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Analysis of triazolopyrimidine herbicides in soils using field-enhanced sample injection-coelectroosmotic capillary electrophoresis combined with solid-phase extraction

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Abstract

In this work, a combined methodology using off-line solid-phase extraction (SPE), on-line field-enhanced sample injection (FESI) and coelectroosmotic capillary electrophoresis with UV detection (CE-UV) is developed for the trace analysis of five triazolopyrimidine sulfonanilide pesticides (i.e., flumetsulam, florasulam, cloransulam-methyl, diclosulam and metosulam). An adequate background electrolyte (BGE) was obtained for the separation of these pesticides using hexadimethrine bromide (HDB) as electroosmotic flow (EOF) modifier. This BGE consisted of 0.00042% HDB, 11 mM formic acid, 16 mM ammonium carbonate and 2.5 mM α-CD solution at pH 7.6. The use of this running buffer together with the FESI preconcentration method provided limits of detection (LODs) in the low μg/L range (i.e., between 13.0 and 31.5 μg/L). The optimized FESI-CE-UV method was combined with off-line SPE using C_{18} cartridges and applied to the determination of the selected group of pesticides in soil samples. Recovery percentages ranged between 50 and 84% in these samples with LODs between 18 and 34 μg/kg. This work shows the great possibilities of the combined use of SPE-FESI-CE-UV to improve CE sensitivity allowing the achievement of LODs similar to other analytical techniques as GC or HPLC.

Keywords: Solid-phase extraction; Field-enhanced sample injection; Capillary electrophoresis; Pesticides; Soil

1. Introduction

Analysis of pesticides is a difficult task since frequently they are found in very low concentrations in complex environmental matrices such as soils, sediments, foods, etc. This difficulty has brought about the necessity of developing separation methods with high efficiency, unique selectivity and high sensitivity. Capillary electrophoresis (CE) can meet many of these requirements, for this reason during the last decade CE has been gaining importance in separation science including the environmental field [1–5]. However, one of the main limitations of CE is its inherent low sensitivity, usually in the mg/L range, which is related to both the low sample volumes injected (normally between 1 and 10 nL) and the short optical path length employed for on-capillary detection. To overcome this problem, different strategies have been developed [6–8]. Among these strategies, the use of preconcentration strategies as on-line stacking or sweeping [9–11] or off-line procedures as solid-phase extraction [12], solid-phase microextraction [13], cloud-point extraction [14] seem to provide the most promising results for pesticide analysis by CE.

Recently, on line preconcentration methods have gained considerable interest due to the significant sensitivity improvement that they provide [9–11]. This is afforded by manipulating the composition and ionic strength of the sample matrix and BGE. One of these techniques is field-enhanced sample injection (FESI), first described by Chien and Burgi [15], which is an on-line sample preconcentration procedure based on the electrokinetic injection of a sample with a lower conductivity compared with the background electrolyte (BGE). In

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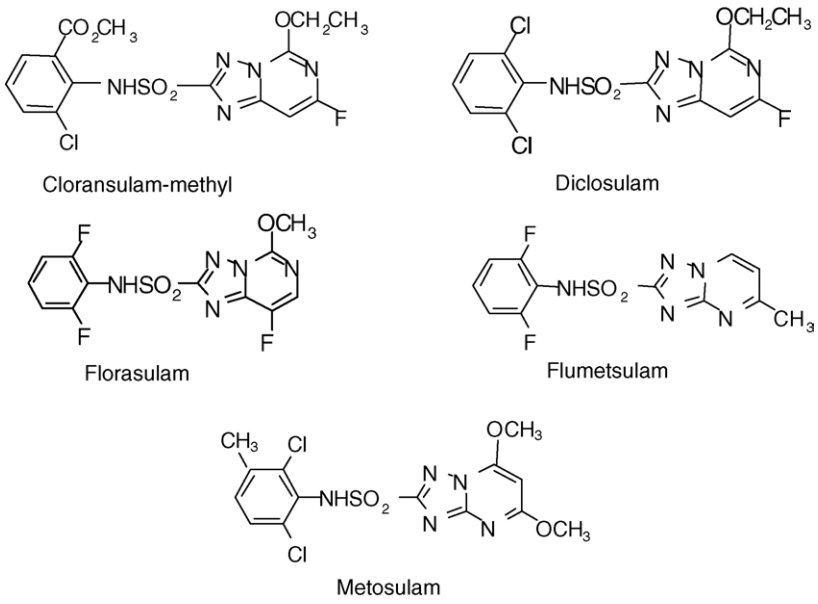

