M.J. Wen, J.M. Liu, Y.Q. Cai, G.B. Jiag, Determination of sulfonylurea herbicides by continuous-flow liquid membrane extraction on-line coupled with high-performance liquid chromatography, J. Chromatogr. A 955 (2) (2002) 183–189.
[15] Q. Zhou, W. Wang, J. Xiao, Preconcentration and determination of nicosulfuron, thifensulfuron-methyl and metsulfuron-methyl in water samples using carbon nanotubes packed cartridge in combination with high performance liquid chromatography, Anal. Chim. Acta 559 (2006) 2000–2006.
[16] E.T. Furlong, M.R. Burkhardt, P.M. Gotes, S.L. Werner, W.A. Battaglin, Routine determination of sulfonylurea, imidazolinone, and sulfonamide herbicides at nanogram-per-liter concentrations by solid-phase extraction and liquid chromatography/mass spectrometry, Sci. Total Environ. 248 (2000) 135–146.
[17] C. Li, A. Lu, J. Wang, Determination of five sulfonylurea herbicides in environmental waters and soil by ultra high performance liquid chromatography with tandem mass spectrometry after extraction using grapheme, J. Sep. Sci. 37 (2014) 3414–3721.
[18] R. El-Debs, R. Nehemé, B. Claude, Coated capillaries with highly charged polyelectrolytes and carbon nanotubes co-aggregated with sodium dodecyl sulphate for the analysis of sulfonylureas by capillary electrophoresis, J. Chromatogr. A 1367 (2014) 161–166.
[19] Z.L. Chem, R.S. Kookana, R. Naidu, Determination of sulfonylurea herbicides in soil extracts by solid-phase extraction and capillary zone electrophoresis, Chromatographia 52 (2000) 142–146.
[20] F. Larras, A. Bouchez, F. Rimet, B. Montuelle, Using Bioassays and Species Sensitivity Distributions to Assess Herbicide Toxicity towards Benthic Diatoms, PLoS One 7 (8) (2012) 1–9.
[21] A. Sulkowska, Interaction of drugs with bovine and human serum albumin, J. Mol. Struct. 614 (2002) 227–232.
[22] Y.V. Ilichev, J.L. Perry, J.D. Simon, Interaction of ochratoxin A with human serum albumin, Preferential binding of the dianion and pH effect, J. Phys. Chem. B 106 (2002) 452–459.
[23] J.J. Aaron, A. Coly, Luminescence methods in pesticide analysis. Applications to the environment, Lumin. Spectrosc. 28 (2000) 699–707.
[24] P.J. Shea, Chlorsulfuron dissociation and adsorption on selected adsorbents and soils, Weed Sci. 34 (1986) 474–478.
[25] A. Gure, F.J. Lara, A.M. García-Campaña, Vortex-assisted ionic liquid dispersive liquid–liquid microextraction for the determination of sulfonylurea herbicides in wine samples by capillary high-performance liquid chromatography, Food Chem. 170 (2015) 348–358.
[26] P. Ling Chang, M. Hsieh, Recent advances in the determination of pesticides in environmental samples by capillary eectrophoresis, Int. J. Environ. Res. Public Health 13 (2016) 409–429.
[27] A. Coly, J.J. Aaron, Photochemically-induced fluorescence determination of sulfonylurea herbicides using micellar media, Talanta 49 (1999) 107–117.
[28] K. Marvatova, J. Martinez Calatayud, A fully automated assembly using solenoid valves for the photodegradation and chemiluminometric determination of the herbicide chlorsulfuron, Anal. Lett. 38 (2005) 179–194.
[29] N.O. Mchedlov-Petrossyan, Y.V. Kholin, Aggregation of rhodamine B in water, Russ. J. Appl. Chem. 77 (2004) 414–422.
[30] P. Ilich, P.K. Mishra, S. Macura, T.P. Burghrdt, Direct observation of rhodamine dimer structures in water, Spectrochim. Acta, Part A 52 (1996) 1323–1330.
[31] N.O. Mchedlov-Petrossyan, N.A. Vodolazkaya, A.O. Doroshenko, Ionic equilibria of fluorophores in organized solutions: the influence of micellar microenvironment on protolytic and photophysical properties of Rhodamine B, J. Fluoresc. 13 (2003) 235–248.
[32] I. Moreno-Villosalada, M. Jofré, V. Miranda, pH dependence of the interaction between Rhodamine B and the water-soluble poly (sodium-4styrenesulfonate), J. Phys. Chem. B 110 (2006) 11809–11812.
[33] J.C. Miller, J.N. Miller, Statistics for Analytical Chemistry, fourth ed., Ellis-Howood, New York, 1994.

Please cite this article as: M. Alesso, et al., Talanta (2016), http://dx.doi.org/10.1016/j.talanta.2016.07.053