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# Determination of herbicides in mineral and stagnant waters at ng/L levels using capillary electrophoresis and UV detection combined with solid-phase extraction and sample stacking

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**Abstract**

In this work, the combined use of solid-phase extraction (SPE) and on-line preconcentration strategies as normal stacking mode (NSM) and stacking with matrix removal (SWMR) for the ultrasensitive and simultaneous capillary electrophoresis-ultraviolet analysis (CE-UV) of five triazolopyrimidine sulfonanilide pesticides (i.e., diclosulam, cloransulam-methyl, flumetsulam, metosulam and florasulam) in different types of water is investigated. An adequate separation electrolyte for the separation and stacking of these pesticides was obtained, considering also its compatibility with MS detection, which consisted of 24 mM formic acid and 16 mM ammonium carbonate at pH 6.4. It was observed that the use of this running buffer together with the SWMR preconcentration method provided the best results in terms of sensitivity (between 6.54 and 11.9 μg/L) and peak efficiency (up to 550 000 theoretical plates per meter, NTP/m). When this on-line preconcentration procedure was combined with an off-line sample preconcentration step as SPE using $C_{18}$ cartridges, the selected herbicides could be detected in the ng/L range. The optimized SPE-SWMR-CE-UV method was applied to the determination of the selected group of pesticides in spiked and non-spiked mineral and stagnant waters. Recoveries ranged between 55 and 110% and limits of detection between 131 and 342 ng/L. This work shows the great possibilities of the combined use of SPE-SWMR-CE-UV to overcome the sensitivity problems usually linked to CE analysis.


*Keywords:* On-line concentration; Stacking; Capillary electrophoresis; Pesticides; Water

## 1. Introduction

Pesticides are nowadays among the priority pollutants to be monitored in a wide variety of matrices because their residue incorporation into waters, soils and crops may represent a serious hazard to human health. Several pesticides can be used as herbicides, plaguicides, fungicides, etc. Certain herbicides are post-emergence products, which are foliage-applied to control weeds that have emerged in competition with the developing crop. However, many of these herbicides still show residual activity in the soil, and therefore, they can control late-germination weeds. These types of herbicides together with pre-emergent ones are mostly applied to soils or sprayed over crops and, as a result of their large production and high stability, they can enter as pollutants into rivers, streams or lakes directly from drainage of agricultural lands. Less than 0.1% of applied pesticides actually reach the targeted pests, while the rest (99.9%) has the potential to move into other parts of the environment, including ground and surface waters [1]. Since water is the primary stream in which pesticides are transported, the need for monitoring herbicides

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in natural waters is essential for achieving good water quality. Moreover, in most European countries and in the USA, groundwater is the major source of drinking water [2].

Triazolopyrimidine sulfonanilide herbicides include cloransulam-methyl, metosulam, flumetsulam, florasulam and diclosulam [3], which are frequently used as pre-emergence and/or post-emergence herbicides in soybeans, peanuts, etc. in different countries. Its mode of action is through the inhibition of acetolactate synthase (ALS). Cloransulam-methyl, for example, is a broadspectrum herbicide, applied to the soil surface or incorporated in pre-emergence and post-emergence in soybeans to control broadleaf weeds [4]. This herbicide, together with diclosulam and flumetsulam, which has been detected in Midwestern US rivers [5,6], is frequently used in US and, therefore, registered by the US Environmental Protection Agency (EPA) [7]. Cloransulam-methyl is likely of slight persistence in the surface, but more persistent when leached into the subsurface. Florasulam, however, is also registered by the European Union (EU) [8], which recommends paying particular attention to the potential of groundwater contamination when florasulam is applied in regions with vulnerable soils and/or specific climatic conditions. Metosulam, indeed, is registered and used in several countries around the world. To our knowledge, there is not an EPA-method allowing the simultaneous determination of these pesticides in waters.

