Talanta 129 (2014) 233–240

Contents lists available at ScienceDirect

Talanta

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

Application of a fully integrated photodegradation-detection flow-batch analysis system with an on-line preconcentration step for the determination of metsulfuron methyl in water samples

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ARTICLE INFO

Article history:
Received 17 March 2014
Received in revised form
14 May 2014
Accepted 16 May 2014
Available online 27 May 2014

Keywords:
On-line solid phase extraction
Flow-batch analysis
Photoinduced degradation
Fluorescence
Metsulfuron methyl

ABSTRACT

This work presents the development of a fully automated flow-batch analysis (FBA) system as a new approach for on-line preconcentration, photodegradation and fluorescence detection in a lab-constructed mixing chamber that was designed to perform these processes without sample dispersion. The system positions the mixing chamber into the detection system and varies the instrumental parameters according to the required photodegradation conditions. The developed FBA system is simple and easily coupled with any sample pretreatment without altering the configuration.

This FBA system was implemented to photodegrade and determine the fluorescence of the degradation products of metsulfuron methyl (MSM), a naturally non-fluorescent herbicide of the sulfonylurea's family. An on-line solid phase extraction (SPE) and clean up procedure using a C18 minicolumn was coupled to the photodegradation-detection mixing chamber (PDMC) that was located in the spectrofluorometer. An enrichment factor of 27 was achieved.

Photodegradation conditions have been optimized by considering the influence of the elution solvent on both the formation of the photoproduct and on the fluorescence signal.

Under optimal conditions, the calibration for the MSM determination was linear over the range of 1.00–7.20 μg L^{-1}. The limit of detection (LOD) was 0.28 μg L^{-1}; the relative standard deviation was 2.0% and the sample throughput for the entire process was 3 h^{-1}. The proposed method was applied to real water samples from the Bahía Blanca's agricultural region (Bahía Blanca, Buenos Aires, Argentina). This method obtained satisfactory recoveries with a range of 94.7–109.8%.

1. Introduction

Since the development of automated analytical methods, different applications have been performed to transform batch processes into automated processes. After the development of segmented flow analysis (SFA) [1] and flow injection analysis (FIA) [2], flow-analysis methodologies have been implemented in a variety of analytical techniques [3–7]. Among these techniques, flow-batch analysis (FBA) systems draw upon the useful features of batch and multi-commutation approaches [8]. FBA also offers an excellent alternative to traditional processes for the automation of analytical procedures because of its flexibility and versatility (multi-task characteristics). The main component of a FBA system is the mixing chamber in which different processes, such as sample conditioning, analyte-reagent addition and mixing, are performed. Moreover, one of the main advantages of using the mixing chamber is that compounds of interest can be detected in the chamber, avoiding the transport of material to the detector and the resulting dispersion. Several analytical applications have been developed using the FBA methodology [9].

Because of the public concern with the environmental and human effects of analytical methods, new sample preparation techniques have been developed [10] to incorporate procedures that reduce the use of hazardous chemicals. Therefore, photoradiation is a promising alternative to chemical reagents. Flow methodologies have already shown high potential for the automation of photochemical derivatization methods. These methods are being exploited for the quantification of various analytes upon photodegradation [11,12].

Metsulfuron methyl (MSM) is a sulfonylurea selective systemic herbicide for the post-emergent control of broadleaf weeds and brush, and MSM is added to diverse crops, such as autumn-winter

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http://dx.doi.org/10.1016/j.talanta.2014.05.024
0039-9140/

cereals, rice, maize, and soybean. MSM is moderately persistent in water and highly mobile in soils and has the potential to enter surface waters from field drainage or runoff water. The persistence and mobility of this compound may cause serious damage to the environment and human health. Because of its widespread use in global agricultural production, particularly in the region surrounding Bahía Blanca, Argentina, the MSM level in water sources intended for both animal and human consumption must be monitored.

Many studies have focused on determining the concentration of this herbicide using different techniques. One of the first attempts to determine the concentration of MSM at trace levels in natural waters employed a gas chromatography technique with electron capture detection [13]. Because of the chemical properties of MSM, high-performance liquid chromatography (HPLC) is one of the most used techniques [14–16] combined with off-line preconcentration techniques (dispersive liquid–liquid microextraction, DLLME, or solid phase extraction, SPE) and spectrophotometric detection (DAD). Recently, ultra-high-performance liquid chromatography (UHPLC) with mass spectrometry detection [17] was employed to determine the concentration of this herbicide. Other methods, such as capillary electrophoresis [18,19], bioassays [20], and enzyme immunoassays [21], have often been use in previous studies. Additionally, the photochemical behavior of metsulfuron methyl in aqueous and organic media has been reported [22]. Since MSM is a naturally non-fluorescent herbicide, Coly et al. [23] determined the concentration of this analyte through photochemically induced fluorescence (PIF) detection in an aqueous micellar mobile phase using a flow injection analysis (FIA) system for the detection of MSM after off-line preconcentration employing successive extraction steps. Another study performed by López Flores et al. [24] proposed a flow injection system to preconcentrate and determine the concentration of the MSM photoproduct instead of MSM using solid-phase fluorescence spectroscopy. A suitable solid support was placed inside a flow cell to preconcentrate and retain the photoproduct for detection.

