Determination of ametryn in soils via microwave-assisted solvent extraction coupled to anodic stripping voltammetry with a gold ultramicroelectrode

Oriza Tavares Æ Simone Morais Æ Paula Paı´ga
Cristina Delerue-Matos

Abstract

An extraction-anodic adsorptive stripping vol- tammetric procedure using microwave-assisted solvent extraction and a gold ultramicroelectrode was developed for determining the pesticide ametryn in soil samples. The method is based on the use of acetonitrile as extraction solvent and on controlled adsorptive accumulation of the herbicide at the potential of 0.50 V (vs. Ag/AgCl) in the presence of Britton-Robinson buffer (pH 3.3). Soil sample extracts were analysed directly after drying and redis- solution with the supporting electrolyte but without other pre-treatment. The limit of detection obtained for a 10 s collection time was 0.021 lg g^{-1}. Recovery experi- ments for the global procedure, at the 0.500 lg g^{-1} level, gave satisfactory mean and standard deviation results which were comparable to those obtained by HPLC with UV detection.

Keywords
Ametryn Æ Gold ultramicroelectrode Æ Stripping voltammetry Æ Spiked soil samples Æ Microwave-assisted solvent extraction

Introduction

Triazine herbicides form a wide group of substances that are among the most common agrochemicals applied to pre- and post-emergence weed control (about 30% of all agricultural herbicides are triazines) [1]. They are ubiq- uitous environmental pollutants in soils and waters. Their use has caused great concern because they are mobile and soluble in water and can also be strongly sorbed into soils [2]. Surveys of the distributions of triazine herbicides, such as ametryn (2-methylthio-4- ethylamino-6-isopropylamino-1,3,5-triazine) and atra- zine (2-chloro-4-ethylamino-6-isopropylamino-1,3, 5-triazine), in the environment are generally performed using gas chromatography, high performance liquid chromatography (HPLC) and thin-layer chromatogra- phy [3]. Among the electrochemical methods, polarog- raphy is the most commonly-used technique [4–12]. In addition to chromatographic methods, adsorptive stripping voltammetry (AdsV), the most sensitive elec- troanalytical technique currently available [13], has been proven to be suitable for trace analysis of pesticides [14]. Only mercury electrodes have been tested as working electrodes in AdsV, where they were used in the cathodic AdsV determination of *s*-triazine [4–6, 10–12]. No study concerning anodic AdsV detection can be found in the literature. In the procedures reported, the substances to be analysed were removed from water by solid phase extraction [5, 8, 10, 12], and from wastewaters [6] and from soils by liquid extraction [12].

The main objectives of the present study were to inves- tigate the anodic adsorptive behaviour of ametryn on a gold ultramicrodisk surface and to study the feasibility of the combination of microwave-assisted solvent extraction (MASE) and anodic stripping square-wave voltammetry in order to obtain a simple, fast, highly sensitive and selective procedure for ametryn analysis in soil samples. Ultramicroelectrodes have a large number of attractive features and are gaining increasing importance in envi- ronmental electroanalysis [15]. MASE coupled with the application of ultramicroelectrodes provides methods that are considerably less aggressive environmentally, since minimal amounts of solvents are used and, in this investi- gation, the use of mercury as electrochemical substrate was avoided.

Experimental

Reagents

Stock standard solutions of ametryn and atrazine (Riedel-de Haë n, Germany; certified purity higher than 98.2% and 99.2%, respectively) were prepared in methanol or in acetonitrile (for HPLC assays) by weighing. For HPLC calibration plot standards, sub- sequent dilutions were made with acetonitrile and water in order to obtain a final ratio of 70:30, v/v (composition of the mixture selected to perform the isocratic elution). Solutions were stored at 4 °C and protected from light.

The supporting electrolyte was Britton-Robinson buffer [16], pH=3.3, prepared with $4.00 \cdot 10^{-2}$ mol l^{-1} acetic acid, $4.00 \cdot 10^{-2}$ mol l^{-1} phosphoric acid and $4.00 \cdot 10^{-2}$ mol l^{-1} boric acid. For pH studies, required pH values were adjusted by addition of 0.500 mol l^{-1} or 5.00 mol l^{-1} hydrochloride acid or sodium hydroxide.

