

# Determination of amitrole and urazole in water samples by capillary zone electrophoresis using simultaneous UV and amperometrical detection

M. Chicharro<sup>a,\*</sup>, M. Moreno<sup>a</sup>, E. Bermejo<sup>a</sup>, S. Ongay<sup>a</sup>, A. Zapardiel<sup>b</sup>

<sup>a</sup> *Departamento de Química Analítica y Análisis Instrumental, Facultad de Ciencias, Universidad Autónoma de Madrid, Paseo Tomás y Valiente, 7, 28049 Madrid, Spain*

<sup>b</sup> *Departamento de Ciencias Analíticas, Facultad de Ciencias, Universidad Nacional de Educación a Distancia, 28040 Madrid, Spain*

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## Abstract

In this paper, capillary zone electrophoresis with amperometric detection (CZE-AD) was first applied to the simultaneous separation and determination of amitrole and urazole in water samples. A simple end-column electrochemical detector was used in combination with a commercially available capillary electrophoresis instrument with UV detection. The effects of several important factors were investigated to find optimum conditions. A carbon disk electrode was used as working electrode. Separation and determination of these compounds in water samples were performed in 0.030 mol l<sup>-1</sup> acetate buffers at pH 4.5, 25 kV as separation voltage and the samples were introduced by hydrodynamic mode for 1.5 s. Most of the studies realized showed that the direct electrochemical detection is more sensitive and selective than UV detection. Under the optimum conditions, excellent linearity was observed between peak amperometric signal and analyte concentrations in the range of 0.19–1.35 mg l<sup>-1</sup> for amitrole and 0.20–1.62 mg l<sup>-1</sup> for urazole. The detection limits were 63 and 68 µg l<sup>-1</sup> for amitrole and urazole, respectively. The utility of this method was demonstrated by monitoring water samples, and the assay results were satisfactory. The detection limits using a previous preconcentration step for amitrole and urazole in spiked mineral water samples were 0.6 and 1.0 µg l<sup>-1</sup> for amitrole and urazole, respectively.

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## 1. Introduction

The intensive use of pesticides in the recent years has increased the agricultural productivity, but at the same time it has generated pesticide residues in natural waters at levels which exceed the legal limits. Amitrole (3-amino-1,2,4-triazole) is a well-known pesticide, which is often used in combination with other active agents in weed control via its inhibition activity on carotenoid biosynthesis [1–4]. The EPA cancelled all use of amitrole in food crops in 1971 as it was identified as a cancerous agent in animals [5]. The most recent studies of the environmental fate of amitrole in terrestrial and aquatic model ecosystems shown that under aerobic conditions have mineralization of amitrole is the main degradation pathway [4,6]. The experiments of these authors revealed that the leaching behaviour is low in the presence or the absence of dissolved organic matter (DOM)

despite the high water solubility of amitrole. Under anaerobic conditions the addition of DOM increases the transport of amitrole in soil columns. These results are more realistic assessments of the amitrole mobility than the previous studies described in literature and by the EPA of the USA [5]. This actual situation creates the need for rapid, simple and reliable methods for measuring amitrole. Various attempts have been made to determine amitrole at trace level demanded by the EU Drinking Water Directive but only one method for liquid chromatography and tandem mass spectrometry with pre-column derivatization has allowed the determination amitrole at this level [7]. In recent years, some authors have demonstrated that the principal degradation product of amitrole is the compound urazole [8].

The lack of data in environmental water is easily explained by the difficulty in determining this compound at trace levels in water, because there is no efficient analytical procedure allowing its extraction from aqueous samples. Its solubility is low in non-water miscible organic solvents 0.011 g l<sup>-1</sup> in methylene chloride and less than 0.001 g l<sup>-1</sup> in hexane and 280 g l<sup>-1</sup> in water, so its extraction from aquatic media using liquid–liquid

\* Corresponding author. Tel.: +34 91 4974041; fax: +34 91 4974931.  
E-mail address: [manuel.chicharro@uam.es](mailto:manuel.chicharro@uam.es) (M. Chicharro).

extraction is practically impossible [9,10]. The logarithm of its water–octanol partition coefficient is  $-0.5$ , so that this analyte is certainly too polar for being sufficiently retained by the widely used C18 silica in solid-phase extraction system. This behaviour explains why it is not surprising that most reported methods for concentrating this compound apply evaporation of water [9–11]. The analysis of the compound by gas chromatography is also difficult owing to its high polarity and low volatility. A method based on acetylation with acetic anhydride has been reported [10,12]. Liquid chromatography is more convenient for this polar analyte, but UV detection is not sensitive owing to the small extinction coefficient of the molecule. Liquid chromatography with electrochemical detection or with UV detection after derivatization has been described [7,10,13–15]. However, the study described in literature clearly illustrates the difficulties in coupling these two steps for real-life situations [13,14].

