Electroanalytical Study of the Pesticide Ethiofencarb

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Abstract: A detailed study of voltammetric behavior of ethiofencarb (ETF) is reported using glassy carbon electrode (GCE) and hanging mercury drop electrode (HMDE). With GCE, it is possible to verify that the oxidative mechanism is irreversible, indepen-dent of pH, and the maximum intensity current was observed at +1.20 V vs. AgCl/Ag at pH 1.9. A linear calibration line was obtained from 1.0×10^{-4} to 8.0×10^{-4} mol L^{-1} with SWV method. To complete the electrochemical knowledge of ETF pesticide, the reduction was also explored with HMDE. A well-defined peak was observed at −1.00 V vs. AgCl/Ag in a large range of pH with higher signal at pH 7.0. Linearity was obtained in 4.2×10^{-6} and 9.4×10^{-6} mol L^{-1} ETF concentration range.

An immediate alkaline hydrolysis of ETF was executed, producing a phenolic compound (2-ethylthiomethylphenol) (EMP), and the electrochemical activity of the product was examined. It was deduced that it is oxidized on GCE at +0.75 V vs. AgCl/Ag with a maximum peak intensity current at pH 3.2, but the compound had no reduction activity on HMDE.

Using the decrease of potential peak, a flow injection analysis (FIA) system was developed connected to an amperometric detector, enabling the determination of EMP over concentration range of 1.0×10^{-7} and 1.0×10^{-5} mol L^{-1} at a sampling rate of 60 h^{-1}. The results provided by FIA methodology were performed by comparison with results from high-performance liquid chromatography (HPLC) technique and demonstrated good agreement with relative deviations lower

than 4%. Recovery trials were performed and the obtained values were between 98 and 104%.

Keywords: Ethiofencarb, oxidation, reduction, square wave voltammetry, flow injection analysis, amperometric detection

INTRODUCTION

Ethiofencarb (ETF) (Fig. 1) is a systemic carbamate insecticide used worldwide in agriculture to control parasites (aphids) on vegetables, fruits, and corn (Tomlin 1997). The photodegradation of ETF in solar light is very rapid and sulfoxide and sulfone are the main degradation products. This pesticide and the product derived from its degradation give rise to residues that may spread through the environment and are particularly frequent contaminants in surface water and groundwater, in soil, and in agricultural and food products (Vialaton and Richard 2000).

Phototransformation of ETF was investigated in aqueous media. Half-lives were measured and photoproducts assessed by chromatography (GC) with mass spectrometry (MS) as detector, allowing the establishment of cleavage mechanism (Vialaton and Richard 2002; Climent and Miranda 1996).

A comparative photodegradation kinetic study of ETF in aqueous and non-aqueous media was carried out. ETF and its metabolites were analyzed by GC in combination with nitrogen-phosphorus detector (NPD) and MS (Sanz-Asensio et al. 1999). A kinetic study of the alkaline hydrolysis of ETF has been carried out using GC-NPD detection (Sanz-Asensio et al. 1997).

A method for monitoring pesticides in apple samples including Soxhlet extraction, an evaporation step, and capillary GC-NPD was applied to a decay study of ETF (Clavijo et al. 1996). Three other extraction procedures such as liquid-liquid extraction (LLE), solid-phase extraction (SPE), and micro-extraction (ME) in water samples were compared. In all cases, the determination was performed by GC-NPD (Barrio et al. 1996). Sometimes the LLE of ETF from fruits and vegetables is not efficient and the extract must be purified by Florisil column chromatography (Takahashi et al. 1995) or with gel permeation chromatography (GPC) (Ueno et al. 2002). Alternatively, the determination of residues of ETF can be performed using high-performance liquid chromatography (HPLC) with ultraviolet (UV) detection (Bicchi et al. 1996).

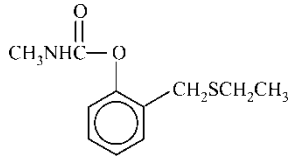

Figure 1. Structural formula of ethiofencarb.

A diode-array detector (DAD) was used to monitor ETF at two wavelengths simultaneously and to acquire spectra instantly (Scaroni et al. 1992). Derivatization of ETF to fluorescent derivatives was achieved by HPLC with fluorescence detection (Tsumura et al. 1995; Kok et al. 1992). Considering analytical techniques and sample complexity, the pretreatment is necessary and the methodologies are time consuming and expensive. To reduce these characteristics, an automatic system using a stopped flow procedure was described. The method is based on the reaction between p-aminophenol and the phenolic compound obtained from the alkaline hydrolysis. A spectrophotometric UV detector was selected (Garcia et al. 1995; Khalaf et al. 1996).