Fig. 1. Structures of the selected pesticides.

this case, only charged analytes or neutral analytes interacting with charged micelles can be concentrated. This on-line preconcentration strategy has also been applied to the analysis of pesticides several times [16–18] providing good sensitivity improvements.

Solid-phase extraction (SPE) has been used for the extraction of pollutants from different environmental matrices [12,19]. Concerning pesticide analysis it has proven to be a very effective tool for off-line preconcentration prior to CE. Besides, combination of SPE and CE has even been carried out in the on-line mode [20].

The pesticides studied in this work, cloransulam-methyl, metosulam, flumetsulam, florasulam and diclosulam (Fig. 1) belong to the triazolopyrimidine sulfonanilide family of herbicides [21]. They are frequently used as pre-emergence and/or post-emergence herbicides in soybeans, peanuts, etc. in different countries. Cloransulam-methyl, together with diclosulam and flumetsulam, which has been detected in Midwestern USA rivers [22,23], are frequently used in USA and registered by the US Environmental Protection Agency (EPA) [24]. Florasulam, however, is also registered by the European Union (EU) [25]. Metosulam, indeed, is registered and used in several countries around the world. In spite of the frequent combination of these herbicides for weed management, these compounds have mostly been analyzed individually by different techniques as metosulam by enzyme-linked inmunosorbent assay (ELISA) [26], cloransulam-methyl by HPLC [27], florasulam by MS [28], flumetsulam by GC–MS [29] and marked diclosulam by radio metric procedures [30]. Our group has recently demonstrated that CE can be a suitable analytical technique to analyze this type of pesticides in water samples [31].

Concerning environmental analysis, soils constitute nowadays one of the samples of major interest and complexity, especially for pesticide analysis. As a result, determination of pesticides and their degradation products in soils is mainly carried out by gas chromatography (GC) or high performance liquid chromatography (HPLC), e.g., the recent review by Andreu and Pico [32]. Although CE has also been used to determine pesticides in soils, there is a very low number of articles concerning this topic. As an example, sulphonylureas [33–35], phenoxyacids [36,37] and quats [38] have been determined in soils by CE. To our knowledge, there is not any analytical method developed for the simultaneous determination of this group of triazolopyrimidine sulfoanilide pesticides in soil samples.

In this work, we propose the simultaneous and trace determination of the five triazolopyrimidine sulfonanilide herbicides (diclosulam, cloransulam-methyl, flumetsulam, metosulam and florasulam) in soil samples by developing a new analytical strategy that combines off-line SPE, on-line FESI and coelectroosmotic CE-UV.

2. Experimental

2.1. Chemicals and samples

All chemicals were of analytical reagent grade and used as received. Ammonium carbonate and formic acid from Merck (Darmstadt, Germany). Acetonitrile, 2-propanol, 1-propanol, methanol, acetone and 1-butanol (HPLC-grade) were from Merck (Darmstadt, Germany). Cetyltrimethylammonium chloride (CTAC), hexadimethrine bromide (l,5-dimethyl-l,5-diazaundecamethylene polymethobromide, HDB), α-cyclodextrin and β-cyclodextrin were from Sigma–Aldrich (Madrid, Spain). 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[l,2,4]triazolo[l,5-*c*]pyrimidin-2-yl)sulfonyl]amino}benzo-