Because of the low levels of MSM present in environmental samples, a preconcentration step is required even for methods with high sensitivities [25]. Furthermore, a clean-up process is also necessary because of the complexity of the sample. Among the extraction techniques, SPE is the most widely used to preconcentrate MSM because of its easy implementation and high preconcentration capabilities. In addition, SPE is able to be automated, which allows a reduction in the analysis time and prevents exposure of operator to potential hazards. In previous studies, however, this process was performed primarily off-line.

The aim of this study was to develop a simple flow manifold to fully automate SPE-photodegradation-detection. The new FBA system for MSM determination implemented both the photodegradation process and the detection step in the mixing chamber that was placed instead of the cell holder in the spectrofluorometer. The proposed system was employed to determine trace levels of MSM in different water samples. For this purpose, an on-line solid-phase extraction (SPE) procedure was coupled to the developed manifold. Generally, photodegradation in flow systems is performed in a reactor coiled around an UV lamp and photoproducts are then, propelled to the detector [11,12,26]. To the best of our knowledge, this study provides the first demonstration of a photodegradation and detection procedures being performed in a flow-batch mixing chamber (PDMC) employed as a photoreactor and as a cell.

2. Experimental

2.1. Reagents

Solutions were prepared using analytical-grade reagents and ultra-pure water (18 MΩ cm^{-1}). Methanol, MeOH (99.8%, HPLC grade, Fluka, Germany) and acetonitrile, ACN (≥ 99%, Sigma Aldrich, Germany) were used as the organic solvents.

A 140 mg L^{-1} MSM (Sigma-Aldrich, Germany) stock solution was prepared in ACN and stored in a dark bottle at 4 °C. Working solutions were prepared daily by appropriately diluting the stock solution.

An appropriate volume of a 0.10 mol L^{-1} sodium dodecyl sulfate (SDS) (Anedra, Argentina) solution was added to the MSM working solutions to obtain the critical micelle concentration (CMC).

The pH of the medium was increased using a 0.10 mol L^{-1} NaOH (Merck, Germany). A 0.025 mol L^{-1} NaOH solution was prepared by diluting the concentrated solution. The pH of the samples was decreased using a 0.01 mol L^{-1} HCl (Merck, Germany) solution.

To evaluate possible interfering substances, solutions of sulfometuron methyl (SMM), chlorsulfuron methyl (CSM), ethoxysulfuron (ETS), nicosulfuron (NCS), deltamethrin, cypermethrin, malathion, fenitrothion and α- and β-endosulfan (all from Sigma-Aldrich, Germany) were prepared in the adequate solvent and diluted with water.

The SPE minicolumn (30 mm × 4 mm i.d.) was constructed by packing a glass cylindrical tube with 200 mg of the sorbent Polygoprep 60-80 C18 (Macherey-Nagel, Germany) with a particle size of 63–100 μm, and the column was sealed with cotton frits at both ends.

2.2. Apparatus and software

The spectrofluorometric measurements were performed on a Jasco® FP 6500 spectrofluorometer. The fluid was pumped with a Gilson® Minipuls 3 peristaltic pump. NResearch® three-way solenoid valves were used to handle all of the solutions in the system.

Tygon® tubes were used in all of the pumping channels. Tubes with an i.d. of 1.14 mm were used for ACN, water and NaOH, whereas tubes with an i.d. of 1.30 mm were used for the sample and waste channels. The remaining tubing was made of Teflon® (0.5 mm i.d.).

The PDMC was constructed with Teflon® and was designed in our laboratory to prepare the solutions and perform the photodegradation and detection in the same location. Detection windows of the PDMC were made of quartz. A lab-constructed stirrer system was designed to improve the mixing inside the PDMC. An electronic actuator (EA) connected to a Pentium® 4 microcomputer was used to control the peristaltic pump, solenoid valves and stirrer system. A schematic diagram of the proposed FBA system is shown in Fig. 1.

The software used to control the FBA system was developed in the LabVIEW® 5.1 visual programming language. The developed software controlled the solenoid valves, peristaltic pump and magnetic stirrer.

2.3. Flow-batch analyzer system

The PMDC could be used to perform photodegradation (using the lamp in the spectrofluorometer) as well as the detection cell for spectrofluorometric measurements. As shown in Fig. 2, the lab-constructed PMDC was designed with two inlets for the incoming solutions and one output for emptying. The PMDC was equipped with two quartz windows at a 90° angle to each other, which were located at the bottom of the chamber to ensure that the photodegradation and detection could be accomplished for the final expected volume (0.90 mL). The inner volume was 1.5 mL. Additionally, a small magnetic stirring system was constructed using a cooler fan motor obtained from an Intel® microprocessor (DC12V, 0.06A) and placed below the PDMC.