In recent years, capillary electrophoresis (CZE) has been developed as a highly effective analytical method in environmental areas because of its low sample consumption, short analysis time, high separation efficiency and relatively simple instrumentation [16]. Most frequently a UV detector is used, which is the standard of commercial capillary electrophoresis instruments. Determination of amitrole by CZE with UV detection has been previously investigated [17–19], but the main problem in the application of CZE with UV detection for the analysis of amitrole is the low detection sensitivity due to the short optical path length joined to small extinction coefficient of the compound. The detection limit allowed using a previous preconcentration step of amitrole in water by CZE with UV detection has been  $4 \mu\text{g l}^{-1}$  [17]. CZE with mass spectrometric detection has been also used for amitrole determination [20]. The shortcoming can be overcome by using electrochemical detection (ED). ED shows higher sensitivity and selectivity than UV; especially the amperometric detection can remove the interferences caused by electro-inactive substances [21–23], so it is suitable to be used with CZE in environmental analysis. ED has the advantage that the detection limits are not compromised by miniaturization. Steady-state measurements with perfectly prepared voltammetric microelectrodes may even lead to lower detection limits than the ones that are obtained with macroelectrodes. The required components for amperometric detection are rather simple and inexpensive. Moreover, ED is applicable to a broad range of important analytes, owing to the variety of electrode materials and electrochemical processes that can be used for the detection. However, the method of simultaneous separation and determination of amitrole and urazole with CZE-ED technique has not been reported.

In our study, CZE with simultaneous UV and amperometric detection has been employed for the separation and detection of amitrole and its degradation product, urazole. A handy, simple and versatile electrochemical detection cell for a commercially available capillary electrophoresis system has been used. This device has many advantages and has been described in different previous papers [24]. Effects of several important factors were investigated to find the optimum separation conditions. The proposed method has been applied to determine amitrole and urazole in mineral water samples.

## 2. Experimental

### 2.1. Reagents

Amitrole and urazole were purchased from Riedel de Hën (Sigma–Aldrich, Madrid, Spain) and were used without further purification. The compound's stock solutions  $0.010 \text{ mol l}^{-1}$  were prepared by dissolving an appropriate amount of the compound in purified water. All stock solutions were kept away from the light and stored under refrigeration. Diluted solutions were prepared daily from the stock solutions. All other chemicals used for the buffer and supporting electrolyte preparation were of analytical reagent grade. Water used for preparing solutions was purified with a Milli-Q Milli-RO water system (Millipore, Spain). Buffers and samples were micro filtered through a  $0.45 \mu\text{m}$  MFS-13 filter (Advantec MFS Inc., CA, USA) before to be used.

### 2.2. Apparatus

All electrochemical measurements were performed in the three-electrode mode using an electrochemical analyzer BAS 100B connected to a Pentium 4/PC computer. The three-electrode system consisted of carbon working electrodes, an Ag/AgCl reference electrode (BAS Model RE-5B) and a platinum wire auxiliary electrode (BAS, West Lafayette, IN, USA). The electrodes joined the cell through holes in its Teflon cover. Electrochemical experiments were carried out in a 5 ml voltammetric cell at room temperature.

A capillary electrophoresis with dual detection system (UV and electrochemical) has been described previously [24,25]. Capillary electrophoresis experiments were carried out with a SpectraPHORESIS 100 (Thermo Quest Corporation, Spain) equipped with a SC100 variable-wavelength UV–vis detector. Data acquisition and processing were accomplished using a Pentium 2/PC equipped with two channels and a Chrom-Card software package. No variation was introduced on the original commercial setup. A 92 cm fused silica column with a 2 cm Nafion tubing decoupler [26] was used for electrophoresis separations with amperometric and UV detection (effective length 60 cm). This column had an I.D. of  $75 \mu\text{m}$  and an O.D. of  $365 \mu\text{m}$  and was supplied by Supelco, cat. no. 77500 (Supelco, Bellefonte, USA). Amperometric detection was followed in a BAS amperometric detector LC-4C connected to the second channel of the Chrom-Card software package.