This work reports the study of electrochemical behavior of ETF at a glassy carbon electrode (GCE) and at a hanging mercury drop electrode (HMDE) using cyclic voltammetry (CV) and square wave voltammetry (SWV). The ETF oxidation occurs at a relatively high potential, and the alkaline hydrolysis produced 2-ethylthiomethylphenol (EMP) as metabolite, which oxidation is easier concerning the potential decrease of the oxidation peak. However, an important drawback of the voltammetry on solid electrodes is adsorption processes. In fact, successive records of ETF oxidation process on the same electrode surface produce a significant decrease in the analytical signal, probably due to an accumulation of products from the electrochemical reaction, which reduces the electrode active surface (Fernández-Abedul and Costa-Garcia 1996). This means that frequent cleaning of electrode surface is necessary, making this unsuitable for routine determinations and might lead to irreproducible analysis.

To surmount these difficulties and provide the easier oxidation capacity of 2-ethilmethilphenol, a flow injection analysis (FIA) system was developed linked to an amperometric detector. The samples were directly injected into the system and the hydrolysis occurred inside without any pretreatment with the production of phenol derivative. The short time of contact of the active substance with the electrode and the continuous passage of the carrier stream, which cleans the electrode surface, is another advantage of the FIA system, because it diminishes the adsorptions effects at the electrode surface.

The proposed voltammetric method allows the interpretation of ETF electrochemical process and the FIA methodology permits the drastic reduction of analysis time. The FIA system was applied to the determination of ETF in spiked natural water samples.

EXPERIMENTAL

Apparatus

All voltammetric measurements were performed using a 663 VA Metrohm cell containing a GCE (Metrohm 6.1204.000) (d = 2.0 mm) for the oxidation studies, or HMDE for the reduction studies, a glassy carbon rod counter

electrode (Metrohm 6.1247.000), and an Ag/AgCl/KCl 3.00 mol L^{-1} reference electrode (Metrohm 6.0728.000) attached to an Autolab PSTAT 10 potentiostat/galvanostat (Ecochemie) running with model GPS.

The pH measurements were determined with a Crison 2002 μpH with a Sentek 71728 combined glass electrode.

The FIA system comprised a Gilson Minipuls 3 peristaltic pump to propel the solutions, a four-way Rheodyne-type 5020 injection valve, and an amperometric detector. It consists of a 641 VA Metrohm detector linked to a 656 Metrohm wall jet containing a three-electrode system—a Metrohm (GCE) as the working electrode 6.0805.010 (d = 3.0 mm), a Metrohm Ag/AgCl/KCl 3.00 mol L^{-1} as the reference electrode (6.07027.000), and a Metrohm gold counter-electrode (6.530.320). To link the different components of the FIA set-up, polytetrafluoroethylene (PTFE) tubing (Omnifit, Teflon, 0.8 mm i.d.) and Gilson end fittings and connectors were used. Additional confluence point was constructed as reported earlier (Alegret et al. 1987). The analytical signals were recorded on a Kipp & Zonnen 112 recorder.

Glassy carbon working electrodes were mechanically cleaned before each experiment by polishing its surface using a polishing kit (Metrohm 6.2802.010), first with α-Al_2O_3 (0.3 μm) until a shining surface was obtained and after with only water.

HPLC analysis were performed by a Sykam A 1210 liquid chromatograph equipped with a model 3200 UV detector tuned to 194 nm. Separation of sample components was accomplished on a Supercosil LC-18 column (250 × 4.6 mm, 5 μm particle size) from Macherey-Nagel, Germany.

Reagents and Solutions

ETF (Pestanal grade, 99.9%) was purchased from Riedel-deHaen and used without further purification. All other chemicals were Merck pro-analysis grade and all solutions were prepared using purified water (conductivity $<0.1\ \mu S\ cm^{-1}$) obtained from a Barnstread E-pure 4 system.

In the voltammetric system, the electrolyte buffer solutions according to Britton-Robinson (BR), ranging between pH 1.9 and 11.5, were prepared by mixing different volumes of a phosphoric, acetic, and boric acid stock solution (containing each acid component at 0.16 mol L^{-1}) and a 0.8 mol L^{-1} NaOH solution in order to obtain the required pH (Fernández and Marti 1977). The ionic strength was adjusted with 1.34 mol L^{-1} KNO_3.

In the FIA system, acetate buffer solutions of pH 3.4 to 5.9 were used as support electrolyte and were prepared by mixing different volumes of acetic acid and sodium acetate solutions, both 2.0 mol L^{-1}, until the desired pH was reached. Subsequent dilution was performed to furnish solutions with a final ionic strength of 0.2 mol L^{-1}.

For the HPLC method, all the solvents used were of HPLC grade. Prior to use, the solvents were filtered and the air removed with helium.