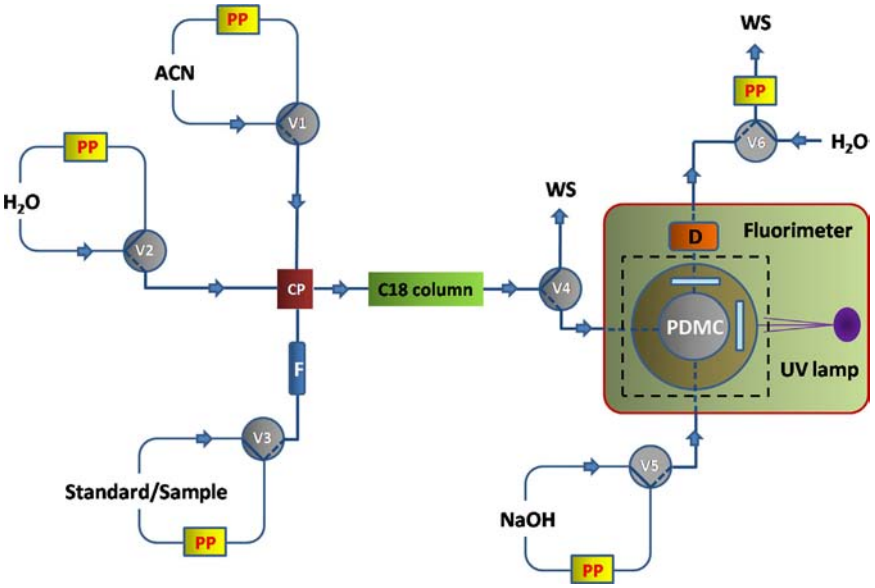

Fig. 1. FBA system for preconcentration, photodegradation and fluorescence determination of MSM. *V1–V6*: solenoid valves; F: syringe filter; CP: confluence point; PP: peristaltic pump; PDMC: photodegradation-detection mixing chamber; D: detector; and WS: waste.

To clearly explain the entire procedure, the process was divided into two parts: the *preconcentration procedure* and the *photodegradation-detection procedure*. Table 1 shows the flow rates and valve-switching time intervals for the complete procedure.

2.3.1. Preconcentration procedure

The preconcentration component of the system consisted of three channels: C_1, C_2 and C_3. These channels correspond to ACN, water and the sample, respectively. The flow rate of ACN and water was 1.22 mL min^{-1}; and the flow rate for the sample was 1.37 mL min^{-1}. The direction of the flow in each channel was controlled by a three-way solenoid valve. When the corresponding valve (i.e., V_1, V_2 and V_3) was switched OFF, the solution was recycled to the respective flask; when the valve was ON, the solutions were pumped to the minicolumn. Additionally, a filter (0.45 μm) was introduced in the C_3 channel to filter the sample prior to preconcentration in the C18 minicolumn. A fourth valve (V_4) was placed after the minicolumn. When this valve was in the OFF position (in the conditioning and loading steps), the solutions that passed through the minicolumn were directed toward the waste. When this valve was ON, ACN (eluting step) was directed toward the PDMC.

The C18 minicolumn was washed with 2.50 mL of ACN and 3.70 mL of water. Thus, the V_1 and V_2 valves were sequentially switched ON for 120 s and 180 s, respectively. After this time, 13.7 mL of the standard solutions or sample was pumped through the C18 minicolumn by switching the V_3 valve to the ON position, and the MSM was retained. The minicolumn was then washed with 2.50 mL of water by switching the V_2 valve to the ON position for 120 s.

Finally, the elution of MSM was performed using 0.50 mL of ACN. In this case, the V_1 valve was switched to the ON position for 46 s, that include pre-elution time (time required to displace the volume of water that reminds in column and channels) and the time for elution and filling the PDMC (25 s). During pre-elution time, V_4 remained in the OFF position while during elution and filling step the PDMC was switched ON to direct the flow to the PMDC.

2.3.2. Photodegradation-detection procedure

As mentioned previously, when the V_4 valve was in the ON position, the eluted MSM (in ACN) flowed to the PMDC. In this component, the system consisted of two channels: C_5 and C_6. These channels had flow rates of 1.22 mL min^{-1} and 1.37 mL min^{-1}, respectively. In C_5, NaOH flowed to the PMDC, and the V_5 valve controlled the direction of the flow. When this valve was OFF, the solution was recycled to the respective flask. When the valve was ON, the NaOH solution was pumped to the PDMC. The sixth valve (V_6) was used to control the emptying of the PDMC. Additionally, a flask containing water was connected to V_6, and this flask was used to ensure that the valve operated correctly when fluids were not carried from the PMDC to the waste.