### 2.3. Electrodes

Graphite disk electrodes with  $900 \mu\text{m}$  diameter were prepared by covering a pencil lead (Pentel, Japan) with Chemsearch, a non-conductive insulator varnish (Chemsearch, Madrid, Spain). Glassy carbon electrodes (Goodfellow, 1 mm diameter) were prepared in the same way. One side was inserted into a flow injection analysis (FIA) fingertight nuts and filled with carbon paste (prepared by mixing graphite powder Acheson #38 (Fischer Scientific, Madrid, Spain) and mineral oil (Aldrich Chemical, Madrid, Spain), in a 70/30, w/w proportion). The final elec-

trical contact was established with a copper screw. The graphite and glassy carbon electrodes were polished with alumina slurries 0.3 and 0.5  $\mu\text{m}$  (Buehler, Spain) on BAS emery paper.

#### 2.4. Sample preparation

Mineral water samples bought in a local supermarket were spiked at different levels of concentrations and stored at room temperature for 3 h. First, samples were subjected to the clean-up procedure as described below. In all cases, a blank sample was submitted in the same procedure for comparison. Afterwards, the fortified sample (50.0 ml) was cleaned up by passing it onto C18 cartridge, which previously had been equilibrated with 5.0 ml of methanol and 5.0 ml of purified water. The effluents were evaporated to dryness using a vacuum rotary evaporator working at 60 °C and 125 rpm. The dry residue was dissolved in 0.5 ml of purified water. The reconstituted samples were prepared in triplicate and microvials were used to introduce the sample into the electrophoretic system.

#### 2.5. Electrophoretic procedure

The electrophoretic measurements were performed on the capillary electrophoretic system as described previously (see apparatus). The new fused silica capillary was first treated by rinsing with 1.0 mol l<sup>-1</sup> NaOH for 1 h, followed by 0.1 mol l<sup>-1</sup> NaOH for 1 h, then with purified water for 1 h. Everyday before conducting the experiments, the capillary was flushed with 1.0 mol l<sup>-1</sup> NaOH for 5 min, followed by 0.1 mol l<sup>-1</sup> NaOH for 5 min, then with purified water for 5 min, and finally with buffer until the inside current of the capillary reached stability. This was important to get a reproducible electroosmotic flow. Between the runs, the capillary was rinsed consecutively with water and the buffer.

CZE was performed at the separation voltage of 25 kV (13  $\mu\text{A}$ ) with 0.030 mol l<sup>-1</sup> acetate, adjusted at pH 4.5 and used as running buffer. Samples were introduced by hydrodynamic mode for 1.5 s (introduced volume being 49 nl). The UV absorbance detector was adjusted at 200 nm. The amperometric measurements were performed in the electrochemical cell filled with a 0.050 mol l<sup>-1</sup> acetate buffer (pH 4.5). The potential applied to the working electrode was 1050 mV.

### 3. Results and discussion

#### 3.1. Cyclic voltammograms

Cyclic voltammetry is a suitable technique for studying the electrochemical behaviour of electroactive compounds. It can help to select the potential of the working electrode. Fig. 1 shows cyclic voltammograms for amitrole and urazole obtained at glassy carbon electrode in 0.050 mol l<sup>-1</sup> acetate buffer at pH 4.5. According to cyclic voltammograms, the oxidations of both compounds were irreversible with one anodic peak at 1195 mV for amitrole and two anodic peaks at 655 and 1170 mV for urazole. The same behaviour was observed on a graphite electrode (not shown).