Standard and Sample Preparation

Stock solutions of ETF (5.0×10^{-3} mol L^{-1}) were prepared with an exact weight of the pure pesticide dissolved in water. The standard solutions used for the optimization studies and plotting calibration curves were prepared by dilution of these stock solutions with water. These solutions were stable for at least 1 week if kept in the dark at $+4^{\circ}C$ when not in use.

Natural water samples were collected from various locations in Porto, Portugal (rivers and lakes), in dark glass bottles. The samples were spiked with ETF and directly analyzed by FIA system using the calibration curve method.

Comparison Method

Results from amperometric analysis were compared with those obtained using an independent method employed by Riedel-deHaen for quality control of pro-analysis grade reagent (Riedel-de-Haen 1999). HPLC was performed at room temperature with a mixture of water and acetonitrile (50:50, v:v) as mobile phase at flow rate of 1.40 mL min^{-1}. Calibration was performed by injection of 20 μL of ETF standard solutions with concentrations of 1.0×10^{-6} to 2.5×10^{-5} mol L^{-1}.

Procedures

The electrochemical behavior of 3.0×10^{-4} mol L^{-1} ETF was studied in BR buffer solutions of 0.3 mol L^{-1} ionic strength over a wide pH range (1.9–12.2) at GCE using CV and SWV. A known volume of the ETF solution, together with 10.0 mL of the BR buffer, were transferred to an electrochemical cell, and this solution was purged with purified nitrogen for 2 min. The electrode surface was polished between two consecutive scans.

In the reduction studies, 6.0×10^{-6} mol L^{-1} ETF in BR buffer solutions over a wide pH range (1.9–12.2) at HMDE using SWV technique were used. A known volume of the ETF solution, together with 10.0 mL of the BR buffer, were transferred to an electrochemical cell, and this solution was de-oxygenated with purified nitrogen for 10 min in the first cycle and 30 sec for each successive cycle. In this case, the electrode surface is automatically renewed between two consecutive scans.

The manifold used for the determination of ETF with amperometric detection has two confluence points and is depicted in Fig. 2.

A volume sample ($I = 400$ μL) was introduced in an ultrapure water carrier stream (R_1) without previous treatment, and the sample plug was then conveyed to the confluence X where NaOH solution ($R_2 = 0.04$ mol L^{-1}) was added to the flow. The alkaline hydrolysis occur in the coiled

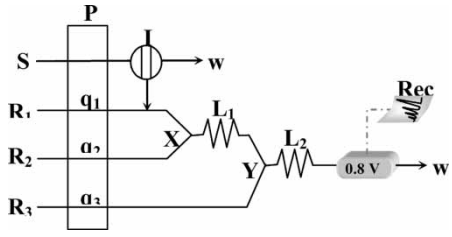

Figure 2. Flow injection system with amperometric detection: P, peristaltic pump; S, sample; I, injection volume (400 μL); R_1, carrier stream (water); R_2, sodium hydroxide solution (0.04 mol L^{-1}); R_3, acetate buffer solution (pH = 5.0); X, Y, confluence points; L_n, reactors ($L_1 = 400$ cm, $L_2 = 50$ cm); $q_1 = q_2 = 0.6$ mL min^{-1}, $q_3 = 1.2$ mL min^{-1}; DET, detector; Rec, recorder; W, waste.

tube reactor L_1 (400 cm); the bolus travels to the confluence Y where it merges with buffer acetate solution (R_3, pH = 5.0), and in reactor L_2 (50 cm) the ionic strength and pH adjustment are made as required by the detector.

RESULTS AND DISCUSSION

In this study, the electrochemical behavior of ETF in the zone of oxidation and reduction was initially studied, using for this purpose a glassy carbon working electrode and HMDE, respectively.

Oxidation Study of ETF with Glassy Carbon Working Electrode

The cyclic voltammograms of 3.0×10^{-4} mol L^{-1} ETF in BR buffer at pH 1.9 showed that this pesticide presents a peak of oxidation at potential of +1.20 V vs. AgCl/Ag, exhibiting a single irreversible anodic peak (Fig. 3). The absence of any cathodic peak on the reverse scan indicated the irreversible nature of the electrode reaction of ETF.

According to previous experiments, oxidation of a sulfur derivative may occur at a glassy carbon surface and against the same reference electrode at a potential close to 1.2 V. The loss of an electron occurs, originating a radical that may form a dimmer when two units are combined (Baizer and Feoktistov 1983) (Fig. 4).

The influence of the scan rate on the peak current (i_p) was studied within the range 0.05–0.40 V s^{-1}. The cycles carried out within the increased values of scan rates produced a linear relationship with the square root of the scan rate, indicating that the process at the surface of the electrode was mainly controlled by diffusion.

