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A simple and fast method for chlorsulfuron and metsulfuron methyl determination in water samples using multiwalled carbon nanotubes (MWCNTs) and capillary electrophoresis

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ABSTRACT

A new method to determine metsulfuron methyl (MSM) and chlorsulfuron (CS) in different water samples was developed. It consists in a solid phase extraction (SPE) procedure using multiwalled carbon nanotubes (MWCNTs) as sorbent material in combination with capillary zone electrophoretic determination. To carry out the pre-concentration step, a simple flow injection system was developed and optimized. Thus, 250 μL of aqueous solution containing methanol 50% (v/v) and acetonitrile 2% (v/v) as eluent, 10 mL of sample and a flow rate of 1.15 mL min^{-1} were selected. The CE variables also were optimized. A rapid determination and good resolution of two herbicides were obtained within 9 min using a simple electrophoretic buffer (50 mmol L^{-1} sodium tetraborate with 3% of methanol, pH = 9.0). Under the optimum conditions, the calibration curves were linear between 0.5 and 6 μg L^{-1} for MSM and CS with R^2 = 0.995 and 0.997, respectively. The repeatability of the proposed method, expressed as relative standard deviation (RSD), varied between 4.1% and 5.4% (n = 10) and the detection limits for MSM and CS were 0.40 and 0.36 μg L^{-1}, respectively. Good results were achieved when the proposed method was applied to spiked real water samples. The recoveries percentages of the two analytes were over the range 86–108%.

1. Introduction

Since Iijima's discovery in 1991 till now, the chemical aspects of carbon nanotubes (CNTs) have generated special attention. These characteristics made it possible to use the CNTs in different analytical applications: as starting materials in the development of sensors and biosensors, as pseudo stationary phase in chromatography and capillary electrophoresis, as solid phase extraction, among others [1–3].

The use of CNTs as solid phase extraction (SPE) sorbent, for extraction of both inorganic and organic compounds, is a relatively important field of application, especially in the last years. SPE is a widely used technique in analytical sciences to carry out the pre-concentration of analytes or/and the clean-up of samples. In this way, the sensibility and selectivity of the applied method are increased, and it is possible to automate and to simplify the pre-treatment procedure.

CNTs have proven to be an excellent sorbent material due to their strong adsorption capacity towards a wide variety of compounds, together with their large specific surface area. The non-covalent interactions established between the analyte and the nanoparticles include ionic interactions (e.g., dipole–dipole), hydrogen bonds, π–π stacking, dispersion forces, dative bonds, and the hydrophobic effect [2].

There are several examples in the literature of the use of CNTs for the pre-concentration of analyte traces. Multiwalled carbon nanotubes (MWCNTs) have been used for the determination of triazines in water samples [4], sulfonamides residues in food of animal origin [5], extraction and determination of polycyclic aromatic hydrocarbons (PAHs) in environmental waters [6], tetracyclines residues in surface water [7]. Likewise, single-walled carbon nanotubes (SWCNTs) have been used for determination of butyltin compounds in seawater [8] and as alternative, carboxylated single-walled carbon nanotubes (c-SWCNTs) have been proposed as a new sorbent for the pre-concentration of non-steroidal anti-inflammatory drugs [9], among other works.

Lately, capillary electrophoresis (CE) has become important in separation science, because it offers various advantages over other techniques, such as faster separations, higher resolution power and requiring smaller sample amounts. On the other hand, one of the main drawbacks of CE is the low sensitivity obtained when

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UV detectors are coupled. Therefore, a pre-concentration step is usually required to determine low concentrations of analytes in biological, food or environmental samples.

Herbicides are often used to improve the agricultural production. Their great consumption can cause environment pollution due to their accumulation. Sulfonylurea herbicides, which were firstly introduced in the 1980s [10], are used for weed control in many crops. Two of the most used pesticides of this family in our region are chlorsulfuron (CS) and metsulfuron methyl (MSM). They are widely used in the production of wheat, soybean and corn. Therefore, their residues can be found in water sources that can be potentially used for human and animal consumption. For this reason, it is important to develop rapid and simple methods to determine sulfonylurea residues at low levels.