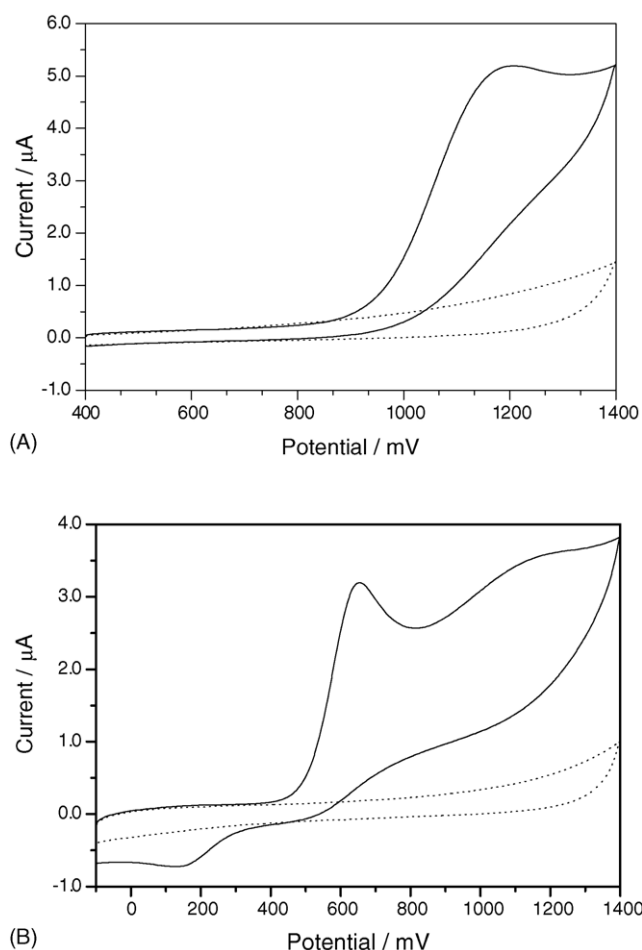


Fig. 1. Cyclic voltammograms of  $1.0 \times 10^{-3}$  mol l<sup>-1</sup> amitrole (A) and urazole (B) in 0.050 mol l<sup>-1</sup> acetate buffer solution at pH 4.5, at a glassy carbon electrode (1.0 mm diameter). Scan rate 50 mV s<sup>-1</sup>.

The effect of the scan rate, between 5 and 150 mV s<sup>-1</sup>, on the analytical signal was also investigated for 50 mg l<sup>-1</sup> of compounds in the acetate buffer of same concentration. A proportional dependence of the peak current on the square root of the scan rate was observed in both cases (not shown). This fact is indicative of a diffusional process.

#### 3.2. Analytical conditions of separation and quantification

In order to obtain the optimum capillary electrophoresis conditions, it is important to examine the effect of nature, concentration and pH of the running solution. Several buffers with a pH between 4.0 and 6.0 were tested (acetate, phosphate, MES, etc.). When the MES buffer was used the background signal went down just at the same time when the migration times of both compounds appeared. Under this situation the amitrole and urazole detection was not possible. When the phosphate buffer was used, only the separation of the compounds was possible between 5.5 and 6.0 pH. This behaviour is because the pH being lower than 5.5, the electrochemical signal of both compounds decreased with the increase in the analysis number, this behaviour may be due to a possible poisoning of the electrode

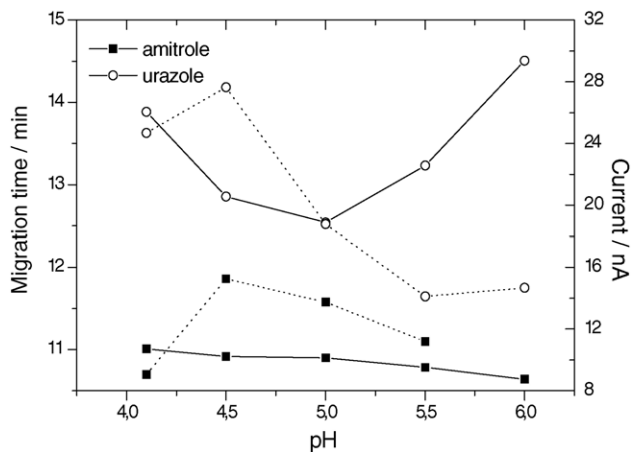


Fig. 2. Evolution of the migration time (solid lines) and peak current (dotted lines) with the pH of the running buffer. Fused silica capillary column 75  $\mu\text{m}$  I.D.  $\times$  100 cm length. Working electrode: 1.0 mm diameter glassy carbon electrode; applied voltage: 950 mV. Running buffer: 0.020 mol l<sup>-1</sup> acetate at pH 4.5. Separation voltage 25 kV. Hydrodynamic injection 2.0 s. Sample concentration: 3.0 and 4.0 mg l<sup>-1</sup> of amitrole and urazole, respectively.

surface. At pH higher than 6.0, the electrochemical signal of amitrole was split into two peaks. Acetate buffer was selected as the running buffer for the subsequent studies. Fig. 2 shows, in solid lines, the influence of pH on the migration times of amitrole and urazole, and in dotted lines, the influence of pH on the amperometric signal.

A pH of 4.5 was selected for the process because it produces the best sensitivity and efficiency and the shortest analysis time in the separation process.

