An integrated on-line method for the preconcentration and simultaneous determination of metsulfuron methyl and chlorsulfuron using oxidized carbon nanotubes and second order fluorescent data

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ABSTRACT

Trace amounts of two sulfonylurea herbicides widely used for crops protection, metsulfuron methyl (MSM) and chlorsulfuron (CSF) were simultaneously determined taking into account the different kinetic photodegradation behavior of their photoproducts in alkaline medium. As the analytes are present at trace concentration levels, a preconcentration by sorption on a mini-column packed with oxidized multiwall carbon nanotubes (ox-MWCNTs) at pH 3.0 was performed. The retained analytes were removed from the ox-MWCNTs mini-column with a mixture of ACN contained 10% (v/v) of NaOH pH 12.5. A total enrichment factor of 26-fold for a 14.50 mL sample volume was obtained. The eluate was photodegraded by UV radiation during 126 s and the fluorescent spectra corresponding to the analytes photoproducts were registered overtime between 300 and 500 nm. The kinetic second order data were analyzed by unfolded-partial least squares-residual bilinearization (U-PLS/RBL) and multidimensional-partial least squares-residual bilinearization (N-PLS/RBL) algorithms. The relative error of prediction (REP %) for N-PLS/RBL was 7.73% for MSM and 6.37% for CSF. In the case of U-PLS/RBL, this statistical parameter was 7.75% for MSM and 7.23% for CSF, respectively. The limits of detection (LOD) were 0.19 $\mu g\,L^{-1}$ for MSM and 1.14 $\mu g\,L^{-1}$ for CSF using N-PLS/RBL and 0.21 $\mu g\,L^{-1}$ for MSM and 1.03 $\mu g\,L^{-1}$ for CSF when U-PLS/RBL was applied.

The entire procedure was performed in an on-line integrated fully automated flow system coupled to a low mercury UV lamp (15 W, 254 nm) and a spectrofluorometer. In this manner, the preconcentration, photodegradation and detection steps were performed in a reproducible way.

After optimization, the method was successfully applied to the analysis of real water samples obtained in the south part of Buenos Aires province and used for irrigation and consumption.

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1. Introduction

The sulfonylurea herbicides (SUHs) are a class of substituted urea herbicides used worldwide and, in particular, in the agricultural region surrounding the city of Bahía Blanca, Argentina. Potential routes of human exposure to these herbicides include consumption of contaminated food or drinking contaminated water. In particular, metsulfuron methyl (MSM) and chlorsulfuron (CSF) are two SUHs that can be found together in several commercial formulations (Alianza 75 WDG, Argus 75 WG, Finesse® WG and others), and their levels in water sources intended for both animal and human consumption must be monitored. Only allowable amounts of SUHs for drinking water are

established. Argentina's regulations stipulated a maximum concentration level of 100 $\mu g\,L^{-1}$ for total pesticides in water sources with conventional treatment [1].

Because MSM and CSF are usually present in complex matrices and has to be detected at low concentrations, the application of extraction and preconcentration procedures to perform the quantitative analysis of them is required.

The simultaneous determination of MSM and CSF using a solid-phase extraction (SPE) as an extraction approach and conventional sorbents (mainly C18) has been performed using different techniques. First attempts to determine both analytes were performed by gas chromatography [2], and by capillary electrophoresis [3]. Usually, high-performance liquid chromatography (HPLC) and ultra-high-performance liquid chromatography (UHPLC) have been the most extensively used techniques for these polar to middle polar and thermally labile compounds determination [4–6]. HPLC or UHPLC coupled with

mass spectrometry (MS) or tandem mass spectrometry (MS/MS) detection techniques, which have the advantages of improved sensitivity and high degree of selectivity, have been proven to be a powerful tool for the determination of trace levels of SUHs [7,8]. Additionally, a capillary electrophoresis method has been proposed by Springer et al. [9] as an alternatively technique to achieve the separation and determination of these compounds using raw MWCNTs as a sorbent.

As a simple approach for the SUHs determination, their fluorescent behavior under UV irradiation in an aqueous micellar mobile phase was exploited. Since MSM and CSF are naturally non-fluorescent herbicides, their photochemical induced fluorescence signal was used to determine their concentrations either individually [10] or through the first-derivative of their binary mixtures [11]. Here, a flow injection analysis (FIA) system was proposed after off-line preconcentration employing successive liquid-liquid extraction steps.

Due to their outstanding chemical and physical properties, carbon nanotubes (CNTs) have been widely used in sorbent-based extraction techniques [12]. To the well-known advantages of using CNTs as sorbents, the benefits of automating conventional SPE procedure were provided. SPE procedure requires several steps to be performed in a reproducible way, and this characteristic can perfectly be achieved with the development of on-line preconcentration techniques. As expected, automation of SPE procedure allows minimize solvent and sample consumption, reduction of the analysis time and avoids exposure to potential hazards since the whole procedure takes place in a close system. Additionally, the quantity of sorbent that is employed when CNTs are used could be reduced compared to conventional sorbents used in SPE cartridges, leading to miniaturization of the process [13].

