



Analytical Methods

Determination of sulfonylureas in cereal samples with electrophoretic method using ionic liquid with dispersed carbon nanotubes as electrophoretic buffer

Valeria H. Springer, Francisco Aprile, Adriana G. Lista^{*}

FIA Laboratory, Analytical Chemistry Section, INQUISUR (UNS-CONICET), Av. Alem 1253, B8000CPB Bahía Blanca, Buenos Aires, Argentina

ARTICLE INFO

Article history:

Received 26 June 2012

Received in revised form 30 January 2013

Accepted 30 July 2013

Available online 8 August 2013

Keywords:

Capillary electrophoresis

Ionic liquid

Single walled carbon nanotubes

Cereal samples

ABSTRACT

A capillary electrophoresis method to determine four sulfonylureas in grain samples was developed using 10 mM of 1-butyl-3-methyl imidazolium tetrafluoroborate (bminBF_4) as electrophoretic buffer solution. 2 mg L⁻¹ of Surfactant Coated-Single Wall-Carbon Nanotubes (SC-SWCNTs) was added to the buffer solution to improve the resolution. In this way, the separation of nicosulfuron, ethoxysulfuron, sulfometuron methyl and chlorsulfuron was carried out in 16 min without using organic solvents. A clean up-preconcentration procedure was done prior to inject the sample into the CE instrument, in order to achieve the established maximum residue limits (MRLs). So, the detection limits (LODs) for each analytes were between 16.8 and 26.6 $\mu\text{g kg}^{-1}$. The relative standard deviations (RSDs) were in the range 1.9–6.7%. A recovery study using the so-called matrix matched calibration demonstrates that no matrix interferences were found throughout the determination. The recovery percentages were ranged between 80% and 113%.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Herbicides are a group of chemical compounds normally used to control weeds in crops. In 1995 it was estimated that herbicides represent 70–80% of the total amount of pesticides used on crop in developed countries. Nowadays, due to the rapidly increasing of the world population and the demand of food, the use of herbicides is crucial for the development of agricultural production (Pacanoski, 2007). Sulfonylureas (SUs) are one of the most used herbicides in many agricultural crops, due to their low application rates, low toxicity to mammals and herbicidal activity (Pimentel & Levitan, 1986). Nevertheless, it is possible that the residues of these herbicides contaminate not only water, soil and air, but also they are accumulated in grains because they are widely applied as selective pre and post-emergence herbicides (Losito, Amorisco, Carbonara, Lofiego, & Palmisano, 2006). Crops treated with SUs include barley, corn, cotton, durum wheat, peanuts, rice, soybeans, spring wheat, and winter wheat (Furlong, Burkhardt, Gates, Werner, & Battaglin, 2000). Therefore, the development of simple and rapid analytical methods for SUs determination in various matrixes is an important challenge to ensure the quality and safety of agricultural products.

Although gas chromatography (GC) is the principal technique used to determine pesticides, liquid chromatography (LC) with different kind of detections is the preferred technique for the deter-

mination of SUs (Moliner-Martínez, Cárdenas, & Valcárcel, 2007; She et al., 2010), because of their polar characteristics, low volatility and thermal stability (Losito et al., 2006). Capillary electrophoresis (CE) is another separation technique that has been used for this determination with UV detection (Chen, Kookana, & Naidu, 2000; Dinelli, Vicari, & Bonetti, 1995; Springer & Lista, 2010). In this technique, the selection of the buffer solution is one of the critical variables because it is related to the simplicity of the electrophoretic mode. Sometimes it is necessary to add some chemical compound to the separation buffer solution to improve the electrophoretic resolution. In this way, organic solvents, dispersed nanoparticles (Cao, Dun, & Qu, 2011) or ionic liquids (Qi et al., 2006) are used. The application of ionic liquids (ILs) during the separation step is due to their properties, such as high thermal and chemical stability, negligible vapor pressure, low toxicity and good electrical conductivity (MacFarlane et al., 2007; Plechkova & Seddon, 2008; Seddon, 1997). ILs are usually defined as salts that melt below 100 °C, being liquids composed solely of anions and cations. Those ILs whose melting point is lower than 25 °C are known as Room Temperature Ionic Liquids (RTILs) and their particular properties (i.e. polarity, viscosity, solvent miscibility or hydrophobicity) can change by means of simple chemical modifications of the nature or size of their ions (Anderson, Armstrong, & Wei, 2006; Carda-Broch, Berthod, & Armstrong, 2003). Currently, the most common ILs are formed by an N- or P-containing organic cation (imidazole, pyrrolidine, pyridine, phosphonium, etc.) in combination with an organic or inorganic anion (tetrafluoroborate, hexafluorophosphate,

^{*} Corresponding author. Tel.: +54 291 4595100; fax: +54 291 4595160.