The influence of the concentration of the separation buffer in the range 0.010–0.050 mol l<sup>-1</sup> on the separation was studied using pH 4.5 acetate buffers. It was found that amitrole and urazole cannot be separated completely when the buffer concentration was less than 0.010 mol l<sup>-1</sup>. But higher buffer concentration also has a negative effect on the separation. With the concentration of buffer increasing, high electrophoretic current generated and the effect of Joule heating becomes more pronounced, this in turn results in peak broadening and migration time lengthening, because the mobility is inversely dependent of the square root of the buffer concentration. For a comprehensive thought, 0.030 mol l<sup>-1</sup> was chosen as the buffer concentration in this work.

The study of the applied voltage was performed between 5 and 30 kV. A voltage of 25 kV (current 13  $\mu\text{A}$ ) was chosen because it produced the shortest analysis time together with the best sensitivity.

In CZE, the volume of injection directly influences the sensitivity of determination and the resolution of the analytes. Hydrodynamic injection was chosen to introduce the sample into the capillary column. The effect of injection time on CZE separation was investigated at two different compound concentrations (0.5 and 3.0 mg l<sup>-1</sup> for amitrole and 0.6 and 4.0 mg l<sup>-1</sup> for urazole). An injection time of 1.5 s (49 nl) provided the best results in both cases. Although in some cases peak area was still linearly related to injection times over 1.5 s and resolution was maintained, peak height response did not increase and peaks

broaden with a dramatic decrease in the number of theoretical plates.

Due to the good resolution between amitrole and urazole, our work focused on the effective capillary length. Different capillary lengths between 100 and 75 cm were tested. Lower capillary lengths were not possible to use because the minimum distance when the dual detection mode was used was 75 cm. An effective capillary length of 92 cm proved to be suitable and was chosen for subsequent studies.

Under the selected separation conditions, the mobilities for amitrole and urazole were evaluated [27]. Five different analysis of sample, containing 1.0 mg l<sup>-1</sup> of each compound were realized. The electrophoretic mobilities were  $1.0 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and  $-0.7 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for amitrole and urazole, respectively. The electro-osmotic mobility was  $5.8 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.

### 3.3. Working electrode and hydrodynamic voltammograms

Amperometric detection in CZE is one of the most sensitive detection modes, but the selection of material used to make the working electrode is decisively significant for the determination of the analytes. In our work, we used glassy and graphite carbon disk electrodes in 0.050 mol l<sup>-1</sup> acetate buffer solution. Moreover, the potential applied to the working electrode greatly affects the sensitivity and detection limits of this method and it is necessary to determine the hydrodynamic voltammograms for the electroactive compounds to obtain the optimum potential.

The hydrodynamic voltammograms obtained with glassy carbon and graphite carbon disk electrodes were very similar. Fig. 3 shows the hydrodynamic voltammograms of the amitrole and urazole using graphite carbon disk electrode (solid lines). The amitrole oxidation start at 800 mV and for higher potential than 1300 mV, the current considerably increases. In the case of urazole oxidation waves, one of them starts at 400 mV and the second one at 800 mV. In both cases when the potential was

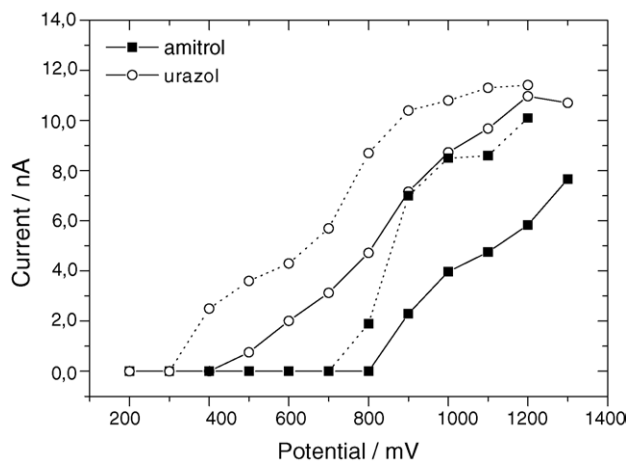


Fig. 3. Hydrodynamic voltammograms for 1.0 mg l<sup>-1</sup> of amitrole and urazole in graphite disk electrode without pre-treatment (solid lines) and with pre-treatment (dotted lines). Fused silica capillary column 75  $\mu\text{m}$  I.D.  $\times$  92 cm length. Running buffer: 0.030 mol l<sup>-1</sup> acetate at pH 4.5. Hydrodynamic injection 1.5 s. Other conditions as in Fig. 2.

higher than 1300 mV the base current too increased. Considering the detection sensitivity of the studied analytes and the background current, 1050 mV was chosen as the optimum working potential.

