



Analytical Methods

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



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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%.

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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,

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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 sulfonyleureas 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 sulfonyleureas 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 (bminBF_4) 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 \times 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 bminBF_4 , 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 $\mu\text{g kg}^{-1}$ and 100 $\mu\text{g kg}^{-1}$ 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.

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