Using this method, 0.50 mL of the eluted solution and 0.40 mL of 0.025 mol L^{-1} NaOH solution were pumped to the PDMC. The mixture was homogenized by stirring for 10 s. The UV lamp of the spectrofluorometer was then switched ON, and the photodegradation of MSM was performed at 240 nm for 30 s. After this step, the fluorescence signal was recorded (λ_{exc}=276 nm; λ_{emi}=385 nm). Finally, the V_6 valve was switched ON for 50 s, and the contents of the cell were aspirated toward the waste. The PDMC was cleaned between measurements. The PDMC cleaning procedure was performed by switching the V_1 and V_4 valves to the ON position and stirring for 60 s. As the PDMC was cleaned, the conditioning of the minicolumn started because V_1 was switched ON. The complete emptying of the PMDC was assured by switching the V_6 valve to the ON position for 65 s.

2.4. Sampling and sample preparation

Diverse waters that are used for irrigation and consumption by humans and animals were sampled from the region surrounding the city of Bahia Blanca located in the Buenos Aires province in southwest, Argentina. Two samples were collected from different locations in the Napostá Grande Creek, one sample was obtained from an artesian well used for human consumption located in Mayo Park, and tap water was collected from the laboratory. In addition, one of the samples was obtained from a well located in a field close to San Martin city, La Pampa province that is used for human and animal consumption. The samples were stored in the dark at 4 °C until the analysis was performed.

The water samples were pre-filtered using 80 μm Whatman™ filter paper to remove any sand and other possible major particles. The samples were then filtered on-line with a 0.45-μm Whatman™

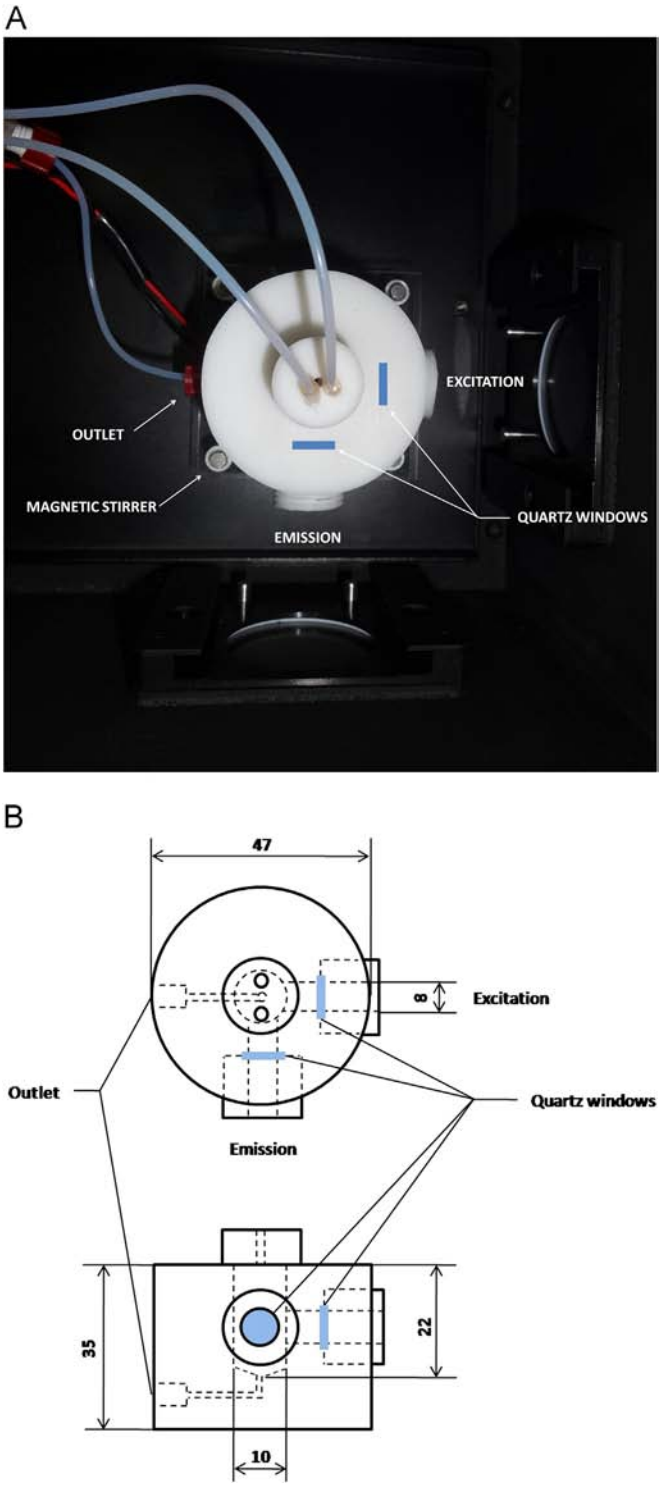

Fig. 2. (A) Top view of the PDMC placed instead of the cell holder in the spectrofluorometer. (B) Schematic diagram of the top and lateral views of the PDMC. Dimensions are expressed in mm.

syringe filter. The pH of the samples was between 6.0 and 7.0. Therefore, the pH of these samples was adjusted to 5.0 with 0.01 mol L^{-1} HCl before the samples were introduced into the SPE column. The samples were analyzed in triplicate.