The reproducibility and stability of the analytical signal for both electrodes were studied for a series of ten sample injections of  $1.0 \text{ mg l}^{-1}$  amitrole and urazole (150 min of analysis time). In the case of the glassy carbon electrode, the signal of urazole decreased gradually from the second analysis and the background current increases with the analysis number. Higher analysis times imply a slight electrode poisoning and a signal decay (52% from the initial signal for analysis times greater than 45 min). On the other hand, the signal of both compounds in graphite disk electrodes was maintained stable (98% from the initial signal) during the 150 min of analysis time, which resulted in a relative standard deviation (RSD) of 9.0 and 6.2% for amitrole and urazole, respectively,  $n = 10$ . The cell provides stable measurements within reasonable long analysis times under the experimental conditions, despite the non-ideal redox behaviour of the electroactive compounds.

Considering that pre-treatments of carbon surfaces in general improve the electrooxidation of different compounds, we studied the influence of potentiostatic pre-treatment performed in NaOH  $0.1 \text{ mol l}^{-1}$  at 1500 mV during 1 min. Fig. 3 shows hydrodynamic voltammograms for amitrole and urazole in a graphite disk electrode without pre-treatment (solid lines) and with pre-treatment (dashed lines). The pre-treatment favoured the electrooxidation, increasing the peak current of both compounds. Therefore, a graphite disk electrode with potentiostatic pre-treatment was selected as working electrode. A typical electropherogram obtained under the optimum conditions using UV and amperometrical detection for a standard solution of amitrole and urazole is shown in Fig. 4.

It has been demonstrated in previous studies [24,25,28] that an electrochemical device used in connection with a commercial CZE system can give very good analytical results, for electrochemically reversible and irreversible analytes, in a simple way without the need of complicated precision apparatus. No distortion in the analytical signal was observed and stable baselines were usually obtained in all measurements. In the present work and under optimal conditions for the electrochemical device already described, one more study was performed. In order to obtain the best signal-to-noise ratio for the electrochemical determination of amitrole and urazole, different buffer solutions and buffer concentrations were tested in the electrochemical detection cell. Our studies found that a poisoning of the buffer solution of the electrochemical cell was not produced in a continuous separation process. In conclusion, the best conditions were obtained using the same solution used in the running electrolyte composition. On the other hand, we also observed that replacing the buffer solution after every seven analyses gives the best signal-to-noise ratio and the best sensitivity.

#### 3.4. Calibration curves and detection limit

Calibration curves using peak current as signal were used to quantify the two compounds. The volume introduced by