E-mail addresses: alista@criba.edu.ar, adriana.lista@uns.edu.ar (A.G. Lista).

nitrate, acetate, etc.). Over the last few years ILs have attracted most attention due to that they are considered as “green” solvents. In CE, ILs have been used as background electrolyte (BGE) additive, especially in MEKC mode (Qin, Wei, & Li, 2003; Xu, Li, & Wang, 2008), or to modify the surface of the capillaries by ILs covalently bonded to the capillary wall (Borissova, Vaher, Koel, & Kaljurand, 2007; Qin & Li, 2002; Qin et al., 2003; Tian, Wang, Chen, Chen, & Hu, 2007; Yanes, Gratz, Baldwin, Robinson, & Stalcup, 2001).

On the other hand, it is well known the physical, electronic and optical characteristics of carbon nanotubes (CNTs). So, their application in analytical processes has rapidly grown (Nilsson, Brinbaum, & Nilsson, 2011; Valcárcel, Cárdenas, Simonet, Moliner-Martínez, & Lucena, 2008). It has been demonstrated that the use of dispersed CNTs in CE, as additive in the run buffer, significantly improves the resolution of the electrophoretic peaks (Springer & Lista, 2012; Suárez, Simonet, Cárdenas, & Valcárcel, 2007).

According to our knowledge, the use of ILs with CNTs as BGE to separate SUs has not been reported. Then, the objective of the present study was to develop a simple and rapid CE method to determine sulfonylureas in wheat and sorghum samples introducing a new composition of the run buffer. These cereals were selected because they are two of the most cultivated grains in the pampean region of Argentina.

Taking into account the established maximum residues levels MRLs (EU Regulation (EC) N° 396/2005) of sulfonylureas in grain samples, any determinative method needs an extraction/preconcentration step. The extraction is commonly carried out using phosphate-buffered solution (PBS), or a combination of it with acetonitrile or methanol. Then, a solid phase extraction by using ion exchangers, RP18, C18 or CNTs as sorbents is normally carried out to preconcentrate the analytes (Kang, Chang, Zhao, & Pan, 2011; Springer & Lista, 2010).

In this work, ethoxysulfuron, nicosulfuron, sulfometuron methyl and chlorsulfuron are simultaneously determined employing 1-butyl-3-methylimidazolium tetrafluoroborate (bminBF₄) with Surfactant-Coated-Single-Wall-CNTs (SC-SWCNTs) as BGE. A very good resolution of peaks was obtained without using toxic organic solvents. Moreover, a simple sample treatment was carried out in order to extract and preconcentrate the analytes.

2. Experimental

2.1. Apparatus

Beckman Coulter (Palo Alto, CA, USA) capillary electrophoresis instrument MDQ equipped with a diode array detector was used. The capillaries were also from Beckman System. Control and data processing was carried out with 32 Karat software.

A centrifuge Rolco (Buenos Aires, Argentina) and a stirring hot plate IKA (Buenos Aires, Argentina) were employed to treat the grain samples.

A Cole Parmer ultrasonic bath (70 W – 60 Hz) (Chicago, USA) was used to disperse the SWCNTs.

Gilson Minipuls – 3 peristaltic pump, 0.5 mm id PTFE tubing, Tygon pump tubing, a Rheodyne 5041 injection valve and a Rheodyne 5011 selection valve were used to carry out the SPE procedure. In this step, a plastic tube (30 mm length × 6 mm i.d.) packed with 100 mg of C18 (Macherey Nagel, Düren, Germany) was placed in the continuous flow system. At the end of the tube, a cellulose frit was used to hold the sorbent material in the cartridge.

2.2. Reagents

All reagents were of analytical grade and ultra pure water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Chlorsulfuron (CS), ethoxysulfuron (ES), nicosulfuron (NS) y sulfometuron methyl (SMM) were purchased from Sigma-Aldrich (Buenos Aires, Argentina). A 20 mg L⁻¹ standard stock solution of each analyte was prepared in acetone and stored at 4 °C. These solutions were stable for at least two months.

The standard working solutions were daily prepared by appropriate dilutions of stock solutions.

Single-walled carbon nanotubes (SWCNTs) with average external diameters of 10–30 nm and purity >95% NTP were provided by Sinatec (Córdoba, Spain). Multi-walled carbon nanotubes (MWCNTs) with average external diameters of 13–16 nm and purity >95% were supplied by Bayer (Leverkusen, Germany). A sodium dodecyl sulfate (SDS) solution with 10% v/v 2-butanol (Sigma, Buenos Aires, Argentina) was used to prepare the dispersion of CNTs which was carried out according to the literature (Moliner-Martínez et al., 2007). 10 mg of CNTs were dispersed in a 17.5 mM SDS solution containing 10% v/v of 2-butanol by using an ultrasonic bath (20 min, 50 W – 60 Hz). This chemical system was stable for a week.