The continuous monitoring of pesticides residues in environmental samples is of great importance and demands high efficiency, selectivity and sensitivity techniques. In this sense, capillary electrophoresis (CE) is increasingly gaining importance in pesticide analysis [9] and represents an attractive alternative technique for their determination [10,11]. However, it is hindered by the short optical path length defined by the column diameter, which yields in a low detection sensitivity (normally in the mg/L range). To improve these low limits of detection (LODs) several on-line preconcentration strategies have been developed [12,13]. One of these techniques is called normal stacking mode (NSM) and consists in the injection of a high amount of sample with lower conductivity than that of the separation buffer. Besides, another on-line preconcentration strategy called stacking with matrix removal (SWMR) has also proven to be effective. In this case, the capillary is filled with the sample previously dissolved in low conductivity matrix. For the analysis of anionic species, once the sample is introduced in the capillary, voltage is applied (inversed polarity) and the matrix is removed from the sample by the EOF, concentrating anionic analytes towards the anode. When the matrix has been mostly removed (the intensity of the current is approximately 97–99% of that of the buffer) polarity is inverted and the separation takes place. The use of this method for the analysis of cationic species requires an anodal EOF that can be achieved by modifying the capillary wall with a suitable cationic surfactant. This technique has been recently applied for the on-line preconcentration of several pesticides [14–16].

Due to their polar nature and ionic character, triazolopyrimidine sulfoanilide pesticides are suitable for their determination by capillary electrophoresis. In this work, we propose the simultaneous determination of five triazolopyrimidine sulfonanilide herbicides (diclosulam, cloransulam-methyl, flumetsulam, metosulam and florasulam)—three of them EPA registered—in water samples using a combination of on-line preconcentration strategies and an off-line preconcentration procedure as solid-phase extraction (SPE). To our knowledge, this is the first time that this group of pesticides is simultaneously determined in water by SPE-CE-UV.

## 2. Experimental

### 2.1. Chemicals and samples

All chemicals were of analytical reagent grade and used as received. Ammonium acetate, ammonium carbonate, ammonium hydroxide, acetic acid and formic acid from Merck (Darmstadt, Germany) were tested as CE running buffers at different concentrations. Acetonitrile (HPLC-grade) was from Merck (Darmstadt, Germany). Distilled water was deionized by using a Milli-Q gradient system A10 (Millipore, Bedford, MA, USA).

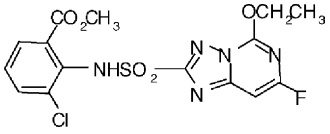
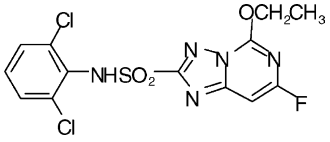
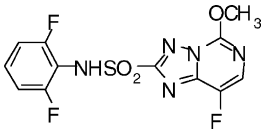
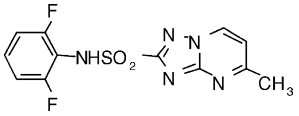
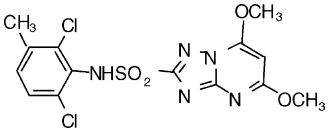
Cloransulam-methyl (methyl 3-chloro-2-{[(5-ethoxy-7-fluoro[1,2,4]triazolo[1,5-*c*]pyrimidin-2-yl)sulfonyl]amino} benzoate), diclosulam {*N*-(2,6-dichlorophenyl)-5-ethoxy-7-fluoro[1,2,4]triazolo[1,5-*c*]pyrimidine-2-sulfonamide}, florasulam {*N*-(2,6-difluorophenyl)-8-fluoro-5-methoxy[1,2,4] triazolo[1,5-*c*]pyrimidine-2-sulfonamide}, flumetsulam {*N*-(2,6-difluorophenyl)-5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine-2-sulfonamide} and metosulam {*N*-(2,6-dichloro-3-methylphenyl)-5,7-dimethoxy[1,2,4]triazolo[1,5-*a*]pyrimidine-2-sulfonamide} obtained from Dr. Ehrenstorfer GmbH (CYMIT QUIMICA, Barcelona, Spain) were used without further purification. Table 1 shows the chemical structures of these compounds as well as some of their chemical and toxicological properties. Standard solutions of each pesticide were prepared in acetonitrile and kept in the dark under refrigeration at 4 °C. Working mixtures of pertinent concentrations were prepared daily by appropriate combination and dilution with acetonitrile.

Mineral water samples purchased from a local supermarket and stagnant water rich in organic matter from a local deposit were spiked at different levels of concentrations (see below) and stored at room temperature for 3 h. Afterwards, samples were subjected to the SPE procedure as indicated under Section 2.3.