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 [11]. The Argentine legislation only establishes a maximum concentration level for total pesticides in 100 μg L^{-1} [12].

Several techniques are used to determine sulfonylureas in water samples. High performance liquid chromatography with UV-V detector [13–15], liquid chromatography coupled to mass spectrometry [16], capillary electrophoresis [17,18], bioassays [19], are among the most frequently reported in the bibliography. When UV-V detectors are used, a pre-concentration is almost always necessary to do. C18, C60 (fullerenes) and CNTs are the most common sorbent materials that are used to carry out the pre-concentration of sulfonylureas [15,20]. CNTs have different properties according to their size and morphology. Only few studies have reported the use of lower outer diameter (o.d.) MWCNTs for SPE of pesticides [21], whereas in most of the works MWCNTs of wide o.d. have been employed (including sulfonylureas). On the other hand, there is a lot of information about the usefulness of using MWCNTs instead SWCNTs to carry out a pre-concentration step.

The present study proposes using lower outer diameter MWCNTs as sorbent material in the SPE pre-treatment of water samples for further determination of sulfonylureas. Afterwards, CE with UV detection is used to determine the analytes.

As CS and MSM are the most widely used herbicides in fields of our region, their concentration determination is the goal. The pre-treatment of the samples is automatized by a simple flow injection system which includes a minicolumn packed with lower o.d. MWCNTs. After this step, the herbicides are analyzed using capillary zone electrophoresis (CZE). By this way, a simple and rapid analysis of this analytes is possible.

2. Experimental

2.1. Chemicals

All reagents were of analytical reagent grade and ultra pure water (>18 MΩ cm^{-1}) was used.

Chlorsulfuron and metsulfuron methyl were purchased from Sigma–Aldrich. A 28 mg L^{-1} standard stock solution of each analyte was prepared in ultra pure water and stored at 4 °C. These solutions are stable for more than 3 months. The standard working solutions were daily prepared by appropriate dilutions of stock solutions.

MWCNTs with average external diameters of 13–16 nm and purity >95% were provided by *Bayer*. Before used, MWCNTs were dried at 120 °C for 2 h, according to the consulted literature [20]. A sodium dodecyl sulfate (SDS) solution with 2-butanol was used to prepare the dispersion of MWCNTs.

The electrophoretic buffer was prepared with sodium borate (Baker), HCl (Merk) and methanol (Biopack).

2.2. Instrumentation

Beckman Coulter capillary electrophoresis instrument MDQ equipped with a diode array detector operating at 231 nm was used. The capillaries were also from Beckman System. Control and data processing was carried out with 32 Karat software.

Gilson Minipuls—3 peristaltic pump, PTFE tubing of 0.5 mm i.d., pump tubing and Rheodyne 5041 injection valve were used. An ultrasonic bath (70 W–60 Hz) was used to disperse the MWCNTs.

The minicolumn used for SPE procedure was prepared by packing a *Tygon*® tube (9 mm length × 2.06 mm i.d.) with dispersed