Methanol and acetone were used to treat the samples. The extraction solution, 0.1 mol L⁻¹ potassium dihydrogen phosphate solution and 20% v/v methanol (PBS-methanol), was adjusted to pH 9.0 with 0.1 mol L⁻¹ sodium hydroxide. Phosphoric acid (85%) was employed to adjust the pH of the sample extracts. All these reagents were purchased from Baker (Chemical Center S.R.L., Buenos Aires, Argentina).

The electrophoretic buffer was daily prepared with 1-butyl-3-methyl imidazolium tetrafluoroborate (Merck, Buenos Aires, Argentina), sodium borate and sodium hydroxide (Baker, Chemical Center S.R.L., Buenos Aires, Argentina).

2.3. CE analysis

The separation was carried out in a fused-silica capillary (54 cm effective length, 75 µm i.d.) with a positive power supply of 15 kV at 21.8 °C. Sample injections were performed in hydrodynamic mode for 15 s at 0.5 psi. The electrolyte buffer was 10 mM bminBF₄, 2 mM sodium borate with 2 mg L⁻¹ SC-SWCNTs. The pH was adjusted at 11 with 0.1 M sodium hydroxide. The capillary was conditioned daily by flushing 0.1 M NaOH (5 min), ultrapure water (3 min) and buffer solution (5 min). All the electropherograms were recorded at 245 nm.

2.4. Sample preparation

Two different types of cereal samples were used. The wheat and the sorghum samples were provided by a cereals industry (Bunge, Buenos Aires, Argentina). In both cases, five subsamples were taken from the aggregated sample and they were carefully mixed. Then, these samples were milled to a fine powder in a grain mill and stored in darkness at 4 °C until analysis.

The samples were analyzed using the whole proposed method and no pesticides were found above the LODs of the method tested. So, the samples were used as blank matrix for all the fortification experiments and also for the matrix effect study.

Sample (2.00 g) was treated with 10 mL of PBS-methanol at pH 9. The mixture was placed on the stirring plate for 30 min. The supernatant was separated by filtration using a vacuum pump. The collected supernatant was centrifuged during 10 min at 4000 rpm. The pH of the samples should be adjusted to 2.5 before the SPE step.

For the recovery studies of both cereals, a new portion of 2.00 g of a homogenized milled sample was weighed. Then, it was fortified homogeneously with a working solution in acetone to reach 50 µg kg⁻¹ and 100 µg kg⁻¹ of the studied herbicides. These fortified samples were allowed to stand at room temperature to dry the solvent. Then, the extraction procedure above depicted was carried out.

2.5. SPE procedure

A continuous flow system was developed to carry out an off-line SPE pre-treatment. In this way, it was possible to preconcentrate the analytes and to clean up the extract of the samples. According to the literature, C18 was selected as sorbent material taking into account the chemical properties of the analytes such as their polarity (Rodríguez, Picó, Font, & Mañes, 2001; Wu et al., 2009; Yan et al., 2011). To this end, a column was packed with C18 and placed into the flow system.

A selection valve (SV) was used for the conditioning step. The column was washed with methanol and ultrapure water. Then, sample extracts were pumped through the column in order to retain the analytes. After retention, SV was switched to wash the column with ultrapure water and an air stream was pumped through the column to remove the water. Finally, the IV was switched to introduce a volume of methanol into an air carrier stream. So, the retained herbicides were eluted. Then, the eluate was evaporated to dryness and the residue was reconstituted in ultrapure water and analyzed by CE-UV at 245 nm.

3. Results and discussion

3.1. Optimization of CE conditions

1-Butyl-3-methyl imidazolium tetrafluoroborate was selected as electrophoretic buffer for the SUs separation taking into account the literature (Qi, Cui, Chen, & Hu, 2004; Qi et al., 2006; Tian et al., 2007) and its chemical properties. Its water solubility compared

with other ILs (1-butyl-3-methyl imidazolium bis (trifluoromethanesulfonyl) imide or 1-butyl-3-methyl imidazolium hexafluorophosphate) is higher. Therefore, this IL is more suitable to be used as BGE in aqueous CE separations. The imidazolium cations coat the capillary walls, thus producing anodic electroosmotic flow (EOF). This effect is increased with the concentration of IL. The separation of SUs was carried out at normal polarity, so the concentration of IL was tested between 5 mM and 20 mM. At this IL concentration range the electrostatic interactions between the added imidazolium cations with the inner surface of the capillary seem to be relatively weak due to a small amount of coating on the wall, and thus could not have influence to the reversal of EOF. Also, with low concentration of IL it is possible to separate SUs at alkaline pH due to the association between the free imidazolium ions in the bulk solution and the negative charged analytes (pKa SUs 3.2–5.2).