For the recovery study, the samples were spiked at two concentration levels in the calibration range of 2.75–5.75 μg L^{-1} following an identical protocol. The recoveries were calculated according to the AOAC definition [27].

3. Results and discussion

3.1. Optimization of experimental conditions

The extraction and FBA variables were optimized based on a higher fluorescence signal and the repeatability of the measurements.

3.1.1. Instrumental conditions and photodegradation time

The instrumental conditions for the photodegradation step were optimized. To irradiate the samples, the slit width on the excitation monochromator was fixed to 20 nm, which is the maximum width in the employed instrument.

Because the degradation of MSM can be achieved with a germicide lamp (254 nm) [23], excitation wavelengths between 220 and 260 were tested, and the highest signal was obtained with an excitation wavelength of 240 nm. Because emission is not involved in this step, the emission wavelength was fixed to 385 nm to monitor the process. The photomultiplier tube (PMT) voltage was fixed to 475 V.

The irradiation time was optimized over the range of 20–60 s. As the photodegradation time increased, an increase in the signal was observed. The largest increase occurred between 20 and 30 s, and, a tendency to form a plateau has being noticed at higher irradiation times. As a compromise between the highest signal acquired and the analysis duration, 30 s was chosen as the optimum value.

After photodegradation was achieved, measurements of the photoproduct were performed by exciting the sample at 276 nm and recording the signal at 385 nm using a slit width of 10 nm for excitation and a slit width of 20 nm for emission.

3.1.2. Effect of chemical variables on fluorescence signal

According to previous studies [23], MSM photoproducts can be obtained in aqueous alkaline media (pH 12.0–13.0) in the presence of micellar solutions of SDS. As was mentioned in introduction part, MSM is presented in low levels in environmental samples and SPE was selected as preconcentration technique considering its intrinsic characteristics. In order to couple both, preconcentration and photodegradation, the eluate must be in the appropriate medium to form the photoproduct. Because MSM solubility at pH above 9.0 is high [28], an aqueous alkaline solution was considered to be used as eluent. However, silica is stable at a pH range between 2.0 and 8.0. Thus, considering the solubility of MSM in different organic solvents, the effect of two possible eluents, methanol and acetonitrile, on the fluorescent signal was studied.

Therefore, 1.25 mg L^{-1} MSM solutions were prepared in different aqueous:organic solvent mixtures and irradiated for 30 s. After irradiation, the fluorescence signal of the photoproduct was measured at λ_{em}=385 nm (λ_{ex}=276 nm). These signals were compared to the signal of a MSM solution that was prepared in 0.01 mol L^{-1} SDS (pH 12.0, adjusted with 0.1 mol L^{-1} NaOH) and irradiated for an identical duration. As shown in Fig. 3, similar signals were obtained using ACN as the organic solvent. Of the two solutions containing ACN, the solution prepared with SDS exhibited a higher signal than that prepared without SDS. Additionally, the inclusion of SDS generated bubbles in the system, which resulted in the need of an additional cleaning step. Therefore, a mixture of 0.01 mol L^{-1} NaOH in ACN was selected as the adequate media to achieve a compromise between the highest signal and the lowest cleaning time.

3.1.3. pH of the photodegradation medium

The pH of the photodegradation medium was optimized between 8.0 and 13.0. The pH was varied by increments of 0.5 units. To select the optimal value, the main criterion was to

Table 1
Valve switching time intervals and delivered volumes.

Valve switching time intervals, *s* (volumes, mL)	V_1	V_2	V_3	V_4	V_5	V_6
Filling channels	**20 (0.40)**	**20 (0.40)**	**20 (0.46)**	OFF	**20 (0.40)**	OFF
Column conditioning						
ACN	**120 (2.4)**	OFF	OFF	OFF	OFF	OFF
Water	OFF	**180 (3.7)**	OFF	OFF	OFF	OFF
Column loading – sample/standard	OFF	OFF	**600 (13.7)**	OFF	OFF	OFF
Column washing	OFF	**120 (2.4)**	OFF	OFF	OFF	OFF
Elution and transport to PDMC						
Pre-elution	**21 (0.43)**	OFF	OFF	OFF	OFF	OFF
Elution and filling PDMC	**25 (0.50)**	OFF	OFF	**25**	**20 (0.40)**	OFF
PDMC cleaning						
Emptying PDMC	OFF	OFF	OFF	OFF	OFF	**50**
Cleaning PDMC	**60 (1.2)**	OFF	OFF	**60**	OFF	OFF
Emptying PDMC	OFF	OFF	OFF	OFF	OFF	**65**
Column conditioning between samples						
ACN	**60 (1.2)**	OFF	OFF	OFF	OFF	OFF
Water	OFF	**180 (3.7)**	OFF	OFF	OFF	OFF

Delivered volumes of each solution, expressed in mL, are indicated between brackets.
ACN: acetonitrile; *V*: solenoid valves; and PDMC: photodegradation-detection mixing chamber.