Acetonitrile, dichloromethane and methanol were HPLC grade (Merck, Germany). All other reagents used were of analytical reagent grade (Merck). Deionised and triply distilled water was used for preparing all solutions.

Apparatus

An AUTOLAB potentiostat/galvanostat, model PSTAT 10, coupled with an ECD module (it is possible to perform measurements at extremely low currents up to 10^{-11} A) from EcoChemie, controlled by a PC through the Model GPES3 software, was used for all electrochemical measurements. The voltammetric studies were performed with a gold ultramicroelectrode (radius=$12.5 \cdot 10^{-6}$ m; purchased from the Department of Chemistry of the University of Southampton and constructed by sealing the gold wire into a glass capillary with epoxy resin) using an Ag/AgCl/3.00 mol l^{-1} potassium chloride reference electrode (to which all the potential values are referred) and a cylindrical carbon counter electrode. Electrical connections were made with low noise coaxial cables and the electrochemical system was placed inside a thick- walled aluminium Faraday cage.

To compare measurements during the determination of ametryn in soil samples, a HPLC system (Sykam 1210 liquid chromatograph) equipped with a 3200 UV/VIS detector configured to detect at 220 nm and connected to a computing integrator with a chromatography data station (PRIME 2.2.6) was used. The system has an injection valve with a 20 µl loop. The chromatographic separations were done on an ET Nucleosil C_{18} column (250 · 4.6 mm; 5 µm particle size) from Macherey-Nagel. Isocratic elution was accomplished at a flow-rate of 1.0 mL/min.

Microwave-assisted extractions were performed with a MARS-X, 1,500 W Microwave Accelerated Reaction System for Extraction (CEM, Mathews, NC, USA) configured with a 14 position carousel. During operation, both temperature and pressure were monitored in a single vessel. Magnetic stirring in each extraction vessel and a sensor registering the solvent leaks in the interior of the microwave oven were also used.

Preparation of the spiked soil samples

Two different soils: type I—pH 7.8, organic matter content 2.2%, water content 0.17%, and type II—pH 5.8, organic matter content 8.4%, water content 1.8%, were collected from two fields in the Chaves re- gion (in the north of Portugal). Samples from each soil type were thoroughly mixed to ensure homogeneity. After air-drying and sieving to a grain size of 2 mm, the soils samples were stored at 4 °C.

For recovery determination assays, the spiked soil samples (n=6) were prepared by adding 1 mL of a $1.10 \cdot 10^{-5}$ mol l^{-1} ametryn standard solution to a portion of 5±0.1 g of soil (for blanks, 1 mL of pure methanol was added). The samples were allowed to stand for 24 h to air-dry and were extracted by MASE thereafter. Fortification was made at the 0.500 µg g^{-1} level.

Microwave-assisted solvent extraction of soil samples

The spiked (n=6) and blank soil samples (n=1) were transferred quantitatively to the glass extraction vessels. After adding 20 mL of the tested MASE solvent to each sample, the vessels were closed. Three solvents were selected: (1) acetonitrile-0.5% ammonia in water (70:30, v/v); (2) acetonitrile, and; (3) dichloromethane-methanol (90:10, v/v). The operational parameters of the MASE apparatus applied were as follows: magnetron power 100%; time to reach settings 10 min; extraction tem- perature 110 °C; extraction duration 20 min; medium speed stirring; maximum vessel pressure cut-off 200 psi. After the extraction, the vessels were allowed to cool to room temperature before they were opened. The super- natants were filtered through a Whatman no. 42 filter paper and, for recovery studies, divided into two por- tions with the same volume: one for HPLC analysis and the other one for voltammetric analysis. The superna- tants were evaporated to dryness under a gentle stream of nitrogen. Immediately before analysis, the residues were redissolved by the addition of 20 mL of the Brit- ton-Robinson buffer (pH=3.3; two-fold dilution) or 1 mL of HPLC eluent (ten times preconcentration).