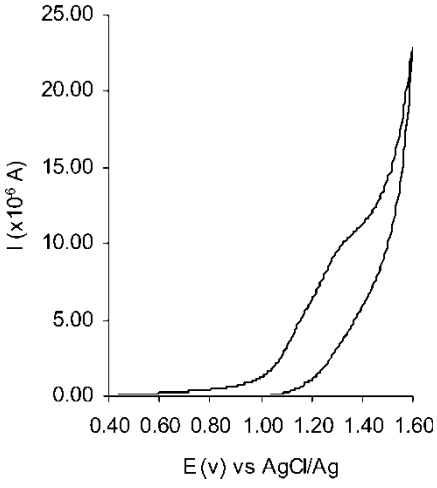

Figure 3. Cyclic voltammogram of 3.0×10^{-4} mol L^{-1} ETF in BR buffer at GCE, pH 1.9 scan rate 50 mV s^{-1}.

After knowing the electrochemical oxidation behavior of ETF, a more sensitive and rapid technique was used, SWV, to evaluate the influence of pH in the ETF peak shape and peak height.

To optimize pH, we used BR buffer solutions of 0.3 mol L^{-1} ionic strength over a wide pH range (1.9–12.2), using a frequency of 50 Hz. It was verified that this pesticide presents a maximum activity at pH 1.9. With the increase of pH, the peak current was found to decrease until the elimination of the peak at pH 10.0 and the peak shape became more and more distorted (Fig. 5). The potential of the oxidation is not dependent of pH values. Using a SWV technique (50 Hz, pH = 1.9), a calibration curve was plotted for ETF standard solutions within the range of 1.0×10^{-4} to 8.0×10^{-4} mol L^{-1} and achieving a linear relation between i_p and ETF concentration with a correlation coefficient of 0.999.

Study of ETF Reduction in HMDE

In order to complete the electrochemical study of this compound, the reduction zone was analyzed through HMDE.

Using HMDE and the SWV technique, the electrochemical behavior of 1.6×10^{-5} mol L^{-1} ETF was examined in BR buffers of different pH values (1.9–12.2) without preconcentration. It was verified that at pH 1.9 ETF is not electroactive, beginning to present electrochemical activity at pH 2.5, with a cathodic peak at potential −1.00 V vs. AgCl/Ag (Fig. 6). By increasing pH, i_p also increased but only until pH 7.0. From this value

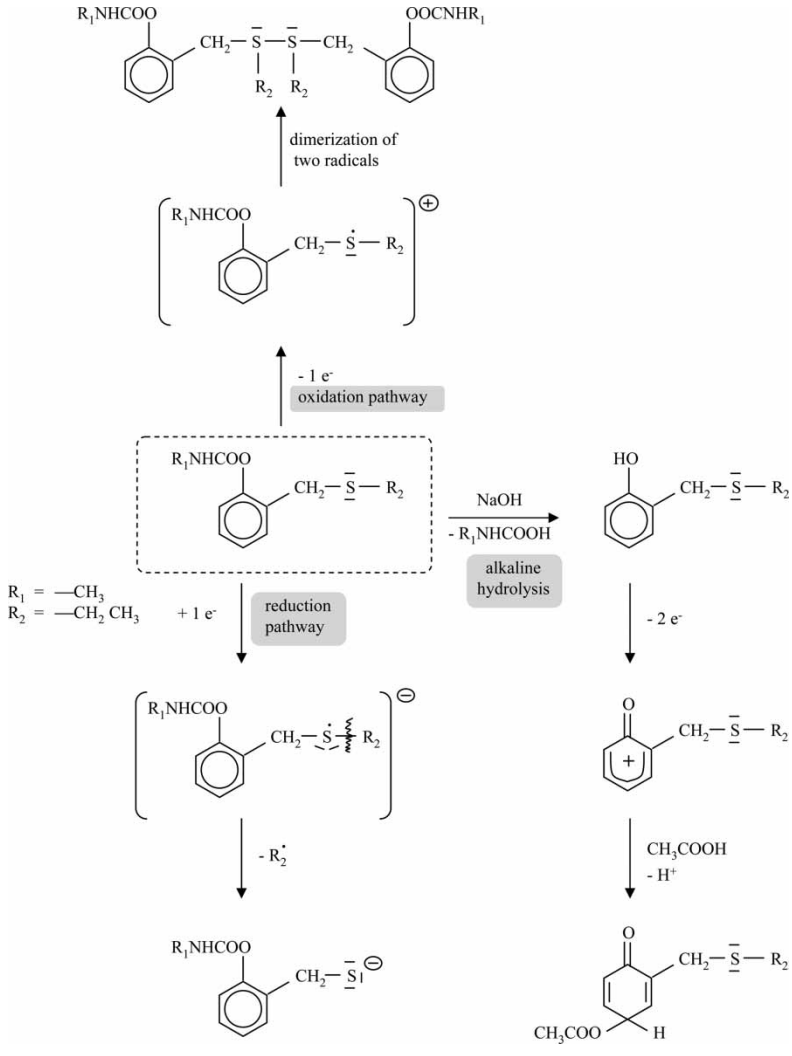

Figure 4. Mechanism for electrochemical oxidation and reduction of ETF and its alkaline derivative.

onward, the i_p decreased (Fig. 7). Because the best peak definition was found at pH 7.0, the BR buffer with this value of pH was selected for subsequent experiments. The potential of the reduction is not dependent of pH values.