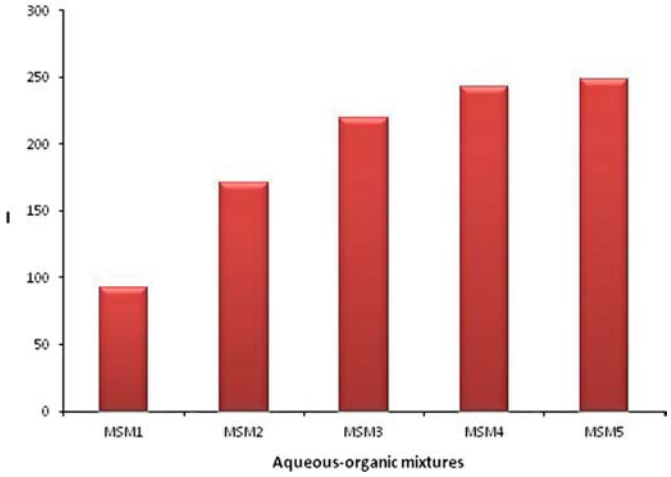

Fig. 3. Effect of different aqueous: organic mixtures used as irradiation-detection media. **MSM1**: 50:50 MeOH: 0.01 mol L^{-1}NaOH; **MSM2**: 50:50 MeOH: 0.02 mol L^{-1} SDS and adjusted to pH 12.0 with 0.1 mol L^{-1}NaOH, **MSM3**: 50:50 ACN: 0.01 mol L^{-1}NaOH, **MSM4**: 50:50 ACN: 0.02 mol L^{-1} SDS and adjusted to pH 12.0 with 0.1 mol L^{-1}NaOH, **MSM5**: 0.01 mol L^{-1} SDS adjusted to pH 12.0 with 0.1 mol L^{-1}NaOH. I: Fluorescence intensity.

achieve the highest signal of the MSM photoproduct with the best repeatability of the measurements. The optimum value was 12.5. At higher pH values, no signal increase was observed.

3.1.4. Extraction procedure

Sample preparation remains a bottleneck in most analyses because it is time consuming and because successive extractions with large amounts of solvents, several of which are toxic, are required in some cases. Additionally, evaporation to dryness and reconstitution is a common resource because of incompatibilities between the pretreatment and the separation or detection techniques that are intended to be employed.

In our method, a single SPE extraction was performed, allowing both sample preconcentration and cleanup without additional steps. Moreover, the extraction solvent was compatible with the photodegradation and detection steps.

Based on previous studies [15], C18 was selected as the sorbent material to perform the sample cleanup and preconcentration of the MSM. The SPE minicolumn was packed with 200 mg of the sorbent. The minicolumn was conditioned with 2.50 mL of ACN (optimized in the range of 1.20–3.70 mL) followed by 3.70 mL of water (1.20–6.10 mL) at a flow rate of 1.22 mL min^{-1}.

The parameters that affected the online preconcentration and elution of MSM were studied. The behavior of the SPE minicolumn was evaluated in terms of sample volume and loading time. The main criterion was to achieve the detection of low concentrations of the analyte with a short analysis time. Thus, 13.7 mL of the sample (1.0–20.0 mL) was passed through the minicolumn at a flow rate of 1.37 mL min^{-1}. Above this volume, the recoveries of the analytes slightly decreased.

As was described in Section 3.1.2, ACN was the solvent with the smallest effect on the photodegradation of the analyte; thus, ACN was selected as the eluting solvent. The elution volume was also studied, and because quantitative recoveries were obtained using 500 μL, this volume was used in the following experiments. Regarding the ratio ACN: NaOH studied in Section 3.1.2, it was noted that the volume of the alkaline solution could be reduced without any change in the optimum pH. Therefore, the dilution of the eluate could be diminished and a 55:45 ACN: NaOH ratio was selected for further experiments. Considering the elution volume, an enrichment factor of 27 was achieved using this method.

3.1.5. Stirring time

When the solutions were delivered to the PDMC, it was necessary to stir the mixtures to obtain good signal reproducibility. Therefore, different stirring times between 3 and 15 s were tested. The best results with respect to signal height and repeatability were obtained when the solutions in the PDMC were stirred for 10 s. The analytical signal did not improve with longer stirring times.

3.2. Analytical performance

The analytical performance of the proposed FBA method was evaluated in terms of the calibration range, sensitivity (evaluated as limit of detection (LOD) and limit of quantitation (LOQ)), sample throughput, reproducibility (expressed as relative standard deviation) and accuracy (expressed as the recovery percentages of spiked samples).

3.2.1. Analytical curve, LOD, LOQ, RSD and sample throughput

Using the proposed FBA method and the optimized values for the physical and chemical parameters, the calibration curve for the MSM determination was constructed over the range of 1.00–7.20 μg L^{-1} (five points). The regression equation was $A = (72.5 \pm 0.7)$ [MSM μg L^{-1}] + (-61.3 ± 3.1) with a correlation coefficient of 0.9995.