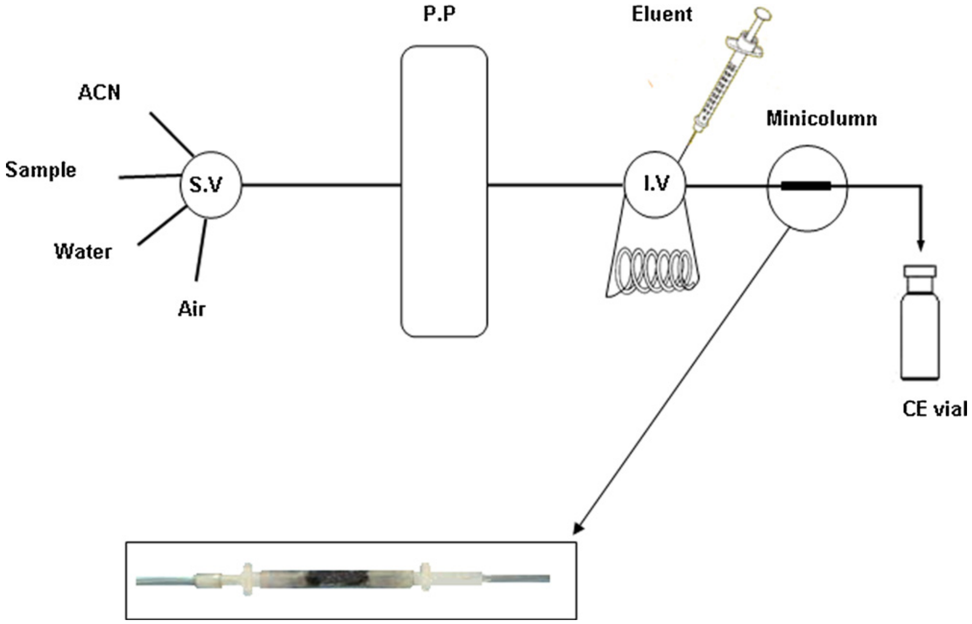

Fig. 1. Continuous flow system for the pre-concentration step. ACN: acetonitrile; SV: selection valve; PP: peristaltic pump; and IV: injection valve.

MWCNTs. At the end of the tube, a cellulose frit was used to hold the carbon nanotubes in the cartridge.

2.3. SPE procedure

A flow injection system was developed to carry out the pre-concentration step (Fig. 1). A minicolumn was packed with 6 mg of dispersed MWCNTs and it was placed in the flow system. The MWCNTs were suspended in a 3 mmol L^{-1} SDS aqueous solution containing 10% (v/v) of 2-butanol, before using it as sorbent material.

The MWCNTs minicolumn was pre-conditioned by washing it with 5 mL of acetonitrile and 3 mL of ultrapure water. Then, 10 mL of sample or standard solutions was pumped through the minicolumn in order to retain the analytes. After retention, the selection valve (SV) was switched to wash the column with 2 mL of ultrapure water. Then, an air stream was pumped through the minicolumn to remove the water. All this steps were carried out at a flow rate of 1.15 mL min^{-1}. Finally, the injection valve (IV) was switched to introduce 250 μL of methanol 50% (v/v) with 2% (v/v) of acetonitrile into an air carrier stream. So, the retained herbicides were eluted. Then, the eluate was analyzed by CE–UV at 231 nm.

2.4. CE analysis

The separation was carried out in a fused-silica capillary (50 cm effective length, 50 μm i.d.) with a positive power supply of 25 kV at 25 °C. Sample injections were performed in hydrodynamic mode for 15 s at 0.5 psi. The electrolyte buffer was 50 mmol L^{-1} sodium borate with 3% (v/v) methanol and HCl 0.4 mol L^{-1} at pH 9.0 The capillary was conditioned daily by flushing it with 0.1 mol L^{-1} NaOH (5 min), ultrapure water (3 min) and buffer solution (5 min). The separation was assisted with pressure (0.3 psi).

3. Results and discussion

3.1. Pre-concentration of analytes

3.1.1. Suspension conditions and packing the minicolumn

As a result of Van der Waals attractions, nanoparticles aggregate easily and, therefore, they were insoluble in common solvents. Because of this, we used long chain surfactants to disperse the MWCNTs to avoid their aggregation and thus, easily fill the minicolumn.

For this purpose, SDS solutions of different concentrations (1–22 mmol L^{-1}) and containing different amounts of 2-butanol were prepared using an ultrasonic bath (70 W–60 Hz) during 15 min. It was observed that SDS concentrations above 10 mmol L^{-1} caused overpressure in the flow system and the frit could not retain the MWCNTs. When the SDS concentration was lower than 3 mmol L^{-1} the MWCNTs suspension was not suitable. So, 3 mmol L^{-1} SDS solution was selected. To maintain a stable suspension of MWCNTs different amounts of 2-butanol were added to the SDS solution. A concentration of 10% (v/v) 2-butanol was optimal. This solution allows MWCNTs being suspended and to fill the minicolumn adequately.