The optimization of IL concentration was carried out by considering the analytes migration time and the electrophoretic resolution. The best results were obtained when 10 mM of IL was used, at pH = 11, but NS and ES appeared together under one peak and the resolution between SMM and CS was not completed.

As pH of the BGE is one of the most important variables in the separation of ionizable analytes, its optimization was carried out working with the selected IL concentration. Although the pKs of SUs are between 3.2 and 5.2, the best separation was found when BGE at pH over 7 was employed. So, separation was performed with alkaline pH (8–11.5). Again, the best migration times were obtained with pH 11, but it was not possible to improve the separation.

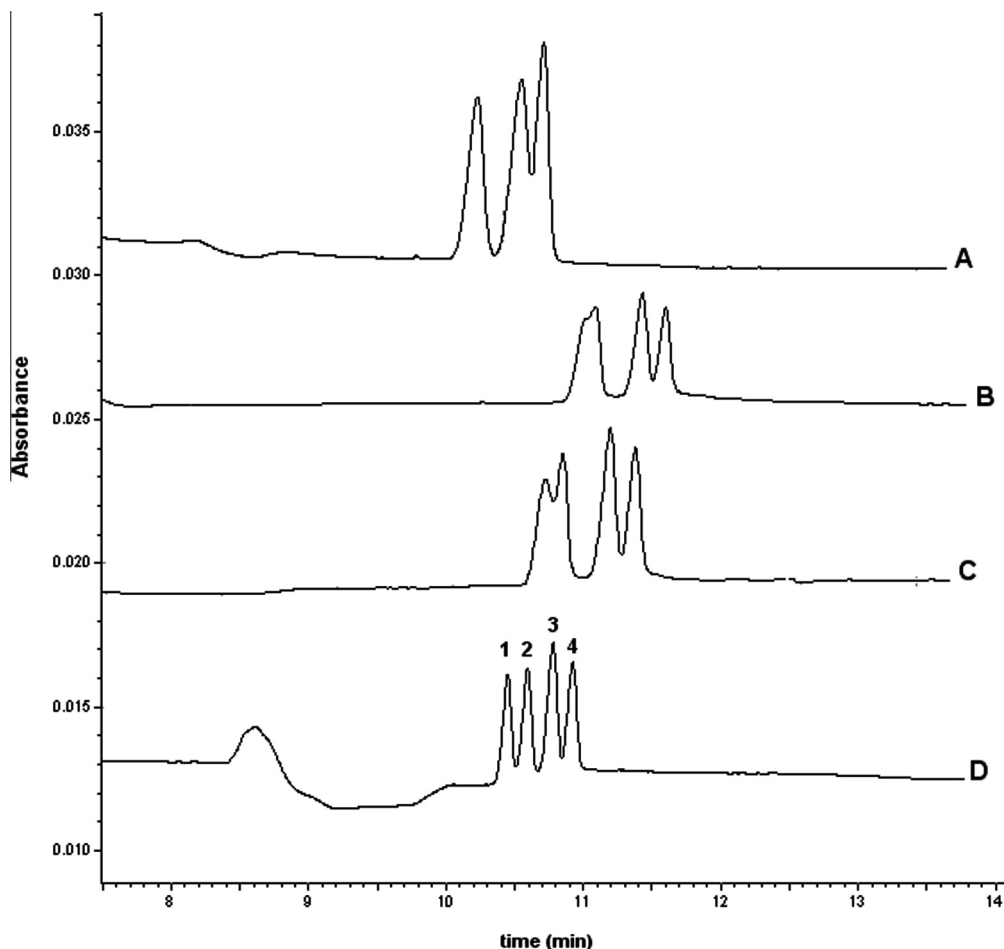


Fig. 1. Electropherograms of standard solution herbicides (2 mg L^{-1} of each analyte) with different BGE. (A) 10 mM IL, pH 11. (B) 10 mM IL and 10% v/v methanol, pH 11. (C) 10 mM IL, and 10% v/v acetonitrile, pH 11. (D) 10 mM IL and SC-SWCNTs (2 mg L^{-1}), pH 11. Peaks: (1) NS, (2) ES, (3) SMM, (4) CS.

3.2. The combined used of *bminBF₄* and SC-SWCNTs as buffer solution

As the resolution of four analytes could not be attained when only *bminBF₄* was used, methanol and acetonitrile were tested as additive in the BGE with the aim to improve the separation. When different quantities of these organic solvents (10–20% v/v) were added, an improvement was noticed, but it was not enough as can be seen in Fig. 1 (electropherograms A, B and C).