Voltammetric procedure

At the beginning of each working day, a gold ultrami- croelectrode was polished with 0.015 µm alumina, and

rinsed abundantly with deionised water until a perfect cyclic steady-state sigmoidal voltammogram was obtained in a solution containing 0.100 mol l^{-1} of potassium hexacyanoferrate(III)/potassium hexacyanoferrate(II) in 1.00 mol l^{-1} of potassium nitrate aqueous solution [17]. Then the working gold ultramicroelectrode was inserted in a 2.5–5 mL aliquot of a soil sample residue redissolved with Britton-Robinson buffer at pH=3.3. For the optimization and atrazine interference studies, blank extracts of soil of type II were redissolved and doped with the desired amount of ametryn and atrazine. The solution was purged with nitrogen (99.99% from LINDE, Portugal) for 15 min.

The preconcentration was accomplished in quiescent solutions at an optimal potential of 0.50 V for a selected deposition time. Following the anodic potential scan, a conditioning potential of 1.0 V was applied to the ultramicroelectrode for 30 s. The square-wave parameters used (except where otherwise stated) were: frequency 50 Hz, amplitude 30 mV; staircase step 3 mV. Voltam- metric quantifications were achieved by the standard additions method.

At the end of the day, the ultramicroelectrode was immersed in concentrated perchloric acid for rv1 min to remove any residues of organic compounds, and it was polished with alumina again.

Results and discussion

Microwave-assisted solvent extraction of soil samples

Simple, rapid and inexpensive methods producing minimum amounts of wastes, preferably wastes free of toxic organic solvents, are needed in environmental analysis. In recent years, sample preparation has attracted special attention, and as a result different instrumental tech- niques such as supercritical fluid extraction (SFE), son- ication and MASE are gaining increasing preference over the traditional laborious techniques of blending and shaking or refluxing (soxhlet) substrates with or- ganic solvents. In fact, among these instrumental tech- niques, MASE is becoming particularly popular due to its simplicity, low cost of operation in terms of required materials and manpower, and rapidity, while it is as accurate as SFE and sonication and superior in terms of precision [18–21]. When optimizing a MASE procedure,
a large number of parameters, such as temperature, ratio of sample/solvent, and extraction time can be consid- ered. These parameters affect extraction efficiency and selectivity. However, in this study, which employs
information available from the literature [22], MASE
method development was focused on the selection of an efficient and convenient solvent for soils with significantly different properties (type I and type II-see the ''Experimental'' section for details). An acetonitrile-0.5% ammonia in water (70:30, v/v) solvent mixture was selected, since this mixture is applied in the conventional procedure [23]. Acetonitrile was chosen a priori because most pesticides dissolve well in it. In order to significantly reduce the duration of the evaporation step with nitrogen after extraction, the applicability of a solvent mixture which included a high content of an organic solvent with a low boiling point, namely dichloromethane-methanol (90:10, v/v), was also investigated. The reference method chosen for quantitative analysis of soil extracts and validation of the proposed AdsV procedure was HPLC. The instrumental conditions were derived from published work [24] (see the ''Experimental'' section), and under these conditions the retention time of ametryn was 4.6 min. A HPLC calibration curve was established between $4.92 \cdot 10^{-6}$ mol l^{-1} and $2.62 \cdot 10^{-5}$ mol l^{-1}, which was fitted by the equation: $A = -1083 + 8.44 \cdot 10^{8}$ [ametryn] (mol l^{-1}); $r = 0.9996$; $n = 8$. The limit of detection (LOD) was calculated, as recommended by IUPAC [25], and a value of 0.028 μg g^{-1} was obtained (redissolution of the soil residues in 1 mL eluent). The mean recovery values of ametryn from soils, type I and type II, spiked with 0.500 μg g^{-1} are shown in Table 1. The conventional extraction, acetonitrile-ammonia in water, resulted in poor recoveries. It can be seen that the highest results were obtained with pure acetonitrile, but the mixture of dichloromethane-methanol also provided acceptable recoveries (>80%). The organic carbon content of the matrix is known to hinder the extraction, owing to strong analyte-matrix interactions that are difficult to disrupt. This fact may explain the somewhat lower values observed for samples of type II soil for the less efficient solvents. Pure acetonitrile was preferred as extraction solvent since it is considered an improvement over another MASE-based method reported for the analysis of triazine residues in soils [22]; in the latter method MASE was carried out in the presence of dichloromethane-methanol. The use of dichloromethane and of other halogenated solvents is slowly being phased out from analytical methods, especially those intended to be used to help protect the environment. Therefore, acetonitrile was tested by analysing fortified soil samples (0.500 μg g^{-1}; six samples for each soil type) stored for 41 days at 4–5 °C. The mean recovery values obtained by chromatographic analysis (Fig. 1) were 103.2±5.7% and 86.3±5.1% for type I and type II soil