It is well-known that, if the columns packed with solid CNTs or with suspended CNTs are small, the simplification of the pre-treatment step is possible.

For this reason, three classes of packing were tested. So, the column was filled with solid MWCNTs, with finely powdered carbon nanotubes, and with suspended MWCNTs. In all cases, a small amount of CNTs was used in order to minimize the formation and dimensions of aggregates.

To evaluate the best type of sorbent packing, UV absorption spectra of eluates were recorded. The column packed with solid MWCNTs gave the best results, but it generated overpressure in the system. For this reason, we choose the column with MWCNTs suspended.

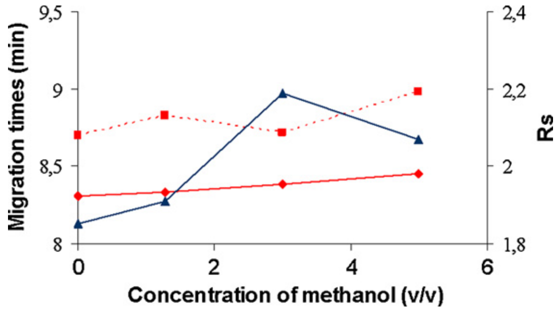

Fig. 2. Effect of methanol concentration in the electrophoretic buffer on the analytes migration times and resolution (Rs) ((------■) CS and (——◆) MSM).

Since, the objective of this work is to minimize the pre-concentration step, a minicolumn of 9 mm of length was selected and different internal diameters (i.d.) were evaluated. It was observed that when i.d. was larger than 2.0 mm, overpressure in the continuous system was generated.

3.1.2. Optimization of extraction conditions

Due to the dimensions of the minicolumn and the amount of MWCNTs used, the selected sample volume was 10 mL. The adsorption of analytes was not complete when the volumes were higher than 10 mL.

The bibliography recommended acetonitrile/acetic acid (90:10) as eluent for sulfonylureas [15,20]. This mixture was tested but it was not compatible with the electrophoretic buffer used in the CZE. So, other solvent mixtures (50% of methanol, 50% acetonitrile, and 50% (v/v) of methanol with different percentage of acetonitrile) were studied. The best elution was obtained with the mixture of methanol 50% (v/v) with 2% (v/v) acetonitrile.

Also, the volume of elution solvent was evaluated within the range of 50–350 μL. From the different UV absorption spectra of eluates, it can be seen that the optimal volume of elution was 250 μL. The elution flow rate also was 1.15 mL min^{-1} as well.

3.2. Optimization of CE–UV analysis

Firstly, it was tested MEKC (micelle electrokinetic chromatography), like recommend the bibliography, to carry out the analytes separation using sodium borate solution and SDS as electrophoretic medium. The obtained results were not good. So, CZE mode was employed.

Taking into account the pK_a values of chlorsulfuron and metsulfuron methyl, a pH range between 6.0 and 10.0 for the electrophoretic buffer was studied. The best resolution was obtained at pH 9.0 using sodium borate solution, as mentioned in Section 2.4. Also, the percentage of methanol added to the buffer was tested between 0% and 5%, in order to obtain the best resolution and an efficient time analysis.

Table 1
Optimum values for CE operational variables.

Optimized variables	Evaluated range	Optimal value
Electrophoretic buffer concentration	20–50 mmol L^{-1}	50 mmol L^{-1}
Buffer pH	6–10	9
% methanol	0–5%	3%
Separation voltage	15–25 kV	25 kV
Applied pressure	0.3–1.0 psi	0.3 psi
Injection time	10–25 s	15 s

Table 2
Analysis of spiked water samples using the proposed method.