When IL and SC-CNTs were combined, an additional interaction between the imidazolium cations and the π -electron network of nanotubes occurs. This interaction improves the dispersion of the CNTs avoiding their possible aggregation, which can clog the capillary and generate an unstable electrophoretic system. Also, a novel interaction between the analytes and nanotubes dispersions was expected to be responsible for the variation of the electrophoretic behavior of SUs and their electrophoretic resolution. It could be observed after the comparison between the electrophoretic separation with and without SC-SWCNTs in the buffer solution (Fig. 1, electropherograms A and D).

So, it was necessary to optimize the type of CNTs that was added to the BGE and their concentration. Surfactant Coated Multi-walled carbon nanotubes (SC-MWCNTs) and Surfactant Coated Single-walled carbon nanotubes (SC-SWCNTs) were tested adding 2 mg L⁻¹ of each one to the electrophoretic buffer. The best resolution was obtained when SC-SWCNTs was used, so three concentrations of this solution (1.0; 2.0; and 2.5 mg L⁻¹) were proved. With 1.0 mg L⁻¹, the peaks for NS and ES were not totally resolved. With 2.0 and 2.5 mg L⁻¹ of SC-SWCNTs it was possible to achieve a complete resolution for the four peaks, so 2.0 mg L⁻¹ was selected as the optimum concentration taking into account the shorter migration times.

On the other hand, the baseline was not sufficiently stable, so a low concentration of sodium borate solution (2 mM) was added to the BGE in order to improve it.

In summary, the BGE composition was: 10 mM *bminBF₄*, 2 mM sodium borate solution and 2 mg L⁻¹ SC-SWCNTs.

The other electrophoretic variables, applied voltage, temperature of the cartridge and the hydrodynamic injection parameters were study. The applied voltage was varied between 15 and 25 kV while the cartridge temperature was changed between 15 and 30 °C. The values that provided an adequate separation in terms of resolution and analysis time were 15 kV and 22 °C. Different times of injection were tested (0.5 psi of pressure): 10 s, 15 s, and 20 s. The best results were obtained injecting during 15 s.

3.3. Extraction procedure optimization

One of the most important variables in this step is the extraction solution. As it has been reported in the literature, different mixtures of acidic or basic solvents and acetonitrile, methanol or acetone were tested for the extraction of SUs from soil and grains

(Kang et al., 2011; Wu et al., 2009). Acidic or basic solvents in extraction process are used because the analytes can be ionized in them. In order to obtain the best extraction solvent, the PB solutions were prepared at different pHs (6, 7, 8.5, 9 and 9.5) taking into account the analyte pK_a values. Then 20% v/v of organic solvents was added and these mixtures were proved during an extraction time of 30 min. When acetone was used, high amounts of pigments in the extracts were observed. Besides, stained sample extracts were obtained when acetonitrile was used. When methanol is added to PB solutions, the cleanest sample extracts were obtained. These tests were performed at the proposed pH range and it was observed that this parameter does not affect the extraction procedure. On the other hand, it is clear that the organic solvent type has an important influence on it. Also, the extraction time was evaluated between 25 and 60 min. When this parameter was above 30 min, the extraction of the analytes was not improved and interferences could be observed in the electropherograms. Magnetic stirring, ultrasonic bath and mechanical stirring were tested in order to obtain the best extraction. It was observed that a high amount of interferences is coextracted with the analytes when the procedure was assisted by ultrasonic bath and the analyte signals were affected. Moreover, mechanical stirring was not useful due to low extraction for all analytes. In short, the best conditions for extraction procedure were: a PBS (pH 9) / methanol mixture with a magnetic stirring during 30 min. This optimization was carried out with wheat sample fortified with 100 µg kg⁻¹ of each analyte. These parameters also were optimal for the sorghum samples.

3.4. Off-line cleanup and preconcentration step

As the concentration of these herbicides in grain samples is low, a continuous flow system with an IV and a SV was developed to carry out an off-line SPE pre-treatment. In this way, it was possible to preconcentrate the analytes and to clean up the samples. For this purpose, the pH of the obtained extract was adjusted at 2.5. Under this condition the SUs are in molecular form and the analytes retention in SPE column is more efficient. A column with 100 mg of C18 was selected. Different volumes of methanol (2–6 mL) and water (1–5 mL) were tested to precondition the column and the best were: 5 mL of methanol and 2 mL of water. Then, an air stream flowed during 5 min at 1.60 mL min⁻¹ in order to dry the column. After that, 10 mL of conditioned extract was passed through the column at a flow rate of 1.25 mL min⁻¹. Next, the column was washed with 5 mL of water (1.60 mL min⁻¹) and then an air stream was pumped through the column to remove the water. All these steps were performed by using a SV. Methanol and acetonitrile were tested as eluent. The best results were obtained with methanol, probably due to the polarity of the analytes and the sorbent material, so different volumes of it were evaluated (500, 700 and 1000 µL). Finally, 700 µL of methanol was injected in an air

Table 1
Analytical parameters of the proposed method.