ate), diclosulam {*N*-(2,6-dichlorophenyl)-5-ethoxy-7-fluoro-[l,2,4]triazolo[l,5-c]pyrimidine-2-sulfonamide}, florasulam {*N*-(2,6-difluorophenyl)-8-fluoro-5-methoxy[1,2,4]triazolo[l,5-c] pyrimidine-2-sulfonamide}, flumetsulam{*N*-(2,6-difluorophenyl)-5-methyl[l,2,4]triazolo[l,5-a]pyrimidine-2-sulfonamide} and metosulam {*N*-(2,6-dichloro-3-methylphenyl)-5,7-dimethoxy[l,2,4]triazolo[l,5-*a*]pyrimidine-2-sulfonamide} obtained from Dr. Ehrenstorfer (Cymit Quimica, Barcelona, Spain) were used without further purification. 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.

2.2. Capillary electrophoresis-UV conditions

CE-UV analyses were performed in a P/ACE system 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 with 50 μm i.d. were purchased from Composite Metal Services (Worcester, UK). The detection length was 60 cm and the total length 67 cm. Injections were made at the cathodic end by electrokinetically injecting the sample for 8 s at −8 kV. Before first use, fused-silica capillary was activated with the following protocol: 0.1 M hydrochloric acid for 2 min, deionized water for 2 min, 0.1 M sodium hydroxide for 5 min, deionized water for 2 min and BGE for 3 min. Capillary conditioning was done every morning by rinsing 3 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 3 min. Electrophoretic separation was carried out at 21 °C and at −20 kV, using a 0.00042% HDB, 11 mM formic acid, 16 mM ammonium carbonate and 2.5 mM α-CD solution at pH 7.6 as separation electrolyte.

2.3. Solid-phase extraction procedure

Soil samples were collected in a rural area of the city of La Laguna, in Tenerife. Two grams of soil were weighted and spiked at different levels with the selected herbicides. After 2 h, they were extracted with 75 mL of water and 300 μL of 0.1 M NaOH in an ultrasonic bath for 20 min. Afterwards, the samples were centrifuged at 4000 rpm for 10 min. The supernatant was then separated, 1 mL of HC1 1 M was added and they were centrifuged again at 4000 rpm for 5 min. Then, 50 mL of the supernatant was 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 of acetonitrile followed by 2 mL 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 of acetonitrile. The organic solvent was then evaporated to dryness in a nitrogen stream. The residues were dissolved in 1 mL acetonitrile and 200 μL of a 16 mM ammonium carbonate solution, and directly injected into the CE instrument.

3. Results and discussion

3.1. CE separation

Since the triazolopirimidine sulfonanilide compounds investigated have pK_a values between 4.00 (diclosulam) and 4.81 (cloransulam-methyl) [39] a buffer at pH 6.4 was found in a previous work that allowed their CZE separation as anions [31]. However, under normal polarity conditions used in that work the stacking technique called *field-enhanced sample injection* (FESI), which has proven to provide high sensitivity improvements [40–42], could not be tested for these anionic compounds. Logically, FESI could be applied for these negatively charged compounds if CE with reverse electroosmotic flow was used providing simultaneous short migration times (reverse EOF and solutes would move in the same direction towards the anode). For this purpose, CTAB, CTAC and HDB have been tested in this work since they are well-known as EOF modifiers [42,43]. In the present work, the use of CTAC (0.1–0.8 mM) added to the pH 6.4 buffer containing 24 mM formic acid and 16 mM ammonium carbonate did not provide suitable separations for the compounds even when different concentration of formic acid and ammonium carbonate were tested. CTAB gave the same separation profile with higher background noise. A different modifier as HDB was tested (0.0001–0.003%) together with different pH values for the BGE. The best combination of HDB, formic acid and ammonium carbonate in terms of CE resolution of the pesticides was 0.00042% HDB, 11 mM formic acid, 16 mM ammonium carbonate at pH 7.6 (see Fig. 2A). Although the proposed method provided a good separation, cloransulam-methyl and diclosulam could not be completely resolved (see peaks 3 and 4 in Fig. 2A). In order to improve the CE resolution, addition of different organic modifiers as 2-propanol, 1-propanol, 1-butanol, acetone, etc. was tested in all cases at concentrations between 1 and 10%. As examples, Fig. 2B and C shows the effect of the addition of different percentages of 2-propanol to the separation electrolyte. As it can be seen, no improvement in the resolution of peaks 3 and 4 was achieved; in fact the resolution was lost increasing the percentage of organic modifier. Furthermore, all the modifiers used provided similar results, that is, an increase in separation time with no improvement in resolution. In fact, higher percentages of modifier provided a decrease in the resolution of nearly all pesticides. Therefore, other compounds like CDs were tested (namely, α-CD and β-CD) at concentrations between 1 and 8 mM in order to improve the separation. Although CDs are normally used as chiral selectors in CE, they have also been used as buffer additives to improve non-chiral separations [44,45] since they can modify the polarity of the BGE. In our case, the use of β-CD did not improve the separation while the use of α-CD at a concentration of 2.5 mM allowed the separation of the five pesticides (see below). Under these last conditions, the temperature effect was also studied between 15 and 25 °C,