	Added ($\mu g\,L^{-1}$)	Found ($\mu g\,L^{-1}$)	Recovery (%)
Lake sample			
MSM	2.5	2.65 ± 0.04	106
MSM	1.0	1.08 ± 0.06	108
CS	2.5	2.19 ± 0.08	87.6
CS	1.0	0.89 ± 0.06	89
Creek sample			
MSM	2.5	2.51 ± 0.06	100.4
MSM	1.0	1.03 ± 0.18	103
CS	2.5	2.31 ± 0.23	92.4
CS	1.0	0.92 ± 0.08	92
Reservoir sample			
MSM	2.5	2.56 ± 0.17	102.4
MSM	1.0	1.02 ± 0.06	102
CS	2.5	2.18 ± 0.19	87.2
CS	1.0	0.88 ± 0.06	88
Underground sample			
MSM	2.5	2.55 ± 0.07	102
MSM	1.0	1.08 ± 0.05	108
CS	2.5	2.54 ± 0.25	101.6
CS	1.0	0.86 ± 0.04	86

As it is shown in Fig. 2, 3% (v/v) of methanol was optimum.

Three different injection times were tested in order to evaluate the effect of this variable on the analytes migration times and on the resolution. A similar resolution was obtained with 15 and 20 s of injection but the migration times were lower with 15 s, so this injection time was selected. The studied ranges and optimum values for the other operational variables are shown in Table 1.

3.3. Analytical parameters and analysis of real samples

Under the optimal conditions above mentioned, high efficient separation and enrichment have been achieved for the quantitative analysis of chlorsulfuron and metsulfuron methyl.

The calibration curves were $y = 838.71x - 18.99$ with $R^2 = 0.997$ and $y = 777.31x - 205.66$ with $R^2 = 0.995$, for CS and MSM, respectively. Each point of the calibration graph corresponds to the average of three individual measurements. The linear range for the both analytes was 0.5–6.0 $\mu g\,L^{-1}$. The LODs calculated as 3 times $S_{y/x}$/slope [22] of the calibration graph were 0.36 $\mu g\,L^{-1}$ for CS and 0.40 $\mu g\,L^{-1}$ for MSM. The precision of the method was evaluated by analysing 10 replicates of the standard solution containing 3 $\mu g\,L^{-1}$ and the relative standard deviation was 5.4% for CS and 4.1% for MSM.

Different water samples were analyzed to prove the applicability of the proposed method to determine CS and MSM. With this purpose, surface (reservoir, lake and creek) and underground real water samples were analyzed. Neither CS nor MSM were detected in the analyzed real samples, so they were spiked with two different concentrations of the analytes. In Table 2, it can be seen the obtained recoveries when the proposed method was applied to real samples and they demonstrated the reliability of the method. Fig. 3 shows a typical electropherogram of surface water sample spiked with 3 $\mu g\,L^{-1}$ of each sulfonylurea.

4. Conclusion

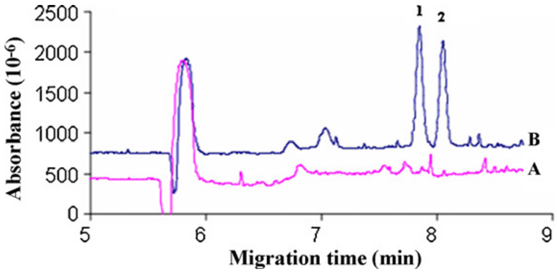

Fig. 3. Electropherogram of lake water sample: (A) sample treated with SPE procedure; (B) the same sample spiked with 3 $\mu g\,L^{-1}$ of MSM and CS, respectively. The peaks were (1) MSM and (2) CS. The experimental conditions were 50 $mmol\,L^{-1}$ sodium borate, 3% methanol at pH 9.0.

A simple and fast procedure to pre-concentrate sulfonylureas using MWCNTs was developed and the analytes are determined by CZE in less than 9 min. The developed flow injection system allows using small amount of MWCNTs to carry out the pre-concentration step. In this way, it is possible to minimize the amount of organic solvents used and the sample volume. Also, the time spent in the sample processing was reduced if compared with other procedures reported in the literature.

Moreover, a simple CZE mode was used employing a common buffer solution. On the other hand, the method presents a good repeatability and the recovery study showed that the proposed method provide satisfactory results when it is applied to different water samples.

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