Herbicide		Slope ± SD	Intercept ± SD	R ²	Linear Range (µg L ⁻¹)	RSD ^a (%)
NS	Sorghum	3.69 ± 0.21	-74.2 ± 35.15	0.994	10–50	6.7
	Wheat	7.39 ± 0.28	-143.25 ± 47.36	0.997	10–50	5.2
ES	Sorghum	6.83 ± 0.31	-61.7 ± 46.76	0.994	5–50	4.8
	Wheat	9.47 ± 0.27	46.9 ± 41.70	0.997	5–50	3.9
SMM	Sorghum	7.64 ± 0.34	335.01 ± 51.12	0.993	5–50	3.6
	Wheat	11.10 ± 0.54	963.88 ± 82.12	0.993	5–50	2.3
CS	Sorghum	9.20 ± 0.35	272.75 ± 56.62	0.995	5–50	2.4
	Wheat	15.38 ± 0.73	713.98 ± 110.97	0.997	5–50	1.9

^a Mean of ten measurements (n = 10) of matrix-matched calibration solution (20 µg L⁻¹ of each SUs).

carrier stream because this volume produced the total elution of the analytes. Before the CE analysis, the eluate was evaporated to dryness at 65 °C and the residue was reconstituted in 300 µL of ultrapure water.

3.5. Analytical parameters and method validation

As it was mentioned in Section 2.4, pesticides were not found in the samples when the whole proposed method was applied. So, the samples were used as blank matrix for all the fortification experiments.

In a preliminary study, the matrix effect (ME) was evaluated for wheat and sorghum samples. It was carried out by comparing the slope of the calibration curves obtained with standards prepared in solvent and the one obtained when matrix-matched standards were used, working at the same linear ranges. The relationship between both slopes (slope matrix/slope solvent) was calculated. It was observed that the ME was important in sorghum samples because the obtained value was not close to 1, but this behaviour was not observed in wheat samples. Moreover, these comparisons were performed by means of a *t*-test and the same results were obtained. As an example it was included the results for the comparison between the slope of calibration curve with solvent standards and that one when matrix-matched standards for NS in sorghum sample was used. The $t_{\text{calculated}}$ value was 9.32 and it is larger than the $t_{\text{tabulated}}$ value ($t_{0.05,6}$), so the slopes are significantly different and this indicates the ME. So, the quantification of the analytes in both matrices was carried out by using matrix-matched standard solutions taking into account the recommendation of DG-SANCO Guidelines (European Commission DG-SANCO, Document No. SANCO/10684/2009). Thus, curves present good linearity for all the SUs with determination coefficients (R^2) higher than 0.99. Each point of the calibration graph corresponds to the average of

three individual measurements. The repeatability of the method was evaluated by analyzing 10 replicates of the matrix-matched calibration solution containing 20 µg L⁻¹ of each analyte. These results are shown in Table 1.

The LODs were calculated as three times $S_{y|x}/\text{slope}$ (Miller & Miller, 2002) of the calibration graph. As can be seen in Table 2, LODs obtained were below the MRLs established by EU for these herbicides.

A recovery study was carried out to check the reliability and the applicability of the method. Thus, wheat and sorghum samples were spiked with SUs at two concentration levels (50 µg kg⁻¹ and 100 µg kg⁻¹) and then were analyzed applying the whole method above described. This procedure was carried out by triplicate. The obtained values of the recovery study for each compound are shown in Table 3. As can be seen, these recoveries varied between 80% and 113%, which were acceptable for these cereal samples and the analytes investigated.

4. Conclusions

A simple CE method using IL and CNTs in the buffer solution, to determine four sulfonylureas in grain samples was developed. It was possible to separate NS, ES, SMM and CS in 16 min and with a high resolution when 10 mM bminBF₄, 2 mM sodium borate solution and 2 mg L⁻¹ SC-SWCNTs, at pH 11 was used as BGE. The main novelty of the method is the use of a low concentration of IL combined with CNTs as buffer solution. This generates a novel interaction with the analytes which produce changes in their electrophoretic behavior. It makes possible an easy separation of SU herbicides without using the organic solvents commonly employed in the electrophoretic solution.

For the extraction of SUs residues, a common solvent mixture was used and the cleanup-preconcentration step was carried out by using a continuous flow system in a few minutes.

The obtained RSD % values are satisfactory and the LODs were lower than the MRLs values for each analyte, including the off-line preconcentration. The reliability and the applicability of the method were obtained applying a recovery study with a matrix matches samples methodology. The recovery values verified that the method can be used for the analysis of these four SUs in these kinds of samples.

Acknowledgements

Financial support from the Universidad Nacional del Sur is gratefully acknowledged. V. Springer acknowledges to Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET).