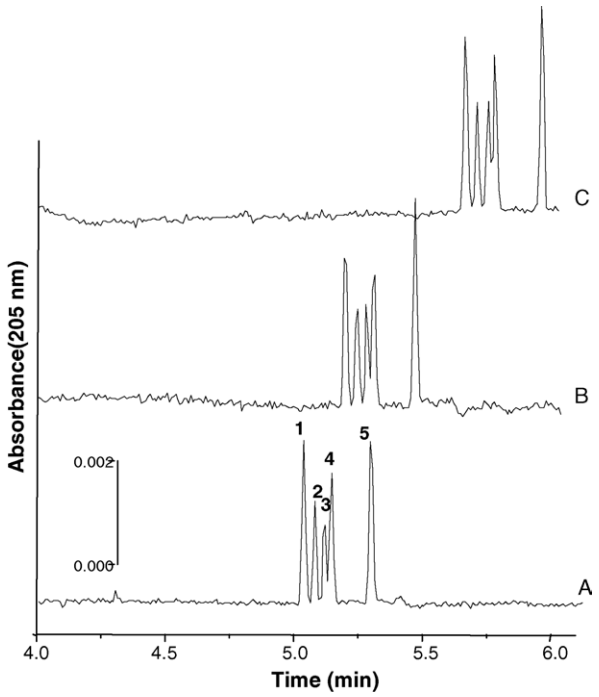

Fig. 2. Influence of organic modifier (2-propanol) in the separation of the selected pesticides. Running buffer: 0.00042% HDB, 11 mM formic acid, 16 mM ammonium carbonate at pH 7.6 and (A) 0% (v/v) 2-propanol; (B) 1% (v/v) 2-propanol and (C) 2.5% (v/v) 2-propanol. (1) Flumetsulam; (2) florasulam; (3) cloransulam-methyl; (4) diclosulam and (5) metosulam. Separation: −21 kV, 25 °C. Injection 5 s at −10 kV. Sample 420 μg/L of each pesticide in acetonitrile:separation buffer 5:1.

providing 21 °C the best results in terms of peak efficiency and resolution.

3.2. Field-enhanced sample injection

As previously indicated, sample preconcentration takes place in the FESI mode, which is accomplished by electrokinetically injecting a sample band with lower conductivity than the BGE. Since pesticides under study have pK_a values between 4.00 and 4.81, the sample matrix should provide both low conductivity and simultaneous ionization of the solutes in order to achieve an appropriate electrokinetic injection. For this purpose, several mixtures of acetonitrile and a solution of 16 mM ammonium carbonate (pH 9.04) or acetonitrile and separation buffer were tested. The use of the ammonium carbonate solution provided the best results in terms of sensitivity. Fig. 3 shows the influence of the percentage of 16 mM ammonium carbonate solution in the sample on the stacking of the analytes. As it can be seen, the highest peak areas were obtained with 17% of 16 mM ammonium carbonate in the sample matrix. Samples with percentages lower than 17% yielded in lower peak areas and also in very irreproducible injections. Moreover, high percentages of the ammonium carbonate solution as, for instance, 50% or 100%, yielded in very low and irreproducible peak areas. Besides, the introduction of a small water plug before the electrokinetic injection as suggested by other authors [15,46] to deeper concentrate the ions in the capillary, was tested without any success. Once