### 2.2. Capillary electrophoresis-UV conditions

CE-UV analyses were performed in a PACE/5510 CE apparatus (Beckman, Fullerton, CA, USA) equipped with a DAD detector working at 205 nm. System Gold Software was used for CE instrument control. Bare fused silica capillaries

Table 1
Chemical and toxicological properties of the selected herbicides

| Pesticide | Formula | p$K_a$[a] | $M_w$ | MRL[b] | Application | Source |
|---|---|---|---|---|---|---|
| Cloransulam-methyl |  | 4.81 | 429.8 | 0.02–0.1 | Soybean, foliage, hay or seed | EPA registered [7] |
| Diclosulam |  | 4.00 | 406.2 | 0.02 | Soybean seed, peanut nutmeat | EPA registered [7] |
| Florasulam |  | 4.54 | 359.3 | 0.01–0.1 | Cereals, fruits, pulses, oil seeds | EU registered [8] |
| Flumetsulam |  | 4.60 | 325.3 | 0.05 | Corn, field, grain, forage and soybean | EPA registered [7] |
| Metosulam |  | 4.80 | 418.3 | – | Cereals | Registered in several countries |

[a] Obtained from [3].
[b] MRL, maximum residue limit (ppm); the authorized MRL values depend on the sample and country.

with 50 μm i.d. were purchased from Composite Metal Services (Worcester, UK). The detection length was 50 cm and the total length 57 cm. Unless otherwise indicated (SWMR) injections were made at the anodic end using $N_2$ pressure of 0.5 psi (1 psi = 6894.76 Pa). Number of theoretical plates (NTP) per meter was calculated using the suitability function of the System Gold Software. Before first use, fused-silica capillary was washed with 0.1 M sodium hydroxide for 30 min and deionized water for 15 min. Capillary conditioning was done every morning rinsing 5 min with running buffer. To achieve a good reproducibility between runs, running buffer was passed through the capillary for 2 min (all rinses were done using $N_2$ pressure at 20 psi) and running buffer vials were renewed every five injections. At the end of the day, water was passed through the capillary for 5 and 2 min more with $N_2$. Electrophoretic separation was carried out at 25 °C and at +23 kV, using a 24 mM formic acid and 16 mM ammonium carbonate solution (pH 6.4) as separation electrolyte.

### 2.3. Solid-phase extraction procedure

Mineral or stagnant water was spiked with the selected herbicides at several concentrations. SPE procedure was performed using a Vac-Master manifold from IST (IST, Hengoed, South Wales, UK). Fifty milliliters volume of this spiked solution with 1 mL of 1 M hydrochloric acid was slowly passed through a $C_{18}$ SPE cartridge (Sep-Pak Plus $C_{18}$ Cartridge) from Waters (Milford, MA, USA) previously activated by flushing with 5 mL acetonitrile followed by 2 mL of 0.01 M hydrochloric acid. After loading the sample into the SPE cartridge, it was dried under vacuum of −10 mmHg (1 mmHg = 133.322 Pa) for 15 min. The retained herbicides were eluted with 10 mL acetonitrile. The organic solvent was then evaporated to dryness at 40 °C using a Rotavapor R-200 (from Büchi Labortechnik, Flawil, Switzerland). The residue was dissolved in 1 mL acetonitrile and directly injected into the CE instrument.

## 3. Results and discussion

### 3.1. CE separation

As mentioned before, to our knowledge, there are no previous works concerning the determination of triazolopyrimidine herbicides by capillary electrophoresis. Therefore, a preliminary study was carried out using standards dissolved in acetonitrile at a concentration of 2 mg/L with UV detection at 205 nm (from the spectra of these compounds dissolved in acetonitrile, a maximum of absorbance was observed at this wavelength and further corroborated by the highest signal/noise ratios obtained by CE-UV at the same wavelength) and hydrodynamic injection at 0.5 psi for 12 s. The selected group of compounds have p$K_a$ values between 4 (diclosulam) and 4.81 (cloransulam-methyl) (see Table 1). Moreover, two

of these compounds (namely, cloransulam-methyl and metosulam) have very similar p$K_a$ values and molecular weights, as can be seen in Table 1, which is expected to complicate their separation. Therefore, in order to achieve a suitable separation, pH higher than 5 should be used. Furthermore, a separation electrolyte with a high pH is suggested in order to achieve a fast separation of the anions. Moreover, an additional constraint was imposed during this optimization study, i.e., non-volatile salts as phosphate, borate, etc. or EOF modifiers as, for instance, CTAC, CTAB, etc. were used in order to obtain a buffer that could be used in the future with a more sensitive and selective detector as a mass spectrometer. Thus, ammonia, ammonium acetate, acetic acid, ammonium carbonate and formic acid were tested as separation electrolytes individually (concentrations between 5 and 80 mM) or in different combinations, in order to obtain separation electrolytes with different pH values (from 5 to 11).