Table 1 Ametryn recoveries from freshly-spiked soil samples (each one was analysed three times) using MASE with three extraction solvents (spiked level 0.500 μg g^{-1})

Solvent	Soil sample type	Recovery and RSD% (number of samples=6)
Acetonitrile-0.5% ammonia in water (70:30, v/v)	I	78.8±8.1
	II	67.8±10
Acetonitrile	I	99.7±2.3
	II	99.6±2.7
Dichloromethane-methanol (90:10, v/v)	I	89.8±2.6
	II	83.3±3.7

RSD: relative standard deviation; Type I soil: pH 7.8, organic matter content 2.2%, water content 0.17%; Type II soil: pH 5.8, organic matter content 8.4%, water content 1.8%

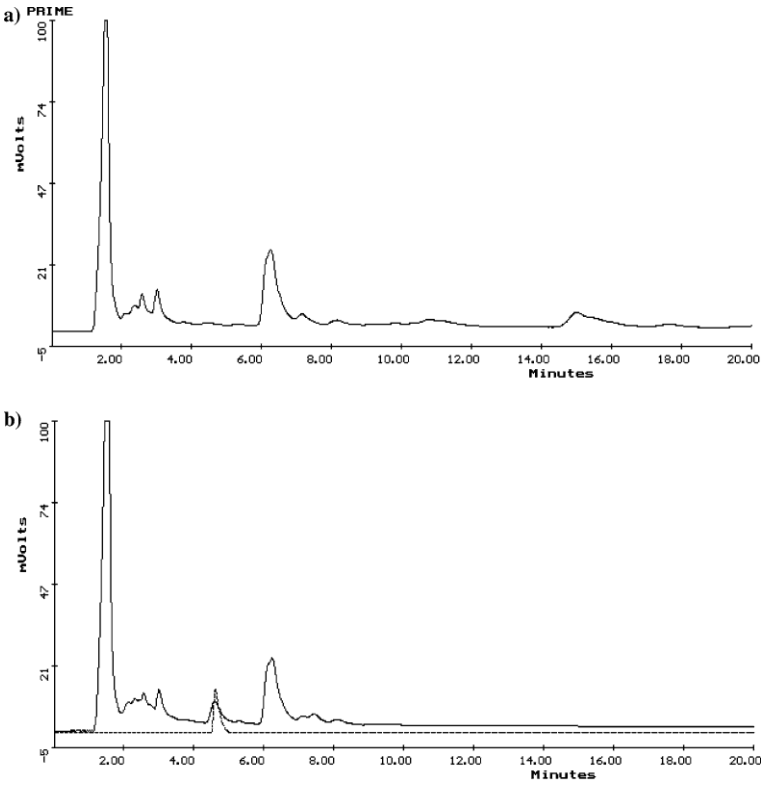

Fig. 1a–b Liquid chromatograms from the analysis of extracts of the richest organic matter soil sample, obtained using acetonitrile as optimum MASE solvent: a blank soil sample; b soil sample spiked with 0.500 **1**g g^{-1} ametryn (overlaid *dotted line chromatogram* corresponds to a $8.36 \cdot 10^{-6}$ mol l^{-1} HPLC standard)

samples, respectively. These results clearly validated the selected MASE procedure.

The ametryn voltammetric optimization studies described below were performed in type II soil extract (obtained with the optimum MASE conditions) residues redissolved with Britton-Robinson (pH=3.3), taking in consideration that the high organic matter content of this soil generates trickier experimental conditions.