According to literature information, the reported results suggest that the reducible unit among the ETF structure would be the sulfur atom. It gains an electron and loses an alquil radical, thus forming a negatively charged structure (Baizer and Feoktistov 1983) (−1 charge at the sulfur atom), as depicted in Fig. 4. This possibility is, however, a mere supposition, because

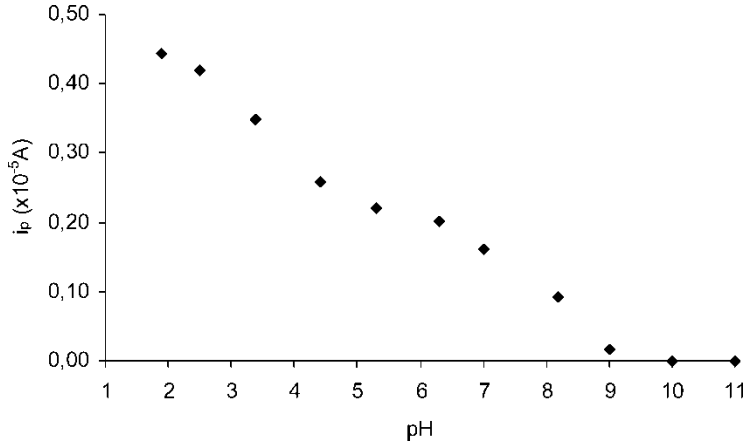

Figure 5. Influence of pH on the square wave voltammetric oxidation peak current (i_p) of 3.0×10^{-4} mol L^{-1} ETF at GCE.

no controlled potential electrolysis and product identification were performed. Several pathways may also be regarded after this stage.

The experimental parameters in SWV are interrelated and have a combined influence on the i_p. Hence, in order to establish the optimal conditions, the influence of parameters such as deposition potential, p_d, and deposition time, t_d, on the height peak of ETF was studied.

The dependence of the i_p (of 4×10^{-6} mol L^{-1} ETF in BR buffer of pH 7.0) on the p_d was identified over the range -0.10 to -0.50 V. A potential of -0.20 V was chosen as the accumulation potential because it gave a more developed peak current. Using the same conditions, the effect of t_d on the

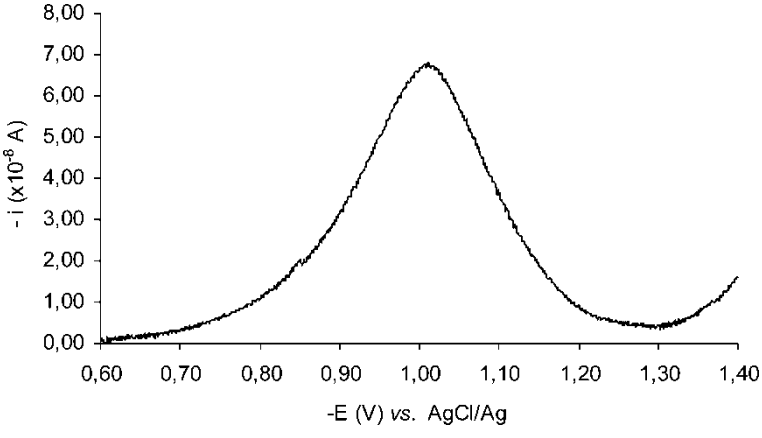

Figure 6. Square wave voltammogram of 1.6×10^{-5} mol L^{-1} ETF in BR buffer (pH 7.0) at HMDE.

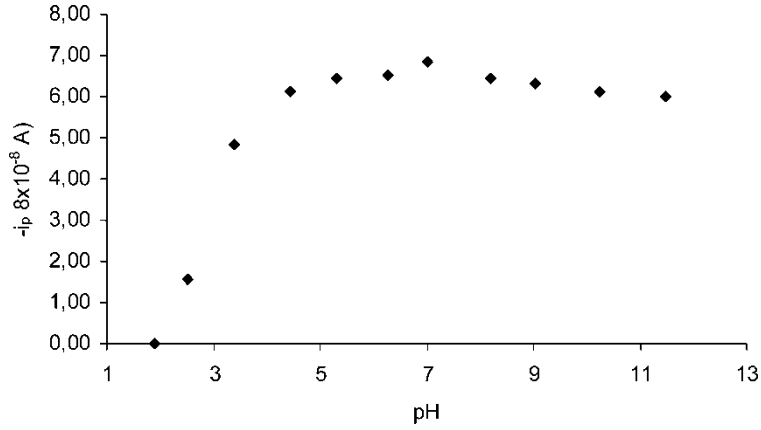

Figure 7. Influence of pH on the square wave voltammetric reduction peak (i_p) of 1.6×10^{-5} mol L^{-1} at HMDE.