None of the mentioned compounds when used alone provided a suitable CE resolution of the selected pesticides. In general, when working at pH values higher than 6.5, overlap of certain compounds, especially metosulam and cloransulam-methyl, occurred. At the same time, electrolytes with a high ionic strength provided very low EOF and therefore high analysis time. The best separation was achieved with 24 mM formic acid and 16 mM ammonium carbonate, which gave a pH of 6.4 and provided an analysis time of 9 min at 23 kV. Concentration of formic acid and ammonium carbonate above the previous ones provided higher analysis time without noticeable resolution improvement. Concentrations below, however, yielded in peak overlap. The use of acetic acid instead of formic acid, although it gave very similar pH, capillary current, peak efficiency and resolution, also provided higher analysis time.

### 3.2. Stacking procedures

Once the separation electrolyte was selected, two on-line stacking procedures were evaluated in order to improve the sensitivity, namely, NSM and SWMR.

#### 3.2.1. Normal stacking mode

In NSM, focusing happens at the interface between the low conductivity matrix and the more conductive background electrolyte (BGE) due to the abrupt change in the local electric field and, as a consequence, the electrophoretic velocity of analytes. In order to obtain a sample matrix with a low conductivity able to provide as much sensitivity as possible, different solutions of each pesticide containing acetonitrile (0.5 mg/L) and separation buffer were tested. Ratios 1:3, 1:1 and 3:1 as well as pure acetonitrile or separation buffer alone were tested. Among them, pure acetonitrile yielded the highest signal to noise ratios and consequently, the lowest LODs. The use of acetonitrile alone for sample stacking, known as acetonitrile stacking, has already been used several times [17–19] with good sensitivity improvements. In our work, by using acetonitrile alone, the sample could be injected in the capillary up to 60 s at 0.5 psi (ca. 4% of the total volume of the capillary). Higher injection times yielded in peak distortion and overlap and, at the same time, higher analysis times due to the high amount of solvent injected. The injection of such a long sample plug yielded in LODs between 133 μg/L for flumetsulam and 195 μg/L for cloransulam-methyl with peak efficiencies between 230 000 and 285 000 theoretical plates per meter (NTP/m) (see Table 2). The LODs obtained for the pesticides using NSM correspond to an improvement between 8 and 11 times relative to non-stacking procedure.

#### 3.2.2. Stacking with matrix removal

The SWMR technique was also tested with samples containing 0.5 mg/L of each pesticide dissolved in acetonitrile or separation buffer alone or combinations 3:1, 1:1, and 1:3 of them. The best results were achieved once more using acetonitrile alone. Samples could be injected up to 18 s at 20 psi. Higher injection times yielded in peak distortion and overlap and also in higher reversal times (the time needed to eliminate the matrix of the sample). LODs obtained (calculated as three times the signal to noise ratio) were between 6.54 μg/L for flumetsulam and 11.9 μg/L for florasulam, which are in the low μg/L level (see Table 2). These low LODs represent an increase of sensitivity up to 20-fold, with respect to NSM injection, and up to 214-fold with respect to non-stacking CE analysis; therefore, this on-line preconcentration strategy was selected for further experiments. Also, in SWMR peak efficiencies are higher than in NSM (between 390 000 and 555 000 NTP/m). Fig. 1 shows the comparison between both preconcentration procedures, NSM and SWMR, for a sample

Table 2
Figures of merit of the CE-UV analysis of the five pesticides under study using NSM and SWMR as preconcentration procedures

| Peak | Herbicide | NSM (60 s, at 0.5 psi) | | | SWMR (18 s at 20 psi) | | |
|---|---|---|---|---|---|---|---|
| | | LOD[a] (μg/L) | NTP/m[b] | Fold[c] | LOD[a] (μg/L) | NTP/m[b] | Fold[c] |
| 1 | Metosulam | 143 | 285 000 | 8 | 10.1 | 480 000 | 117 |
| 2 | Cloransulam-methyl | 195 | 250 000 | 11 | 9.8 | 555 000 | 214 |
| 3 | Diclosulam | 191 | 230 000 | 8 | 10.6 | 390 000 | 143 |
| 4 | Florasulam | 185 | 265 000 | 10 | 11.9 | 440 000 | 148 |
| 5 | Flumetsulam | 133 | 245 000 | 8 | 6.5 | 452 000 | 174 |

[a] Calculated as three times the S/N ratio.
[b] Number of theoretical plates per meter of column.
[c] Fold respect to the non-stacking procedure dissolving the pesticides into running buffer.