LOD was 0.28 μg L^{-1} and was calculated as $3.3S_0$, where S_0 represents the standard deviation corresponding to the predicted concentration of a blank sample [27]. LOQ was 0.85 μg L^{-1} and was calculated as the concentration corresponding to 10 times S_0. The relative standard deviation (RSD %) was 2.0, and this value was obtained from six replicate runs with a 4.25 μg L^{-1} MSM solution.

The sample throughput of the photodegradation and detection steps was 72 h^{-1}, and the sample throughput for the entire procedure, including the SPE procedure and washing steps, was 3 h^{-1}.

It is important to highlight that the linear range could be extended by linear regression, but considering that MSM is presented in low concentrations in water sources, samples could be easily diluted to employ the constructed analytical curve.

3.2.2. Selectivity

The effect of the presence of other pesticides in water samples on the analysis of MSM was examined. For this study, other sulfonylurea herbicides and pesticides with other structures that are employed in Bahía Blanca's agriculture region were tested (Table 2) to include different chemical groups of pesticides.

The entire procedure, including the pre-concentration step, was performed. To reduce the analysis time, the MSM solution and the standard solutions of each possible interfering compound were prepared at a higher concentration (0.01 μg mL^{-1}), loaded onto the minicolumn for a shorter time (5 min), and then subjected to the procedure described in Section 2.3.1. No signal was observed for the standards of the possibly interfering pesticides, indicating that these were not retained on the minicolumn or eluted with ACN or that no fluorescent product was produced or detected after irradiation under the conditions described above.

Concerning sulfonylurea herbicides, photodegradation varying pH and irradiation time was studied, and the kinetics of degradation was different for each tested analyte. Therefore, the optimal conditions for MSM photodegradation were inappropriate for the tested sulfonylurea herbicides.

The identical procedure was repeated with mixed solutions of MSM and each of the examined substances. The ratios of interferent:MSM were 1:1, 10:1 and 100:1, and the MSM concentration was maintained constant. The results are given in Table 2.

Table 2
Pesticides studied as possible interferences for MSM determination.

Pesticide family	Interferent	Tolerance ratio (interferent:MSM)
Sulfonylureas	Ethoxysulfuron methyl	100:1
	Sulfometuron methyl	30:1
	Chlorsulfuron methyl	3:1
	Nicosulfuron	100:1
Pyretroids	Deltametrin	100:1
	Cypermetrin	100:1
Organophosphates	Malathion	100:1
	Fenitrothion	100:1
Organochlorines	α-Endosulfan	100:1
	β-Endosulfan	100:1

The change in the signal due to the presence of the tested pesticide did not exceed the RSD value (2.0%), indicating measurement reproducibility. Two exceptions were observed: the signal of MSM recorded in the presence of higher concentrations of SMM or CSM was significantly higher than that obtained for MSM alone. SMM did not appear to interfere with the MSM signal for SMM: MSM mixtures at ratios below 30:1; however, at a ratio of 50:1, the signal was approximately 2.4-fold higher than the average value measured for MSM. At a ratio of 5:1, the presence of CSM resulted in an approximately 1.5-fold increase in the signal. Because regulations allow the use of sulfonylurea herbicides at similar concentrations to MSM, these pesticides should not be a source of difficulties in real sample analysis.

3.3. Analysis of real samples

The proposed method was tested through the preconcentration and determination of MSM in water samples. Although the samples were collected from different potentially contaminated water sources in which pesticide contamination is expected because of agricultural techniques, MSM residues were not detected. Thus, the samples were spiked as described in 2.4. For both concentration levels, Table 3 shows the added concentrations, the value determined for each sample, and the calculated recovery percentage. The recovery values ranged from 94.7% to 109.8% and were acceptable for determining MSM at μg L^{-1} levels.

The allowable amount of MSM in drinking water is not stipulated by Argentina's regulations; only a maximum concentration level for total pesticides (100 μg L^{-1}) has been established [29]. However, the Drinking Water Directive in the European Union (EU) established a maximum concentration of 0.10 and 0.50 μg L^{-1} for individual and total pesticides, respectively [30]. Because drinking water is derived from a variety of sources, including rivers, reservoirs and groundwater, it can regularly contain trace levels of pesticides in excess of the drinking water standards [31]. Therefore, considering Argentina´s regulations and the fact that pesticides may be present in higher amounts in raw waters, the proposed method is adequate for determining the MSM level in the analyzed samples, with the exception of tap water, which requires higher sensitivity.

3.4. Comparison with previous methods

Table 4 shows different analytical methods that have been proposed for the determination of the MSM concentrations in water samples. The methods are compared by considering the

Table 3
MSM determination in spiked real water samples applying the proposed FBA method.