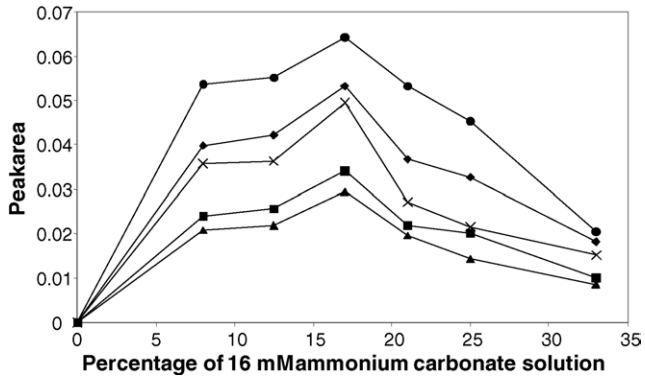

Fig. 3. Influence of percentage of 16 mM ammonium carbonate solution (pH 9.04) on the field-enhanced sample injection (FESI) of the selected analytes. Injection 6 s at −8 kV. Sample 330 μg/L of each pesticide. (◊) Flumetsulam; (■) florasulam; (▲) cloransulam-methyl; (×) diclosulam and (●) metosulam. Each sample was injected three times.

the optimum conductivity of the sample was selected, the injection voltage and injection time were optimized. Injection time was varied between 1 and 40 s and injection voltage between −1 and −10 kV, being the optimum values 8 s and −8 kV. No difference was observed between the use of −8 kV and higher values. In addition, higher injection times yielded in broadening of the peaks and, as a consequence, loss of resolution. Fig. 4 shows the separation of the five triazolopyrimidine sulfoanilide herbicides under optimum injection and separation conditions. Optimum injection and separation conditions provided limits of detection (LODs)-calculated as three times the signal-to-noise ratio in the μg/L range, between 13.0 μg/L for metosulam and 31.5 μg/L for cloransulam-methyl.

3.3. Method validation

Under optimum FESI conditions, the performance of the method was examined by carrying out a reproducibility study at

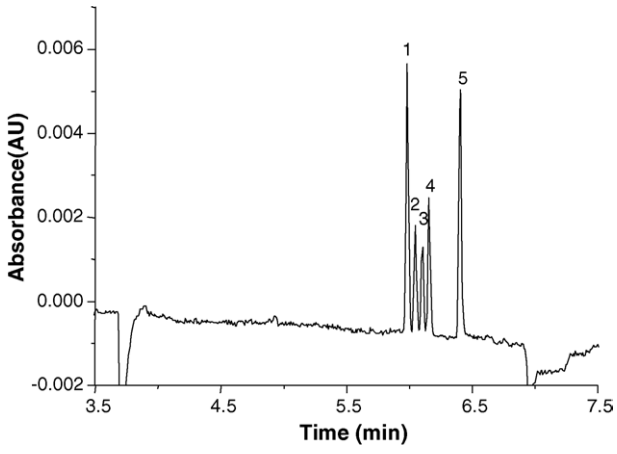

Fig. 4. Electropherogram of the FESI-CE-UV separation of the selected pesticides. Buffer: 0.00042% HDB, 11 mM formic acid, 16 mM ammonium carbonate, 2.5 mM α-CD at pH 7.6. Sample: 200 μg/L of each pesticide in acetonitrile with 17% of 16 mM ammonium carbonate solution. Injection: 8 s at −8 kV. Separation: −20 kV, 21 °C. (1) Flumetsulam; (2) florasulam; (3) cloransulam-methyl; (4) diclosulam and (5) metosulam.