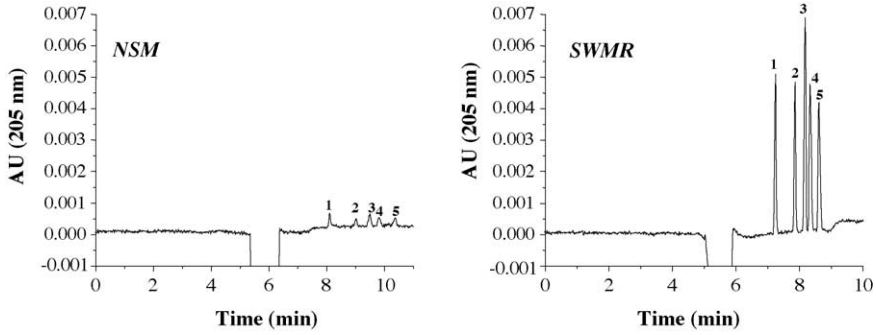



Fig. 1. Electropherogram of the separation of the selected pesticides carried out under NSM: sample in acetonitrile injected 60 s at 0.5 psi; SWMR: sample in acetonitrile injected 18 s at 20 psi, applied potential −23 kV (sample matrix removal), +23 kV (electrophoretic separation); Carrier electrolyte: 24 mM formic acid and 16 mM ammonium carbonate; Total length: 57 cm (50 cm effective length). (1) Metosulam; (2) cloransulam-methyl; (3) diclosulam; (4) florasulam; and (5) flumetsulam. Sample: 0.22 mg/L metosulam, 0.2 mg/L cloransulam-methyl, 0.24 mg/L diclosulam, 0.2 mg/L florasulam, 0.18 mg/L flumetsulam.

containing approximately 200 μg/L of each pesticide. As it can be seen in the figure, the increase in sensitivity provided by SWMR is clearly higher. In the literature, there are several papers that have also applied SWMR to the determination of other pesticides with very similar LODs [14–16]. As an example, in Refs. [14,15] the LODs for the SWMR procedure of quats standards in Milli-Q water were between 10 and 15 μg/L, which are slightly above the ones obtained in this work (between 6.5 and 11.9 μg/L).

### 3.3. Method validation

Under optimum SWMR conditions, the performance of the method was examined by carrying out a reproducibility study at three levels of concentration (50, 100 and 200 μg/L) with five consecutive injections during the same day ($n = 5$) and three different days ($n = 15$). Samples of higher concentration values yielded in peak overlap. Table 3 shows the result of the validation procedure for a concentration of 200 μg/L. As it can be seen in Table 3, relative standard deviation values (RSDs) were lower than 2.17% for migration times and lower than 6.31% for peak areas within the same day (i.e., repeatability), while day-to-day precision RSD values were lower than 2.62% for migration times and lower than 8.83% for peak areas, showing that the SWMR procedure is reproducible. Once the reproducibility study was carried out, calibration curves (based on the peak areas) were obtained at a working range of 40–200 μg/L by injecting each standard five times. Table 3 also shows the calibration parameters as, for instance, calibration equation, correlation coefficients ($R$), $S_{y/x}$ (standard deviation of residuals) and limits of quantifications (LOQs) calculated as 10 times the signal to noise ratio. As it can be seen, a good linearity, with correlation coefficients ($R$) higher than 0.9962 was observed.