Optimization of the voltammetric procedure

Preliminary investigations to characterize the electrochemical behaviour of ametryn on the gold ultramicroelectrode were carried out by recording cyclic voltammograms of a soil extract containing $1.20 \cdot 10^{-6}$ mol l^{-1} ametryn at several scan rates ranging from 10 mV s^{-1} to 2,000 mV s^{-1} (n=12). Some voltammograms are showed in Fig. 2. A clearly-defined anodic peak, due to the oxidation of ametryn, is observed at rv0.7 V. On the reverse scan, a poorly defined cathodic peak appears at rv0.37 V. Cycles performed at increasing scan rates gave rise to reduction–oxidation peak currents with intensities that showed increased linearly with scan rates up to 100 mV s^{-1}. The plot of log(i) versus log(scan rate) for the anodic peak is a straight line that follows the relation $\log(i(A)) = 0.548 \cdot \log(\text{scan rate}) - 7.51$; r=0.997; n=5; its slope is very close to that theoretically expected for a dominant diffusion-controlled process, but the value of the origin suggests that the electrode reaction is partly accompanied by adsorption (in most systems adsorption processes are very fast, so under most experimental conditions the rate of adsorption is controlled by diffusion) [26–27]. At

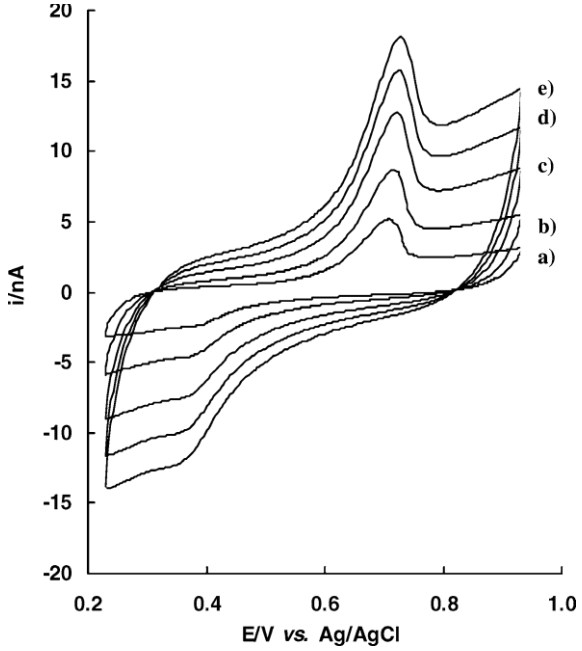

Fig. 2a–e Cyclic voltammograms of a soil extract containing $1.20 \cdot 10^{-6}$ mol l^{-1} of ametryn (pH 3.3) at several scan rates: a 10 mV s^{-1}, b 25 mV s^{-1}, c 50 mV s^{-1}, d 75 mV s^{-1} and e 100 mV s^{-1}

higher scan rates, the current growth of the cyclic voltammetric peaks decreases as a consequence of a rate-determining step such as protonation [4–5]. The anodic and cathodic peak potentials shift toward more positive values and toward less positive potentials with the increasing scan rate, respectively. This behaviour corre- sponds to a typical quasi-reversible system [28].

The anodic peak was selected for performing further optimizations since its definition and current are much higher than those obtained for the cathodic peak and because no anodic voltammetric determination of *s*-triazines was found in the literature.

To determine whether the compound exhibits surface-active properties, which would make the AdsV technique applicable, accumulation studies were carried out by square-wave voltammetry at pH=3.3. The effect of preconcentration potential on the peak height was evaluated by applying a potential, ranging from 0.10 V to 1.0 V, for 10 s to a soil extract spiked with $2.00 \cdot 10^{-7}$ mol l^{-1} ametryn. With the application of an accumulation potential lower than 0.70 V, asignificant increase in peak current (rv200%) (when compared to an open circuit) was obtained. Maximum intensities were reached using 0.50–0.60 V as the deposition potential. From the above results, it can be concluded that amet- ryn is not only oxidized and reduced but also exhibits interfacial adsorptive character on the gold ultramicro- electrode surface.