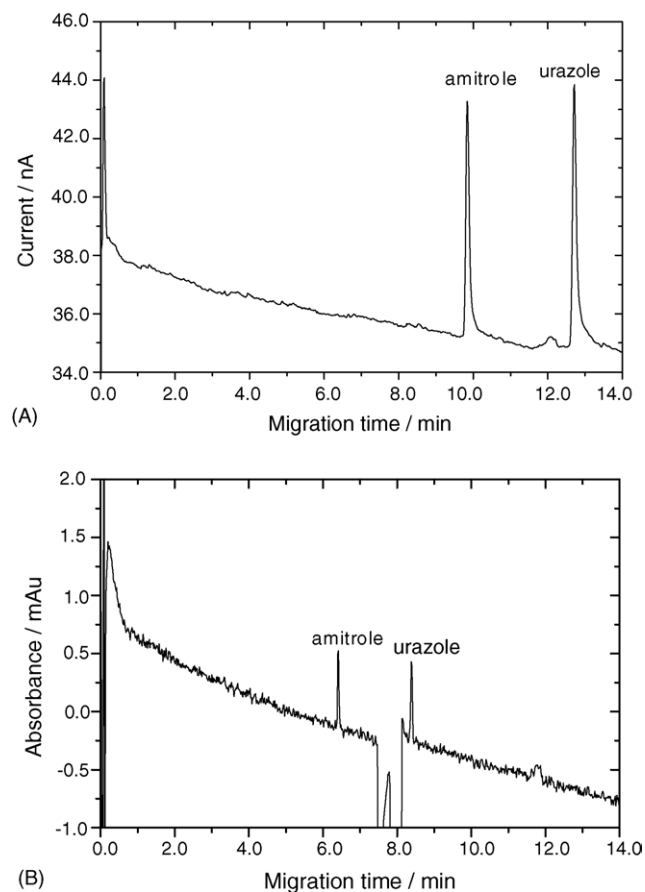


Fig. 4. Electropherograms for the CZE separation of amitrole and urazole under optimal conditions for electrochemical detection in a graphite disk electrode applying a voltage of 1050 mV (A) and for UV detection with a wavelength detection of 200 nm (B). Sample concentration: 1.0 and  $1.2 \text{ mg l}^{-1}$  for amitrole and urazole, respectively.

hydrodynamic injection was 49 nl. In Table 1, the regression equations, correlation coefficients, and detection limits for both compounds in UV and electrochemical detection are listed. Each point was reported as the average of four analysis. The electrochemical detector response at 1050 mV was linear in the sample concentration range from  $0.19$  to  $1.35 \text{ mg l}^{-1}$  for amitrole and  $0.20$  to  $1.62 \text{ mg l}^{-1}$  for urazole, respectively, and the UV detector response at 200 nm was linear in the sample concentration range from  $0.73$  to  $1.35 \text{ mg l}^{-1}$  and  $0.90$  to  $1.62 \text{ mg l}^{-1}$  for amitrole and urazole, respectively. Also, linearity was maintained at higher concentrations, but it was not considered to be of practical use taking into account the expected concentration levels for these compounds in water samples. In both cases the electrochemical detection is more sensitive than UV detection.

The migration time and the peak height reproducibility were evaluated at a concentration of  $1.0 \text{ mg l}^{-1}$  of each compound to check the performance of the CZE system. The RSD values obtained were below 5.6% of the peak height in electrochemical detection, lower than 8.0% in UV detection and below 1.5% in the case of the migration times. The high reproducibility indicates that this method is precise and rugged.

Table 1  
Results of regression analysis on calibration plots and the detection limits

Compound	Detection	Regression equation <sup>a</sup>	Correlation coefficient	Detection limit <sup>b</sup> (mol l <sup>-1</sup> (μg l <sup>-1</sup> ))	% RSD <sup>c</sup>	
					Peak current	Migration time
Amitrole	Electrochemical	$y = -0.2 + (6.4 \times 10^5)x$	0.994	$5.3 \times 10^{-7}$ (45)	4.0	1.0
	UV	$y = -0.02 + (6.2 \times 10^4)x$	0.998	$1.2 \times 10^{-6}$ (100)	7.5	1.3
Urazole	Electrochemical	$y = 0.01 + (7.1 \times 10^5)x$	0.9991	$8.4 \times 10^{-7}$ (85)	5.6	1.5
	UV	$y = 0.04 + (6.1 \times 10^4)x$	0.998	$1.1 \times 10^{-6}$ (110)	8.0	1.1

Working potential was 1050 mV for electrochemical detection and UV detector was adjusted at 200 nm.

<sup>a</sup>  $y$  is peak height peak (electrochemical detection in nA and UV detection in mAu) and  $x$  is the concentration of compounds in mol l<sup>-1</sup>.

<sup>b</sup> The detection limits corresponding to a concentration level equivalent to a signal of  $3\sigma$ .

<sup>c</sup> RSD (%) value based on nine different spiked water samples, using the same capillary ( $1.2 \times 10^{-5}$  mol l<sup>-1</sup> of each compound).

### 3.5. Amitrole determination in water samples

Under the optimum conditions, CZE-AD was applied for the determination of amitrole and urazole in mineral drinking water samples. The low minimum residue level in water samples imposed by the European Community Drinking Water Directive necessitates a preconcentration step of the samples to achieve a fit in the linear range of the proposed method.

In our work, a preconcentration step was carried out using evaporation of the water samples (described in Section 2). Application of the evaporation method to water samples volumes higher than 50.0 ml was not possible because certain compounds of the matrix appearing in the migration zone of the compounds were also preconcentrated.