### 3.4. Solid-phase extraction of water samples

In order to increase the sensitivity of our analytical protocol for its future application to real samples, an off-line SPE preconcentration procedure was developed prior to SWMR-CE-UV analysis using $C_{18}$ cartridges. These cartridges have been selected, according to previous experiments concerning the individual extraction of cloransulam-methyl and diclosulam from waters [20,21]. Moreover, no method has been proposed for the extraction of the other three pesticides from waters. Therefore, a new SPE extraction method was optimized using $C_{18}$ cartridges. Spiked Milli-Q water samples were initially used to optimize the extraction procedure. For this purpose, the volume of solvent used to condition the cartridge, the amount of sample extracted and also the volume of solvent used to elute the analytes were optimized. Optimum

Table 3
Repeatability, day-to-day precision (both expressed as RSD percentage) and figures of merit obtained with the optimized separation buffer and optimized SWMR procedure

| Pesticide | Repeatability (RSD %)[a] ($n = 5$) | | Day-to-day precision (RSD %)[a] ($n = 15$) | | Calibration curve ($n = 5$) | $R$ | $S_{y/x}$ | LOD (μg/L) | LOQ (μg/L) |
|---|---|---|---|---|---|---|---|---|---|
| | $t_R$ | Area | $t_R$ | Area | | | | | |
| Metosulam | 1.91 | 6.31 | 2.25 | 8.53 | $y = 1.593x + 0.0041$ | 0.9965 | 0.0067 | 10.1 | 33.7 |
| Cloransulam-methyl | 1.68 | 4.95 | 2.06 | 8.83 | $y = 1.401x - 0.0013$ | 0.9969 | 0.0036 | 9.83 | 32.8 |
| Diclosulam | 2.17 | 3.34 | 2.45 | 7.68 | $y = 2.858x - 0.0062$ | 0.9977 | 0.0093 | 10.6 | 35.3 |
| Florasulam | 1.83 | 2.08 | 2.62 | 6.47 | $y = 2.066x - 0.0027$ | 0.9962 | 0.0068 | 11.9 | 39.7 |
| Flumetsulam | 1.64 | 6.18 | 2.35 | 8.32 | $y = 2.281x - 0.0021$ | 0.9972 | 0.0051 | 6.54 | 21.8 |

[a] Data given for 100 μg/L.

Table 4
Mean recovery ($n = 3$), RSD (%) values and LODs of the selected pesticides in spiked mineral and stagnant water samples after SPE-SWMR-CE

| Pesticide | Mineral water | | | | | Stagnant water | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1000 ng/L | | 600 ng/L | | LOD (ng/L) | 1000 ng/L | | 600 ng/L | | LOD (ng/L) |
| | Recovery (%) | RSD (%) | Recovery (%) | RSD (%) | | Recovery (%) | RSD (%) | Recovery (%) | RSD (%) | |
| Metosulam | 59 | 7 | 64 | 11 | 328 | 63 | 5 | 55 | 8 | 342 |
| Cloransulam-methyl | 110 | 10 | 92 | 7 | 195 | 104 | 14 | 92 | 16 | 201 |
| Diclosulam | 105 | 9 | 100 | 1 | 207 | 108 | 11 | 85 | 9 | 220 |
| Florasulam | 92 | 5 | 101 | 5 | 247 | 97 | 2 | 91 | 7 | 253 |
| Flumetsulam | 102 | 15 | 98 | 5 | 131 | 104 | 7 | 99 | 10 | 129 |

extraction conditions were as follows: 5 mL of acetonitrile, 2 mL of 0.01 M HCl for conditioning, 50 mL of spiked water samples containing 2 mL of 1 M HCl, vacuum for 15 min and 10 mL elution with acetonitrile as described in Section 2. After evaporation of the acetonitrile in a rotary evaporator at 40 °C, 1 mL of acetonitrile was added and the solution was injected into the CE system for 0.3 min using SWMR conditions. Performance of the SPE was studied by comparing the electropherograms of the spiked samples with standards. Once the SPE procedure was optimized, it was applied to the extraction of spiked and non-spiked mineral and stagnant water at two levels of concentrations (1000 and 600 ng/L). Each sample was extracted three times ($n = 3$) and injected in the CE system three times following the optimized SWMR method. The injection of non-spiked water samples showed that the selected pesticides were not present in the samples. Table 4 shows the mean recoveries and RSD values of the extraction procedure. As it can be seen in Table 4, for spiked mineral water samples, mean recovery values ($n = 3$) were around 100% for all pesticides except for metosulam, which had a recovery between 59 and 64% for mineral water and between 55 and 63% for stagnant water. RSD percentage values ranged between 1 and 16%. As expected, the electropherograms showed that stagnant water samples were not as clean as mineral water (see below). Stagnant water was obtained from a non-potable source (a local deposit) and due to the great amount of organic matter that it has, the electropherograms were not as fine as for mineral water samples. However, the recoveries were very similar for both types of waters. According to these recovery values, LODs of the SPE-SWMR-CE-UV method (see Table 4) range between 131 ng/L for flumetsulam and 328 ng/L for metosulam in mineral water samples and between 129 ng/L for flumetsulam and 342 ng/L for metosulam in stagnant water. It is interesting to mention that these ultrasensitive LODs are similar to the best values reported in literature for pesticides using CE and stacking procedures [14,22,23].