To reduce the fouling of the gold surface due to possible adsorption of the products of reaction, and to enhance the repeatability, an electrochemical cleaning step consisting of applying a conditioning potential of 1.0 V for 30 s was always performed before each new scan. As far as the effect of accumulation time on the peak current is concerned, two concentration levels $2.00 \cdot 10^{-7}$ mol l^{-1} and $7.00 \cdot 10^{-7}$ were studied depositing at 0.50 V. The peak current increased linearly over the periods 0–25 s (n=6) and 0–10 s (n=3), respectively. Then, for both levels, the peak response tended to reach a plateau, indicating that gradual saturation of the gold ultramicroelectrode occurred, following typical adsorption isotherm behaviour. Thus, the preconcentration time of choice will be dictated by the sensitivity needed to assay ametryn in different soil samples. However, it must be emphasized that, due to the enhanced mass transfer attained when using ultramicroelectrodes [17, 29], no forced convection during the deposition step is needed, and the time of analysis is reduced since short deposition times are applied and no equilibration period before the anodic scan was used (the duration commonly used for AdsV performed with conventional electrodes, like HMDE, is in the range of minutes).

According to the literature [30], the pH region below 1 is of no analytical interest since *s*-triazine herbicides hydrolyse rapidly. Figure 3 shows the influence of varying the pH between 2.0 and 6.7, using the Britton- Robinson buffer, on the anodic AdsV peak current of ametryn (Fig. 3 represents the sum of the contributions from the electrochemical reaction and the adsorption

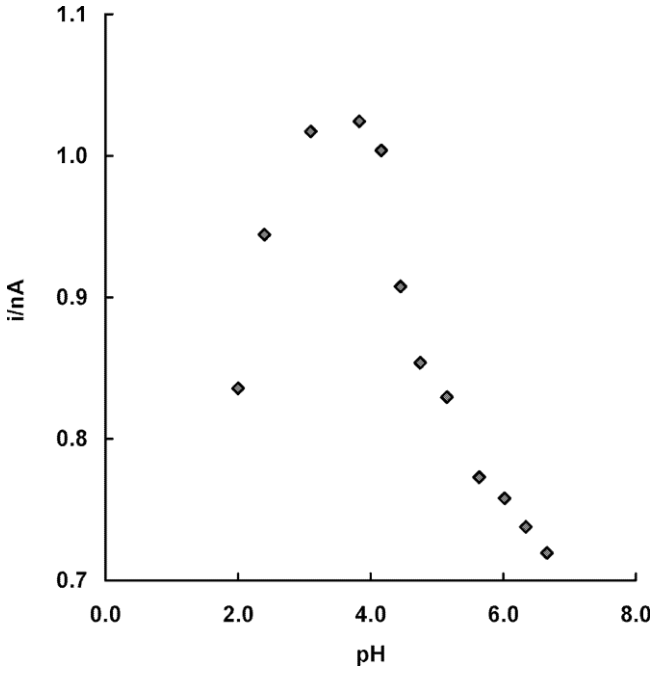

Fig. 3 Effect of varying pH on the anodic adsorptive stripping peak current of ametryn in a soil extract containing $4.00 \cdot 10^{-7}$ mol l^{-1}. Deposition for 10 s at 0.50 V

process, which may have different pH dependencies). This pesticide exhibits a high and regular peak at pH 3.1–4.2. Beyond this region, on both sides, the peak height decreases significantly. A shift of the peak po- tential towards less positive values was observed as the pH increased, indicating the existence of a protonation reaction coupled with the oxidation process [14]. This fact may help to explain the peak decrease observed for pH values higher than 4.2, that may be a consequence of a difficult electrode oxidation due to insufficient activity from the hydronium ions participating in the process. Since the p K_a value of ametryn in aqueous solution [30] is 4.05, it can be concluded that the protonated form of the investigated herbicide is predominantly present in acidic solutions falling within the above mentioned optimal pH region [4, 9]. This also means that the an- ionic (deprotonated) form of ametryn is not the elect- roactive species adsorbed and detected on the gold ultramicroelectrode surface.

The choice of a suitable supporting electrolyte is very important for the determination of triazine herbicides [5, 12]. Previous studies showed that the recommended medium for their determination by AdsV at the HMDE is Britton-Robinson buffer [5]. Variation of the ionic strength and the type of electrolyte have a less pro- nounced effect on the analytical signal when ultramicro- electrodes are utilized [17, 29]. Taking these facts into consideration, the medium selected to carry out further studies was the Britton-Robinson buffer at pH 3.3, which originated an ametryn anodic peak potential at rv0.65 V. The ability to readily assay low levels of concentra- tion was attributed not only to the effective accumula-