On the other hand, due to the sorption/desorption cycles, the compaction of CNTs in the packed column can occur leading to a decrease in the performance of the adsorption process and overpressure in the flow system. One interesting alternative, not only to enlarge their potential but also to enhance their solubility, is the functionalization of the CNTs surface by an acidic oxidative treatment. The oxidation process offers a larger number of oxygen containing functional groups, but also a more hydrophilic surface structure, which makes the CNTs more hydrophilic and suitable for sorption of moderately to polar compounds [14].

The increasing use of chemometrics in environmental studies over the last two decades corresponds to the intensive research dedicated to test and prove how powerful the data processing techniques can be in this field and also to the availability of appropriate software. Nevertheless, the spectroscopic measurement lacks of the required selectivity, particularly when similar chemical compounds must be analyzed in complex samples. The lack of selectivity or the presence of interfering species linked to natural samples demands the application of chemometric methods based on multivariate calibration techniques in order to overcome these limitations and to complement these analytical methodologies [15].

Multivariate calibration methods are focused on the establishment and application of mathematical models that that relate to multivariate instrumental signals with analyte concentrations or sample properties [16]. The possibility to quantify an analyte in the presence of interferences, as long as the interfering compounds are present in the calibration samples during the establishment of the calibration model, is the so-called first-order advantage. The second-order advantage implies that the analyte contribution can be appropriately modelled, quantitatively estimated and resolved in the presence of unknown interferences, absent in the calibration samples [15]. The use of fluorescence and chemometric tools applied to the quantification of pesticides was demonstrated in the literature [17,18].

In a previous article, a flow-batch analysis (FBA) system to automate the preconcentration, photodegradation and fluorescent detection of MSM photoproducts in different water samples was developed. The SPE procedure was performed using a conventional sorbent (C18) and the photodegradation and detection were performed in a chamber [19].

The purpose of this work was to develop a fully automated flow manifold to achieve the simultaneous preconcentration and fluorescent determination of MSM and CSF by a chemometric approach taking into account the different kinetic photodegradation behavior of their photoproducts. The overlapped signals demand the use of algorithms that exploited the second order advantage, such as unfolded-partial least squares-residual bilinearization (U-PLS/RBL) and multidimensional-partial least squares-residual bilinearization (N-PLS/RBL). Because these analytes are present in environmental water samples in trace levels it is necessary to perform a preconcentration step. To accomplish this aim, an on-line SPE procedure was optimized using ox-MWCNTs as a novel sorbent for the selected analytes. The SPE mini-column was coupled to a reactor coiled around an UV lamp and photoproducts were then propelled to the spectrofluorometer to acquire the corresponding over time spectra. To the best of our knowledge, it is the first time that the different kinetics of photodegradation of MSM and CSF were studied and used to determine them simultaneously by a chemometric approach.

2. Experimental

2.1. Reagents

Metsulfuron methyl (MSM) and chlorsulfuron (CSF) were purchased from Sigma-Aldrich, Germany. A 140 mg L^{-1} standard stock solution of each analyte was prepared in acetonitrile (≥99%, Merck, Germany, ACN) and stored in dark bottles at 4 °C. Calibration and validation set solutions were prepared daily by an appropriate dilution of the stock solutions with HCl pH 3.0.

All other solutions were prepared using analytical-grade reagents and ultra-pure water (18 MΩ cm^{-1}).

Nitric and sulfuric acids were obtained from Sigma-Aldrich (Germany). 50.0 mL NaOH (Merck, Germany) 0.10 mol L^{-1} solution was prepared by dissolving a suitable amount of the solid drug in distilled water. A 0.03 mol L^{-1} NaOH solution (pH 12.5) was prepared by diluting the concentrated solution. The pH of the samples was adjusted using a 0.01 mol L^{-1} HCl (Merck, Germany) solution.

Multiwall carbon nanotubes (MWCNTs) with average external diameter of 13–16 nm and purity >95% were provided by Bayer®. Before used, MWCNTs were dried at 80 °C for 2 h.

2.2. Apparatus and software

The spectrofluorometric measurements were performed on a Jasco® FP 6500 spectrofluorometer. The excitation wavelength was 276 nm and the emission spectra were recorded between 300 and 500 nm. The slit width for excitation and emission were 5 and 10 nm, respectively, and the photomultiplier tube (PMT) voltage was fixed to 475 V. The scan rate was 2000 nm min^{-1}. The fluids were pumped with a Gilson® Minipuls 3 peristaltic pump. A Hellma® 178–712-QS flow cell was used. NResearch® three-way solenoid valves were used to handle all the solutions in the system.

Tygon® tubes were used in all of the pumping channels. A tube with an i.d. of 1.14 mm was used for the ACN-NaOH mixture, whereas tubes with an i.d. of 1.30 mm were used for water, NaOH, air and sample. All the flow system connections were made of PTFE (0.5 mm i.d.). A lab-made photoreactor with a Philips® low mercury UV lamp (15 W, 254 nm) was used. In this device, 5.60 m of a PTFE tube was helically coiled around the UV lamp. An electronic actuator connected to a Pentium® 4 microcomputer was used to control the peristaltic pump, solenoid valves and the photoreactor. The software used to control the flow system was developed in the Labview® 5.1 visual programming language.

The infrared measurements were performed on a FTIR-NIR spectrometer Thermo Scientific Nicolet iS50.