In order to show the usefulness of the SPE-SWMR-CE-UV procedure, it was applied to the analysis of trace amounts of these pesticides in mineral and stagnant water spiked at 350 ng/L. Fig. 2A shows the electropherogram of the spiked mineral water. As it can be seen, all the pesticides could be detected at this low level. The injection of the same sample under NSM conditions (Fig. 2B) did not provide an appropriate sensitivity, as indicated previously. Fig. 2C shows the result of the direct injection of the sample (without previous SPE) using the SWMR procedure, demonstrating the necessity of

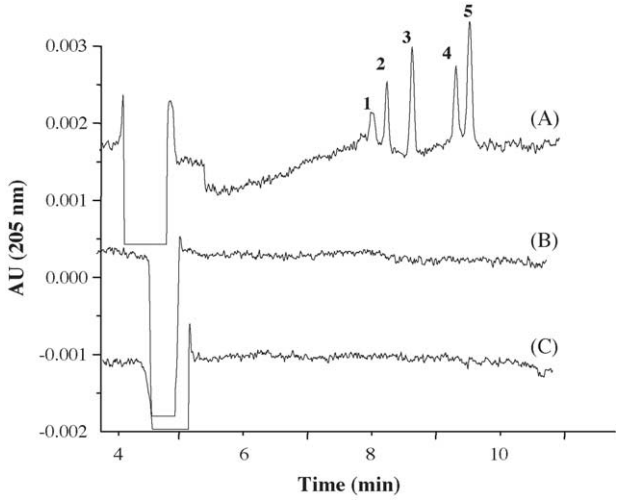



Fig. 2. (A) SPE-SWMR-CE-UV of a mineral water sample containing 350 ng/L; (B) SPE-NSM-CE-UV of a mineral water sample containing 350 ng/L; (C) direct injection using SWMR of a mineral water sample containing 350 ng/L of each pesticide. NSM injection of the same sample gave the same electropherogram. Note that EOF has been modified in order to clarify the figure.

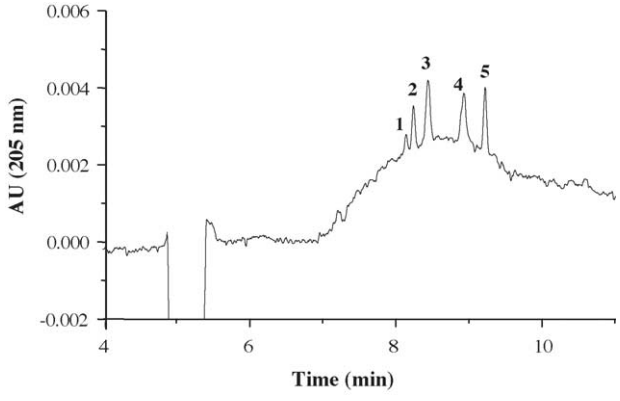



Fig. 3. Electropherogram of a spiked stagnant water sample containing 350 ng/L after SPE-SWMR procedure.

the combined use of SPE-SWMR-CE-UV in order to obtain adequate sensitivity. Fig. 3 shows the SPE-SWMR-CE-UV electropherogram of a stagnant water sample containing 350 ng/L of each pesticide. Once more, the five pesticides could be detected; however, as it has been mentioned before, the electropherogram is not as clean as for mineral water since a baseline displacement after 7 min of analysis appears in the electropherogram together with the selected pesticides. However, this fact seems not to have influence on the recovery and quantification of the analytes, as can be deduced from the results given in Table 4.

## 4. Conclusions

In this work, we propose the combined used of off-line SPE using $C_{18}$ cartridges and the on-line preconcentration procedure SWMR-CE-UV for the ultrasensitive and simultaneous determination of triazolopyrimidine pesticides (cloransulam-methyl, metosulam, flumetsulam, florasulam and diclosulam) in water samples. The proposed method is extremely sensitive for the selected pesticides, allowing their quick and feasible determination in mineral and stagnant waters down to the ng/L level with recovery percentages between 55 and 110%.

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