Sample	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)
A[a]	2.75	2.80 ± 0.01	101.8
	5.75	5.55 ± 0.01	96.4
B[b]	2.75	3.02 ± 0.02	109.9
	5.75	5.44 ± 0.01	94.7
C[a]	2.75	2.85 ± 0.01	103.6
	5.75	6.06 ± 0.01	105.4
D[c]	2.75	3.02 ± 0.01	109.8
	5.75	6.25 ± 0.01	108.7
E[d]	2.75	2.69 ± 0.02	97.8
	5.75	5.61 ± 0.01	97.6

[a] A and C, Naposta Grande creek.
[b] B, San Martín, La Pampa, water well.
[c] D, Water upwelling.
[d] E, Tap water.

Table 4
Brief comparison of the analytical methods for MSM determination in water samples.

	GC/ECD [13]	HPLC [15]	UHPLC [17]	FIA-PIF [23]	FIA-PIF [24]	FBA
Automation	No	Yes	Yes	Partial	Yes	Yes
Pretreatment	SPE	SPE	SPE	LLE	SPE	SPE
Sample volume (mL)	500	10.0	1.5	25.0	2.06	13.7
Eluent volume (mL)	–	0.03	–	–	Continuous	0.50
Enrichment factor	100	330	125	5	–	28
Detection technique	GC/ECD	LC–ESI–MS	MS–MS	Fluorescence	Fluorescence	Fluorescence
Multianalyte[a]	Yes(2)	Yes(6)	Yes(16)	No	Yes(2)	No
Complexity of analysis	High	Medium	Medium	High	Low	Low
Linear range ($\mu g\ L^{-1}$)	0.50–50.0	0.01–1.00	0.007–0.300	0.10–39.0	11.0–400	1.00–7.20
LOD ($\mu g\ L^{-1}$)	0.01	0.03	0.002	0.10	3.30	0.28
LOQ ($\mu g\ L^{-1}$)	0.05	0.09	0.007	Not informed	11.0	0.63
RSD (%)	$\leq$ 12	6.0	8.0[c]	3.7	2.4	2.0
Throughput (h^{-1})	8	3	3.75[b]	80	14[b]	3[b]

[a] Between brackets, amount of determined analytes.
[b] Included preconcentration step.
[c] For 0.01 $\mu g\ L^{-1}$.

automation of the entire procedure, the preconcentration step, the complexity of the analysis and the analytical parameters.

Lower detection limits are achieved with chromatographic methods. However, in most chromatographic analyses, time-consuming off-line preconcentration processes that include a higher number of steps are required. In the FIA-PIF method [23], satisfactory analytical parameters are obtained, but a tedious, long off-line preconcentration is performed involving consumption of high amounts of toxic solvents (such as dichloromethane) due to successive liquid–liquid extractions to clean up the sample. On the other hand, an automated FIA system with SPE preconcentration was proposed, but the preconcentration of MSM photoproducts instead of MSM was achieved [24].

The proposed FBA method is a simple and fully automated system with short SPE clean-up and preconcentration steps followed by a photodegradation process and the detection of the MSM fluorescent active photoproduct. Additionally, the entire procedure (including the SPE preconcentration step) was performed on-line. The FBA system required a low sample volume (13.7 mL) and a low ACN volume (6.0 mL, including the volume required for the conditioning of the minicolumn and washing of the PDMC). Compared with chromatographic methods, the FBA method showed a high sample throughput and substantial cost savings because of the minimal consumption of reagents and the low equipment cost. Additionally, the LODs were of the same order of magnitude as the majority of those reported previously in the literature with the exception of the LODs reported with the HPLC method [15] and the UHPLC MS/MS method [17].

4. Conclusions

The developed FBA method successfully determined the MSM concentration in real surface water samples that were spiked with MSM. The novelty of the proposed configuration allowed the photodegradation and detection processes to occur in the same chamber without any loss or dispersion of the sample. Additionally, the inherent advantages of using a FBA system (e.g., low consumption of reagents, decrease of waste generation, and reproducibility) were compounded with the advantages of using UV light as the decomposition agent. The combination of these two processes resulted in a significant decrease in the amount of the chemicals employed in the analysis. This decrease in consumption is one of the most important principles in green chemistry.

Furthermore, a simple SPE procedure was coupled to the FBA system, allowing the realization of the sample clean-up and analyte extraction and preconcentration more rapidly without any additional steps. This process obtained a satisfactory enrichment factor of 27. Moreover, the inclusion of an organic solvent did not significantly affect the formation of the photoproduct or the fluorescent signal and thus facilitates the completely on-line determination of the concentration through the simple fully automated system.

Acknowledgments

The authors gratefully acknowledge financial support of the Bilateral Cooperation between Argentina and the Czech Republic, Project no. 7AMB12AR008 (ARC/11/03). I. Šrámková and H. Sklenářová would like to acknowledge the co-financing of this publication by the European Social Fund and the State Budget of the Czech Republic, TEAB, Project no. CZ.1.07/2.3.00/20.0235. I. Šrámková would like to acknowledge the financial support of the Project SVV 260 063. B. Fernandez Band, M. Grünhut and C. Acebal also would like to express their gratitude to National Council of Scientific and Technical Research (CONICET).

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.05.024.

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