preconcentration was also studied for a range of 0–20 sec. After 20 sec of accumulation, it was noticed that the i_p is at its maximum, which keeps approximately constant for higher values of t_d.

Having optimized experimental parameters (pH, p_d, t_d) and using a frequency of 50 Hz, a calibration curve was plotted for standard solutions of ETF in the range of concentration 4.2×10^{-6} to 9.4×10^{-6} mol L^{-1}, obtaining a linear relation between i_p and ETF concentration.

Electrochemical Study of Reaction Products of Alkaline ETF Hydrolysis

Considering that the potential obtained for ETF oxidation is fairly high (+1.20 V vs AgCl/Ag), the electrochemical behavior of the oxidation and reduction of the reaction products of alkaline ETF hydrolysis was analyzed.

In order to know the electrochemical behavior of the ETF derivative, cyclic voltammograms were done in the range of scan rate of 0.020–0.200 Vs^{-1} for hydrolyzed solution of 7.0×10^{-4} mol L^{-1} ETF with pH 3.2. A very well-defined anodic peak at + 0.75 V vs. AgCl/Ag and of irreversible nature was found (Fig. 8). According to literature, this peak corresponds to the oxidation of a phenolic derivative (Baizer and Feoktistov 1983; Guiberteau et al. 1995). This intermediate compound may suffer further stabilization in acetic medium after nucleophilic addition of acetate (Fig. 4).

The plot of i_p vs. $v^{1/2}$ is linear and passes through the origin, which proves that the oxidation reaction is controlled by a diffusion process.

In order to optimize the best experimental conditions (alkaline hydrolysis reaction time, basis concentration NaOH, pH) of hydrolyzed 3.0×10^{-4} mol L^{-1} ETF standard solutions, the SWV technique was used.

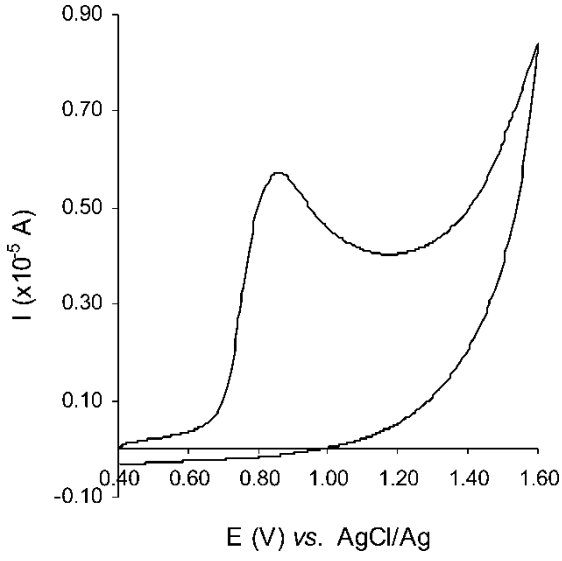

Figure 8. Cyclic voltammogram of the product of alkaline ETF hydrolysis (3.0×10^{-4} mol L^{-1}) at GCE. Scan rate 50 mV s^{-1}.

The optimization of the optimum value of pH was done for a range of 1.9–5.4 pH units. For this range, EMP always presented electrochemical activity with a maximum i_p at pH 3.2 (Fig. 9). It was also concluded (unlike what happened with ETF) that in this case the peak potential (E_p) is dependent of pH. A displacement of E_p to less positive values with the increase of pH indicated the involvement of protons in the electrode reaction. A plot of E_p (mV) vs. pH was linear with an equation of best fit of: [E_p (mV) = −36.9 pH + 848.5 mV; R = 0.989].

The reaction kinetics of alkaline hydrolysis were studied for a range of time of 0–30 min. For this time, i_p is independent of hydrolysis reaction time, and the reaction is almost instantaneous. For future tests, the time value of 0 min was chosen.

To perform an alkaline hydrolysis of an ETF solution, a strong basis (NaOH) was used. To optimize this parameter, the concentration of NaOH was changed between 2.0×10^{-3} and 2.0×10^{-2} mol L^{-1}. It was concluded that by increasing NaOH concentration, i_p also increases until it reaches a maximum at a concentration of NaOH of 1.0×10^{-2} mol L^{-1}. From this concentration point onward, i_p stays almost constant.