Table 1
Repeatability, day-to-day precision (both expressed as RSD percentage) and figures of merit obtained with the optimized separation buffer and optimized FESI procedure

Peak	Pesticide	Intra-day precision (RSD%)[a] (n = 3)		Day-to-day precision (RSD%)[a] (n = 15)		Calibration curve (n = 5)	R	$S_{y/x}$	LOD (μg/L)	LOQ (μg/L)
		t_m	Area	t_m	Area					
1	Flumetsulam	0.21	4.04	1.29	8.33	$y = 0.5527x - 0.0073$	0.9973	0.0080	14.9	49.7
2	Florasulam	0.21	4.33	1.21	8.55	$y = 0.3518x - 0.0050$	0.9969	0.0054	26.0	86.7
3	Cloransulam-methyl	0.20	3.74	1.28	9.33	$y = 02869x - 0.0034$	0.9948	0.0057	31.5	105
4	Diclosulam	0.19	6.71	1.24	7.60	$y = 0.4541x - 0.0062$	0.9962	0.0077	20.2	67.3
5	Metosulam	0.20	5.54	1.29	9.60	$y = 0.6688x - 0.0129$	0.9965	0.0109	13.0	43.3

[a] Data given for 125 μg/L.

three concentration levels (125, 250 and 400 μg/L) with three consecutive injections during the same day (n = 3) and three different days (n = 9). Table 1 shows the result of the validation procedure for a concentration of 125 μg/L. As it can be seen in Table 1, relative standard deviation values (RSDs) were lower than 0.21% for migration times and lower than 6.71% for peak areas within the same day (i.e., repeatability), while day-to-day precision RSD values were lower than 1.29% for migration times and lower than 9.60% for peak areas, showing that the FESI procedure can be considered as reproducible. Once the reproducibility study was carried out, calibration curves (based on the peak areas) were obtained at a working range of 100–500 μg/L by injecting each standard three times. Table 1 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 0.9948 was observed in all cases.

3.4. SPE procedure of soil samples

As mentioned previously, to our knowledge there is not a SPE protocol for the simultaneous extraction of these five pesticides from soil samples. As a first step, we have tested the SPE procedure developed by our group for water samples [31]. For this purpose, several spiked soil samples (500 ng/g) from an agricultural area of La Laguna, which contained a high amount of organic matter, were ultrasonicated with 75 mL of Milli-Q water for several minutes and later centrifuged. One millilitre of HCl 0.1 M was added to the supernatant, filtered and submitted to the SPE protocol. With this protocol, pesticides could be extracted from the soil but with very low recovery values, around 15%. After several attempts to optimize the extraction, it was found that all the pesticides could be extracted at higher levels by using 75 mL of Milli-Q water at which 300 μL of 0.1 M NaOH were added. Since these pesticides have pK_a values between 4.00 and 4.81, at basic pH the pesticides are ionized and they can easily be extracted with deionized water. Optimum extraction time was found to be 20 min. Afterwards, samples were centrifuged, and 1 mL of 0.1 M HCl was added to the supernatant. In this step, precipitation took place (fulvic acids), and centrifugation was again carried out. This new supernatant was filtrated through a 0.45 μm filter and submitted to the already optimized SPE protocol, which was not changed. Fig. 5A, shows the CE-UV electropherogram of a spiked soil sample containing 200 μg/kg of each pesticide after the SPE and the FESI procedure. Fig. 5B shows the electropherogram of the same non-spiked soil sample after SPE-FESI-CE-UV. It can be seen that the selected pesticides are not present in the soil samples and also that no interfering peaks appear in the electropherogram. The SPE procedure was repeated three times with spiked soil samples at two levels of concentrations (200 and 500 μg/kg). As it can be seen in Table 2, recovery percentages (n = 3) range between 50 and 84%, and the LOD range between 18 μg/kg for flumetsulam and 34 μg/kg for cloransulam-methyl. These LODs values are similar to those reported in the literature for other pesticides and in some cases even lower than what were obtained by GC or LC methods as was reported in the review article previously mentioned [32]. At this point, it should also be stated, that although the proposed method is useful for the determination of these pesticides in soils, more work needs to be done in order to improve the recoveries and also to demonstrate its application to other different types of soils.