tion step (deposition potential and accumulation time) performed at the optimum pH, but also to the improved sensitivity of the applied waveform used to monitor the accumulated herbicide. A comparison [31] of square- wave and differential-pulse voltammetry for reversible and irreversible cases indicates that the square- wave currents are 4 and 3.3 times higher, respectively, than their analogous differential-pulse responses. The application of a square-wave waveform to ultramicro- electrodes presents very special features, namely: (1) the ohmic drops are greatly diminished, so sample treatment is minimized and in situ assays become possible; (2) the capacitive charging currents are highly reduced, allowing a better discrimination of the faradaic current;
(3) the reduced values of resistance and capacitance of ultramicroelectrodes lower the cell-time constant, and therefore allow the working electrode to apply the potential on very short time scales; (4) the small size of the ultramicroelectrodes enables analysis of very small sample volumes. These points have been documented in connection with trace analyses of: several metals in in vitro cell cultures [32–37]; the anti- depressant venlafaxine in urine [38]; pesticides in soils [39, 40].

The square-wave AdsV response depends markedly on the parameters of the excitation signal. Optimization of the square-wave parameters indicates that an ampli- tude of 30 mV, a staircase step of 3 mV and a frequency of 50 Hz are the most suitable for ametryn quantifica- tion in soil extracts, taking in consideration the peak definition and height.

Voltammetric analytical characteristics and application

Once the influences of all the variables that affect the square-wave voltammetric signal had been determined, and their optimum values established, the proposed procedure for quantitative assay of ametryn in soil ex- tracts of type II was validated by evaluating the linear working range, the LOD, the repeatability, the selec- tivity and the recovery of the system.

With a 10 s deposition time, and using the standard addition method (performing three replicates at each concentration), the concentration was found to be linearly dependent on the ametryn peak current within the range $4.60 \cdot 10^{-8}$ mol l^{-1} to $7.20 \cdot 10^{-7}$ mol l^{-1}. The LOD was calculated, as recommended by IUPAC [25], using the following equation for this linear region: $i(A) = 1.08 \cdot 10^{-10} + 2.35 \cdot 10^{-3}$ [ametryn] (mol l^{-1}); $r = 0.9995$; $n = 10$. The value obtained, 0.021 **1**g g^{-1}, confirmed the high sensitivity of the environmentally-friendly procedure developed here, using a deposition time of only 10 s (redissolution of soil residues in 20 mL of Britton-Robinson buffer).

In order to characterize the repeatability, measurement cycles were repeatedly carried out using a deposition time of 10 s in a soil extract containing $2.00 \cdot 10^{-7}$ mol l^{-1} of ametryn. The results from 50 successive measurements showed gave a relative standard deviation of just 3.3% (0.627±0.021 nA).

The selectivity of the optimized procedure was tested in the presence of the most common herbicide from the *s*-triazine family, atrazine. In the literature, it is well established that traditional mercury electrodes are not adequate for selectively determining pesticides from this class [4–12]. When the mixture contains more than one triazine compound, only one polarogaphic cathodic peak is detected because the peak potential values are very close together [4–12]. In this case, the peak current