Table 2
Comparison between obtained LODs with the MRLs established by EU.

Herbicide	LOD (µg kg ⁻¹)		MRLs ^a (µg/kg ⁻¹)
	Wheat	Sorghum	
NS	19.2	26.6	50
ES	16.8	20.5	50
SMM	22.2	20.0	NP*
CS	21.6	21.8	100

^a According to EU legislation [Regulation (EC) No 396/2005].

* NP: not permitted.

Table 3
Analysis of spiked grain samples using the proposed method.

Added concentration (µg kg ⁻¹)	Sample			
	Wheat		Sorghum	
	Found concentration (µg kg ⁻¹) ^a	Recovery (%)	Found concentration (µg kg ⁻¹) ^a	Recovery (%)
50				
NS	50.5 ± 0.2	101	46.7 ± 1.2	93.4
ES	54.4 ± 0.6	109	53.8 ± 1.5	108
SMM	54.1 ± 1.7	108	40.0 ± 0.6	80
CS	54.8 ± 1.2	110	56.6 ± 1.4	113
100				
NS	94.1 ± 1.2	94.1	92.6 ± 0.7	92.6
ES	108.5 ± 0.9	108	93.3 ± 1.6	93.3
SMM	105.3 ± 0.9	105	104.7 ± 1.3	105
CS	102.8 ± 0.6	103	106.8 ± 0.7	107

^a Mean of three measurements (mean ± SD).