It should also be indicated, that the CE-UV LODs obtained in this work using FESI are slightly higher than the ones obtained in our previous work [31] (6.5–11.9 μg/L) for the analysis of the

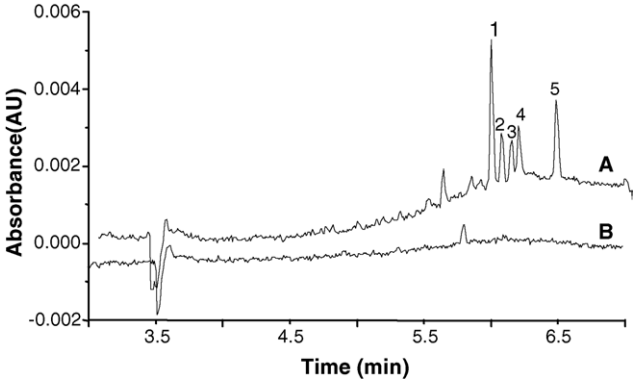

Fig. 5. Electropherogram of (A) a spiked soil sample containing 200 μg/kg after SPE-FESI procedure; (B) a non spiked soil sample after SPE-FESI procedure. All the conditions as in Fig. 4.

Table 2
Mean recovery ($n = 3$), RSD (%) values and LODs of the selected pesticides in spiked soil samples after SPE-FESI-CE-UV

Pesticide	Soil sample				
	500 μg/kg		200 μg/kg		LOD (μg/kg)
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Flumetsulam	70	2	76	13	18
Florasulam	77	6	80	8	30
Cloransulam-methyl	82	10	84	3	34
Diclosulam	57	8	65	15	30
Metosulam	57	15	50	10	22

same group of pesticides by using stacking with matrix removal SWMR-CE-UV. However, in [31] in which a SPE-SWMR-CE-UV method was used for the determination of these pesticides in mineral and stagnant waters, it was observed that when analyzing stagnant waters, which had a very high content in organic matter, the electropherograms were not as clean as when analyzing mineral waters. In fact, a baseline displacement was observed but still the pesticides could be analyzed. In the case of soil samples, the amount of organic matter is really high, much higher than in stagnant waters, and the use of SPE-SWMR-CE-UV was not found suitable for the analysis of these soil samples. In fact, it can be observed in this work that the recovery of the analytes are slightly lower than in [31], which can be attributed to the high organic matter content of the soil samples. Apart from that, electrokinetic injection, is more selective than the SWMR procedure developed in [31] and it is simpler and less time consuming than SWMR in which polarity should be switched at some stage and, in some of the available instrumentation, polarity switching must be carried out manually. In addition, as it can be seen in Fig. 5A and B, the electropherograms obtained by the FESI procedure are very clean and no baseline displacement was observed as when analyzing stagnant waters in [31]. Therefore, although the SWMR-CE-UV procedure provided slightly lower LODs, the FESI-CE-UV method is more suitable for the analysis of soil samples (concerning their high organic matter content of the samples) and its combination with SPE, provides LODs (18–34 μg/kg) very similar and even lower than for other groups of pesticides by GC or LC techniques, which is not usual.

4. Conclusions

In this work, a combination of off-line SPE and on-line sample stacking as FESI have been used together with coelectroosmotic CE-UV for the trace and simultaneous determination of triazolopyrimidine sulfoanilide pesticides (flumetsulam, florasulam, cloransulam-methyl, diclosulam, metosulam) in soil samples. The LODs achieved are in the μg/kg level with recovery percentages between 50 and 84%. This work shows the usefulness of the combination SPE-FESI-CE-UV to achieve low LODs, in some cases even lower than the obtained by GC or LC for other pesticides.

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