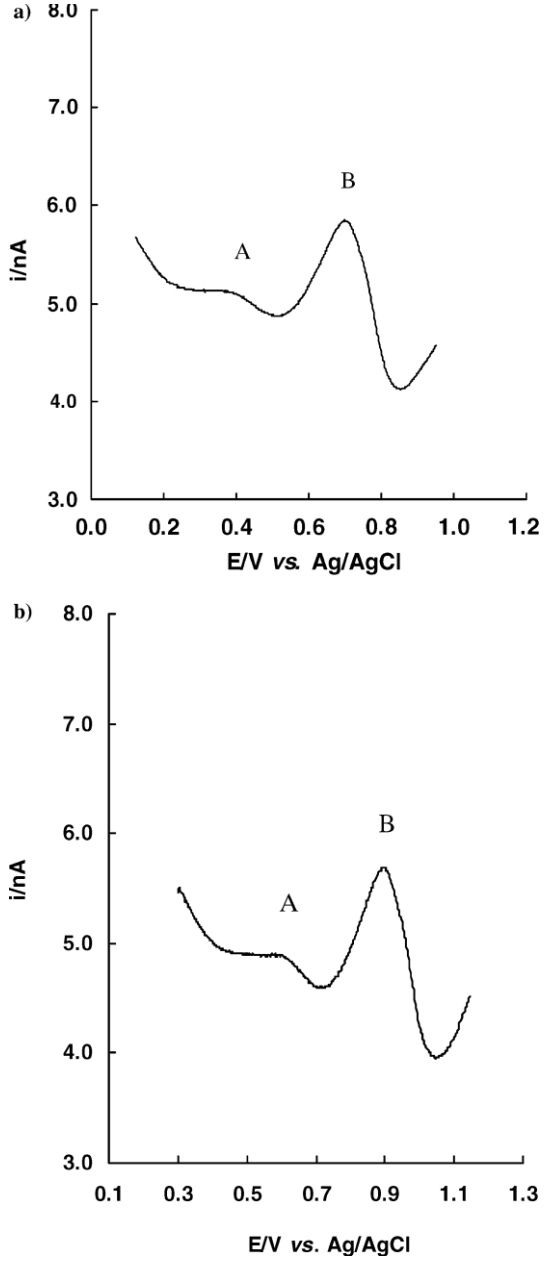

Fig. 4a–b Square-wave voltammograms for type II soil extracts, showing the atrazine (A) and ametryn (B) peaks obtained at (a) pH=3.3 depositing at 0.50 V and at (b) pH=2.0 accumulating at 0.35 V respectively

represents the sum of currents from all separate re- sponses [4–12]. Detection of the oxidation peak on the gold ultramicroelectrode surface enhances the selectivity enough to obtain well-separated peaks for ametryn (0.70 V) and atrazine (0.40 V) in soil extracts contami- nated with both pesticides (Fig. 4a). Furthermore, if the experimental conditions are changed to the optimum values for atrazine (pH=2.0; deposition potential 0.35 V; all of the other parameters the same as for a- metryn), the ametryn and atrazine potentials shift to 1.90 V and 0.60 V respectively, but selectivity remains (Fig. 4b). In line with the definition of the robustness of a procedure (the ability to remain unaffected by small changes in its operational parameters [41]), these results also mean that the developed methodology is robust.

After MASE (using acetonitrile, the optimum extraction solvent, under the conditions described in the ''Experimental'' section), filtration of the supernatant, drying, and redissolution of the residues with 20 mL Britton-Robinson buffer (pH=3.3) or 1 mL HPLC eluent, the proposed voltammetric procedure was suc- cessfully applied to the determination of ametryn in three soil samples of type II spiked with 0.500 lg g^{-1} (a commonly-applied dose). Validation of the results was confirmed by comparing them with to mean values ob- tained via a HPLC method, as reported in the literature [24] for the same set of samples. In anodic AdsV, the pesticide content was assessed by performing three standard additions of $1.00 \cdot 10^{-7}$ mol l^{-1} and an accu- mulation time of 10 s. Three replicates at each concen- tration were performed in both techniques. The average recoveries and standard deviations for the global pro- cedure achieved by MASE-square-wave voltammetry and by MASE-HPLC were 99.1±2.1% and 98.9±4.6% respectively.

Conclusions

In this work, a MASE procedure for extracting ametryn from two significantly different soil types was first established. Soil samples (freshly spiked and with aged residues) were extracted under optimal conditions, and the obtained results obtained show that stronger MASE conditions are not required for aged residues. Then an easy square-wave AdsV method based on the oxidation of ametryn at a gold ultramicroelectrode was developed for determining ametryn in soil extract solutions. The proposed procedure provides an important environ- mentally-friendly improvement of the AdsV methods already published, since the use of mercury was avoided, and this improved technique provides a similar LOD to these previous methods [4]. In addition, the selectivity is enhanced using this technique, allowing two herbicides from the *s*-triazine family to be distinguished. If real samples with very low ametryn concentrations are to be analysed, one approach is to redissolve the soil extract residues in a volume less than 20 mL (2.5 mL is enough to permit quantification with a ultramicroelectrode) or to increase the accumulation time significantly. If the sensitivity achieved is still not sufficient, a preconcen- tration step should be introduced, as used in previously published *s*-triazine polarographic studies [5, 8, 10–12].

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