From the optimized values (pH = 3.2, hydrolysis reaction time of 0 sec, and NaOH concentration of 1.0×10^{-2} mol L^{-1}) and using the SWV technique with a frequency of 50 Hz, calibration curves were plotted for ETF hydrolyzed solutions in the range of concentration from 1.0×10^{-4} to 6.0×10^{-4} mol L^{-1}. For this concentration interval,

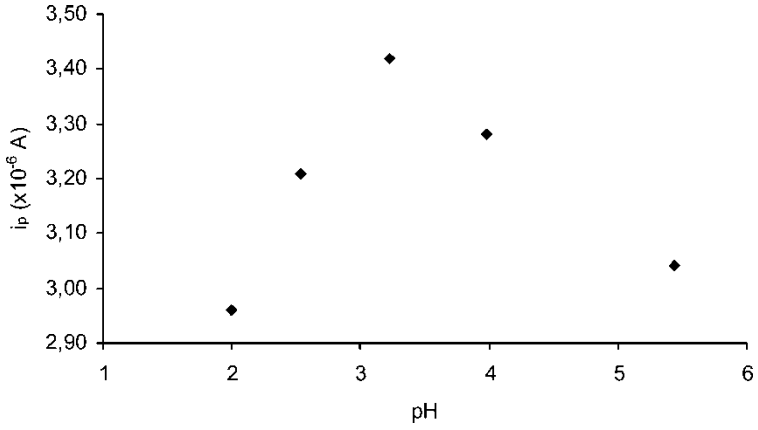

Figure 9. Influence of pH on the square wave voltammetric oxidation peak (i_p) of the product of alkaline ETF hydrolysis (3.0×10^{-4} mol L^{-1}) at GCE.

i_p varies linearly with concentration, obtaining a coefficient of correlation of 0.999.

The reduction of hydrolyzed solutions of ETF in HMDE was also studied thoroughly, but the product of this hydrolysis did not present electrochemical activity. The inability of a sulfur reduction after the alkaline hydrolysis and within the studied potential ranges suggested that the –S– "group" suffered chemical alteration. So, the –S– "group" of the alkaline derivative may not be exactly as represented in Fig. 4, which follows information from reference (Guiberteau et al. 1995).

Optimization of FIA System

The FIA manifold used in the determination of ETF was gradually optimized by the univariant method with the purpose of allowing the introduction samples without pre-treatment and maximizing the sensitivity, reproducibility, and sample rate.

The influence of several parameters, namely, pH of supporting electrolyte, working electrode potential, concentration of sodium hydroxide, flow rate, injection volume, and length of the reactors, was assessed. The study of the best working conditions of the FIA manifold was made using 1.0×10^{-5} mol L^{-1} of ETF.

Because the hydrolysis product is readily oxidized at the glassy carbon electrode, the optimization was started by investigating the effect of pH of the support electrolyte. Based on the previous results of the voltammetric study, the potential was fixed at +0.80 V and the pH was varied from 3.4–5.9. Within this pH range, the best results—higher absolute response and better reproducibility—were obtained at pH = 5.0.

With acetate buffer solution of pH 5.0 as the support electrolyte, the potential of the working electrode was optimized studying the variation of the current peak height with an applied fixed potential between +0.50 and +1.50 V. The peak current increased until a maximum at the potential of +0.75 V, and between +0.75 and +1.20 V this peak remained virtually constant. Above +1.20 V, the analytical response decreased significantly and reproducibility suffered accordingly. Thus, the value of +0.75 V was chosen and used in subsequent trials.

Following the optimization of support electrolyte pH and the oxidation potential, the next step was to study the effect of changing the concentration of sodium hydroxide used in the alkaline hydrolysis. The sodium hydroxide concentration is a fundamental parameter for the optimization of this FIA system; therefore, a wide range of strengths was tested (5.0×10^{-3} through 6.0×10^{-2} mol L^{-1}). Up to 4×10^{-2} mol L^{-1}, the analytical signal increased with the concentration, thus this level was chosen for subsequent runs. EMP was formed in reactor L_1, and so five lengths (50–500 cm) were tested. The length of 400 cm was chosen, because smaller ones decreased the sensitivity and reproducibility due, presumably, to insufficient mixing of the sample with the NaOH solution and because with longer ones the sensitivity and sampling rate decreased due to the dispersion effect. The bolus travels to the confluence Y where it merges with buffer acetate solution, and in reactor L_2 the ionic strength and pH adjustment are made as required by the detector. The length of reactor L_2 was fixed at 50 cm to give the best compromise between sensitivity and reproducibility. Both reactors (L_1 and L_2) were coiled to improve radial mixing and minimize the dispersion of the sample plug (Ruzicka and Hansen 1988).