References

- Anderson, J. L., Armstrong, D. W., & Wei, G. T. (2006). Ionic liquids in analytical chemistry. *Anal. Chem.*, 78, 2892–2902.
- Borissova, M., Vaher, M., Koel, M., & Kaljurand, M. (2007). Capillary zone electrophoresis on chemically bonded imidazolium based salts. *J. Chromatogr. A*, 1160, 320–325.
- Cao, J., Dun, W., & Qu, H. (2011). Evaluation of the addition of various surfactant-suspended carbon nanotubes in MEEKC with an in situ-synthesized surfactant system. *Electrophoresis*, 32(3–4), 408–413.
- Carda-Broch, S., Berthod, A., & Armstrong, D. W. (2003). Solvent properties of the 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid. *Anal. Bioanal. Chem.*, 375, 191–199.
- Chen, Z. L., Kookana, R. S., & Naidu, R. (2000). Determination of sulfonylurea herbicides in soil extracts by solid-phase extraction and capillary zone electrophoresis. *Chromatographia*, 52(3–4), 142–146.
- Dinelli, G., Vicari, A., & Bonetti, A. (1995). Separation of sulfonylurea metabolites in water by capillary electrophoresis. *J. Chromatogr. A*, 700, 195–200.
- EU legislation: Maximum pesticide limits for food products for human consumption and animal feedingstuffs. Regulation (EC) No 396/2005.
- European Commission DG-SANCO: Method validation and quality control procedures for pesticide residue analysis in food and feed, Document No. SANCO/10684/2009, 1 January 2010.
- Furlong, E. T., Burkhardt, M. R., Gates, P. M., Werner, S. L., & Battaglin, W. A. (2000). 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, 135–146.
- Kang, S., Chang, N., Zhao, Y., & Pan, C. (2011). Development of a method for the simultaneous determination of six sulfonylurea herbicides in wheat, rice, and corn by liquid chromatography–tandem mass spectrometry. *J. Agric. Food Chem.*, 59, 9776–9781.
- Losito, I., Amorisco, A., Carbonara, T., Lofiego, S., & Palmisano, F. (2006). Simultaneous determination of phenyl- and sulfonyl-urea herbicides in river water at sub-part-per-billion level by on-line preconcentration and liquid chromatography–tandem mass spectrometry. *Anal. Chim. Acta*, 575, 89–96.
- MacFarlane, D. R., Forsyth, M., Howlett, P. C., Pringle, J. M., Sun, J., Annat, G., et al. (2007). Ionic liquids in electrochemical devices and processes: Managing interfacial electrochemistry. *Acc. Chem. Res.*, 40, 1165–1173.
- Miller, J. N. & Miller, J. C. 2002. Estadística y Quimiometría para Química Analítica. (4th ed.). Madrid: Pearson Education S.A (Chapter 5).
- Moliner-Martínez, Y., Cárdenas, S., & Valcárcel, M. (2007). Surfactant coated fullerenes C60 as pseudostationary phase in electrokinetic chromatography. *J. Chromatogr. A*, 1167, 210–216.
- Nilsson, C., Brinbaum, B., & Nilsson, S. (2011). Nanoparticle-based pseudostationary phases in CEC: A breakthrough in protein analysis? *Electrophoresis*, 32, 1141–1147.
- Pacanowski, Z. (2007). Herbicide use: Benefit for society as a whole-A review. *Pak. J. Weed Sci. Res.*, 13, 135–147.
- Pimentel, D., & Levitan, L. (1986). Pesticides: Amounts applied and amounts reaching pests. *BioScience*, 36, 86–91.
- Plechova, N. V., & Seddon, K. R. (2008). Applications of ionic liquids in the chemical industry. *Chem. Soc. Rev.*, 37, 123–150.
- Qi, S., Cui, S., Chen, X., & Hu, Z. (2004). Rapid and sensitive determination of anthraquinones in Chinese herb using 1-butyl-3-methylimidazolium-based ionic liquid with β -cyclodextrin as modifier in capillary zone electrophoresis. *J. Chromatogr. A*, 1059, 191–198.
- Qi, S., Li, Y., Deng, Y., Cheng, Y., Chen, X., & Hu, Z. (2006). Simultaneous determination of bioactive flavone derivatives in Chinese herb extraction by capillary electrophoresis used different electrolyte systems-Borate and ionic liquids. *J. Chromatogr. A*, 1109, 300–306.
- Qin, W., & Li, S. F. Y. (2002). An ionic liquid coating for determination of sildenafil and UK-103,320 in human serum by capillary zone electrophoresis-ion trap mass spectrometry. *Electrophoresis*, 23, 4110–4116.
- Qin, W., Wei, H. P., & Li, S. F. Y. (2003). 1,3-Dialkylimidazolium-based room-temperature ionic liquids as background electrolyte and coating material in aqueous capillary electrophoresis. *J. Chromatogr. A*, 985, 447–454.
- Rodríguez, R., Picó, Y., Font, G., & Mañes, J. (2001). Analysis of post-harvest fungicides by micellar electrokinetic chromatography. *J. Chromatogr. A*, 924, 387–396.
- Seddon, K. R. (1997). Ionic liquids for clean technology. *J. Chem. Technol. Biotechnol.*, 68, 351–356.
- She, Y., Cao, W., Shi, X., Lv, X., Liu, J., Wang, R., et al. (2010). Class-specific molecularly imprinted polymers for the selective extraction and determination of sulfonylurea herbicides in maize samples by high-performance liquid chromatography–tandem mass spectrometry. *J. Chromatogr. B*, 878, 2047–2053.
- Springer V. & Lista A.G. (2010). A simple and fast method for chlorsulfuron and metsulfuron methyl determination in water samples using multiwalled carbon nanotubes (MWCNTs) and capillary electrophoresis. *Talanta*, 83, 126–129.
- Springer, V., & Lista, A. G. (2012). Micellar nanotubes dispersed electrokinetic chromatography for the simultaneous determination of antibiotics in bovine milk. *Electrophoresis*, 33, 2049–2055.
- Suárez, B., Simonet, B. M., Cárdenas, S., & Valcárcel, M. (2007). Surfactant-coated single walled carbon nanotubes as a novel pseudostationary phase in capillary EKC. *Electrophoresis*, 28, 1714–1722.
- Tian, K., Wang, Y., Chen, Y., Chen, X., & Hu, Z. (2007). Application of 1-alkyl-3-methylimidazolium-based ionic liquids as background electrolyte in capillary zone electrophoresis for the simultaneous determination of five anthraquinones in rhubarb. *Talanta*, 72, 587–593.
- Valcárcel, M., Cárdenas, S., Simonet, B. M., Moliner-Martínez, Y., & Lucena, R. (2008). Carbon nanostructures as sorbent materials in analytical processes. *Trends Anal. Chem.*, 27, 34–43.
- Wu, Q., Wang, C., Liu, Z., Wu, C., Zeng, X., Wen, J., et al. (2009). Dispersive solid-phase extraction followed by dispersive liquid–liquid microextraction for the determination of some sulfonylurea herbicides in soil by high-performance liquid chromatography. *J. Chromatogr. A*, 1216, 5504–5510.
- Xu, Y., Li, J., & Wang, E. (2008). Microchip micellar electrokinetic chromatography based on one functionalized ionic liquid and its excellent performance on proteins separation. *J. Chromatogr. A*, 1207, 175–180.
- Yan, C., Zhang, B., Liu, W., Feng, F., Zhao, Y., Yonggang, & Hui, Du. (2011). Rapid determination of sixteen sulfonylurea herbicides in surface water by solid phase extraction cleanup and ultra-high-pressure liquid chromatography coupled with tandem mass spectrometry. *J. Chromatogr. B*, 879, 3484–3489.
- Yanes, E. G., Gratz, S. R., Baldwin, M. J., Robinson, S. E., & Stalcup, A. M. (2001). Capillary electrophoresis application of 1-alkyl-3-methylimidazolium-based ionic liquids. *Anal. Chem.*, 73, 3838–3844.