The mineral water samples bought (BONAQUA) was analyzed. A non-spiked 50.0 ml aliquot of the sample was first analyzed, following the sample procedure to check the presence of our compounds. Qualitative analysis of the concentrated extract of mineral water showed in electrochemical detection one width peak, and in UV detection a width down in the back-

ground followed by a big peak, in both cases these signals did not correspond with any of our compounds. Therefore, subsequent water samples (50.0 ml) were spiked with different quantities of compounds. Fig. 5 shows the electropherograms for the mineral water subjected to a 100-fold preconcentration step. The recovery of spiked samples were  $84 \pm 6\%$  for amitrole and  $67 \pm 5\%$  for urazole ( $n = 3$ ). The detection limits of amitrole and urazole, applying the method in mineral water with the evaporation-step procedure followed in this work were, 0.6 and 1.0 μg l<sup>-1</sup>, for amitrole and urazole, respectively using electrochemical detection. Using UV detection the amitrole and urazole detection at this level of concentration was not possible.

## 4. Conclusions

A new method, based on the amperometric detection of amitrole and urazole using CZE has been presented. The system allows the UV and ED at the same time. The UV detection was performed in its usual configuration, on column, while the amperometric detection was performed in an end-column con-

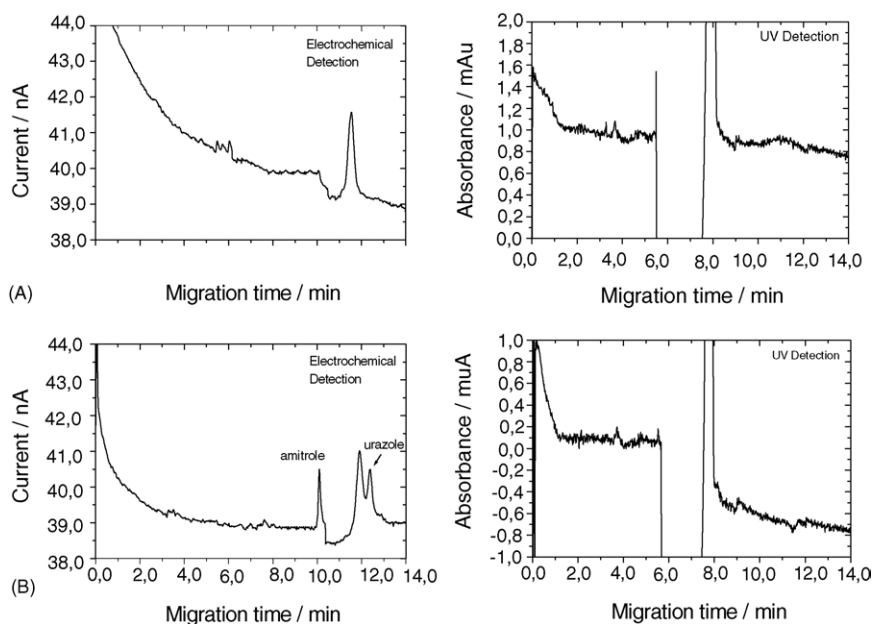


Fig. 5. Electropherograms of mineral water samples after preconcentrated 100-fold by evaporation under optimal conditions. (A) mineral water sample; (B) mineral water sample spiked with 3.3 μg l<sup>-1</sup> of amitrole and 4.7 μg l<sup>-1</sup> of urazole. Other conditions as in the text.

figuration. Such a combined method shows very good versatility and selectivity. This permits electroactive and non-electroactive compounds to be detected by the electrochemical and UV detection systems at the same time.

The data reported show that CZE is suitable for mono- and multiresidue analysis of different kinds of herbicides (in this case aminotriazole herbicide) in water samples using the ED system. Moreover, the data show that ED is more sensitive than UV detection in all cases. The determination of amitrole and its degradation product, urazole, was achieved under the best conditions for their separation and detection. The detection limits of the proposed method using amperometrical detection, without any preconcentration or clean-up steps, were lower than 63 and 68  $\mu\text{g l}^{-1}$  for amitrole and urazole, respectively. With a simple and fast clean-up and evaporation steps, assays close to the minimum residue levels can be carried out without interference from other substances present in mineral water samples. An enrichment factor of 100 was obtained by evaporating 50.0 ml mineral water samples and adjusting to 500  $\mu\text{l}$  extracts. The detection limits were 0.6 and 1.0  $\mu\text{g l}^{-1}$  for amitrole and urazole, respectively.

Due to the small amount of sample used and the buffer volume required, CZE-AD appears to be cheaper and environmentally safer than other analytical methods. The technique shows high separation efficiency and constitutes a good alternative to other analytical techniques for the determination of this kind of compounds.

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