The selection of the most adequate flow rate was dependent on limitations of the wall-jet cell, which has a dead volume of about 1 μL. It was verified that using flow rates higher than 2.4 mL min^{-1} was not satisfactory, because they produce high pressures within the system and, consequently, irreproducible signals, whereas lower flow rates give reproducible signals but compromise the sampling rate. Therefore, the value of 2.4 mL min^{-1} was chosen.

With the purpose of selecting the most adequate injection volume, loops with lengths enabling the insertion of volumes between 100 and 500 μL were prepared for the injection valve. These real volumes (including the internal volume of the injection valve) were determined by titration of the volume obtained from 10 replicate injections of a solution of known concentration. A loop with an injection of 400 μL was selected because of the highest linear sensitivity attained.

Analytical Applications

Calibration plots were constructed using the optimized parameters. The electrode responses for increasing injected concentrations are shown in Fig. 10.

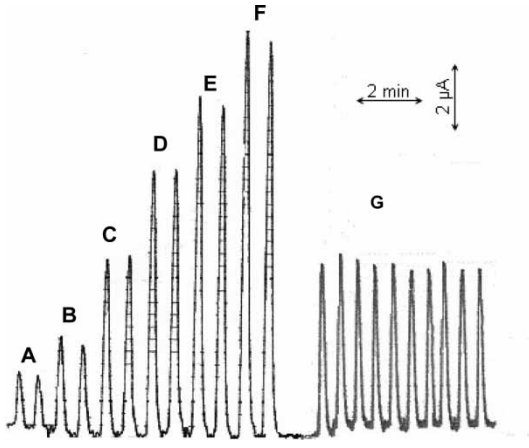

Figure 10. Flow injection signals obtained with the amperometric system corresponding to the injection of a set of standards of ETF and one sample with recoveries. A, 5.0×10^{-7} mol L^{-1}; B. 1.0×10^{-6} mol L^{-1}; C, 2.0×10^{-6} mol L^{-1}; D, 3.0×10^{-6} mol L^{-1}; E, 4.0×10^{-6} mol L^{-1}; F, 5.0×10^{-6} mol L^{-1}; G, sample 1 (in Table 1).

The calibration plot was linear between 1.0×10^{-7} and 1.0×10^{-5} mol L^{-1} with a slope of 1.0×10^{6}, an intercept of 3.5×10^{-1}, and an R^2 of 0.999.

Following the procedure described previously, five samples of spiked water were analyzed in triplicate. A calibration curve was used to quantitate the contents of the sample, and the results are given in Table 1. In order to assess the quality of the results obtained with the developed methodology, determinations of ETF in spiked waters were carried out using FIA and HPLC with UV detection, and the relative errors were always $<5\%$. Recovery trials ranged from 98 to 104%, confirming the accuracy of the developed system. The detection limit of the method calculated under the optimized conditions and according to IUPAC recommendations

Table 1. Comparative analysis carried out for five samples

Sample	FIA ($\times 10^{-6}$ mol L^{-1})	HPLC ($\times 10^{-6}$ mol L^{-1})	RE (%)
1	1.90 ± 0.07	1.95 ± 0.06	−2.6
2	2.52 ± 0.05	2.58 ± 0.06	−2.3
3	2.49 ± 0.06	2.42 ± 0.05	+2.9
4	3.19 ± 0.04	3.07 ± 0.04	+3.9
5	3.15 ± 0.05	3.25 ± 0.05	−3.1

Mean and standard deviation from five and three determinations by FIA and HPLC, respectively.

(Mocak et al. 1997) was $1.0 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$ of pesticide. To assess the precision of FIA procedure, the relative standard deviation was calculated for 10 consecutive determinations and was 1.7% for a concentration level of $2.0 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$ (sample 1, Table 1). The sample capacity of the system is 60 samples $\mathrm{h^{-1}}$, supposing 1 min per injection. The experimentally determined calibration parameters were compared with the theoretically expected values by means of student's t-test; for a confidence interval of 95%, a value of t lower than the critical value was obtained.

CONCLUSIONS

Electroanalytical techniques are suitable to miniaturization ETF and they can be successfully accomplished when associated to automatic methods. Therefore, based on the electrochemical behavior of ETF, one analytical methodology was developed using FIA with amperometric detection at $+0.75\,\mathrm{V}$ vs. Ag/AgCl to quantify the pesticide in spiked natural water samples. The developed method shows a linear correlation with concentration over a broad range; the results have good accuracy and precision. Consequently, the method proved to be a good alternative to the comparative HPLC method. Moreover, the proposed method is simple, easy to operate, inexpensive, and made complex pretreatment of the samples unnecessary. This methodology could replace time-consuming and costly procedures and can be easily implemented in any routine analytical laboratory.

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