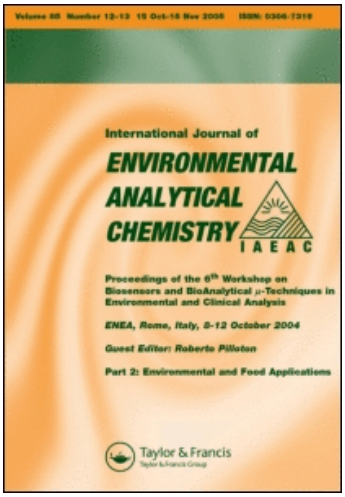

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Electroanalytical Determination of the Herbicide Atrazine in Natural Waters

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ELECTROANALYTICAL DETERMINATION OF THE HERBICIDE ATRAZINE IN NATURAL WATERS

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Differential pulse voltammetry at the static mercury drop electrode was used to establish an electroanalytical procedure for atrazine determinations in pure and natural waters. The cathodic peaks observed are attributed to the reduction of mono and di-protonated species and showed to be pH-dependent, with the maximum peak current values at pH 2.3. In pure water, the detection limit found was 5 μg/L at a scan rate of 2 mV/s and 11 μg/L at 10 mV/s. In natural waters the calculated detection limits at 10 mV/s were 13 μg/L and 16 μg/L for a clean dam and polluted creek waters and 38 μg/L for a typical tropical soil solution, respectively. The higher scan rate used for natural waters analysis allow to improve the detection limit by avoiding the competition of contaminants with the processes occurring at the mercury surface. Hydroxyatrazine, the main chemical and photo-degradation product of atrazine does not interfere in the determination method. The main advantage of this technique is to allow sample analysis without pre-treatments or extraction with solvents. The procedure is adequate for further applications in the study of movement, adsorption and degradation of atrazine in soils.

KEY WORDS: Differential pulse voltammetry, atrazine, environmental waters, herbicides.

INTRODUCTION

Atrazine (2-Chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is one of the pre-emergent herbicides most widely used in the world and has frequently been found as a contaminant in surface and ground waters[1,2]. The Maximum Contamination Level Goal proposed by the United States Environmental Protection Agency for atrazine in drinking water is 3 μg/L[2]. Although the usual range of concentration for atrazine varies between 0.05–100 μg/L[3] values up to 2300 μg/L for surface water and 700 μg/L for ground water have been already reported for isolated samples[4].

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Atrazine is mainly used in the annual control of some grasses and broadleaf weeds in corn, sorghum, sugar cane, pineapple, pinus and other cultures[4]. Due to its low reactivity and water solubility, atrazine is reasonably stable (half life varying among 20 and 100 days[5]), mobile and persistent in water and soil. Residues and metabolites have been found in ground water long time after application[6].

In strong acid or alkaline media, atrazine is slowly hydrolyzed to hydroxyatrazine, a non-phytotoxic product that is decomposed by plants to amines and carbon dioxide[7]. Atrazine also decomposes when submitted to light irradiation and to the action of micro-organisms (microbial degradation). In those cases it is possible that, at some stage of the process, atrazine is transformed into hydroxyatrazine[8].

The main technique used for atrazine determination is gas chromatography[9] but in some cases also liquid[10] and thin layer[11] methodologies have been employed. More recently, immunoassays[12] are becoming available for this kind of analysis while enzyme biosensors[13] and optical fibber sensors[14] are being currently developed. On the other hand, electroanalytical techniques such as voltammetry and polarography have also been used for this purpose but only at a laboratory level[15–18].

The electroactivity of atrazine was first verified in 1967[15]. Studying the s-triazine, simazine, propazine, prometrine and prometone, the authors showed that these herbicides exhibit polarographic reduction waves in acid aqueous solutions. The lower detection limit found was 1.5 mg/L using DC polarography and 150 μg/L for single-sweep polarography.

In another paper[16], a detection limit of 300 μg/L for atrazine was reported with single-sweep polarography in H_2SO_4 (0.2 N). Differential pulse polarography was also used to determine altrazine and other s-triazines in solution with KCl (0.05 M) as the electrolyte[17]. The detection limit obtained was 15 μg/L. The authors showed that the electroanalytical behaviour is strongly dependent on the pH of the solution and that protonated forms of atrazine are reduced in acid medium. The peak current showed a maximum at pH 2.0. A series of s-triazines was analyzed by differential pulse polarography in phosphate buffer aiming to compare the electroanalytical results with those obtained by gas chromatography[18]. The agreement found between the two techniques was excellent. Besides the reduction on mercury, atrazine can be oxidized on platinum electrodes in anhydrous acetonitrile[19]. However the applicability of such procedure to determine atrazine concentration in natural samples is not easy due to the difficulties in using electroanalytical techniques in non-aqueous solutions. Table 1 shows a review of papers using electroanalytical techniques for the detection of s-triazines.

In comparison with gas chromatography, the main technique used at present, the electroanalytical procedures are faster, cheaper and easier to be carried out. Moreover, they can be successfully employed for the analysis of colored materials or samples containing dispersed solid particles[20]. The disadvantages are, in many cases, related to lower selectivity and sensitivity (as can be seen in Table 1) as well as the difficulties encountered when using solid electrodes in relatively dirty environmental samples. This later problem can be minimized by the use of a renewable mercury surface as electrode material.

The aim of this work is to study the electrochemical behaviour of atrazine using differential pulse voltammetry (DPV) on a hanging mercury drop electrode in order to establish an electroanalytical procedure to determine atrazine concentrations in real samples with better sensitivity and selectivity. The procedure will take into account its further application for the study of movement adsorption and degradation of atrazine in soils.

Table 1 Published papers using voltammetric techniques for the detection of s-triazines.

Substance	*Technique*	*Detection limit*	*Reference*
Atrazine Simazine Prometrine Prometone	DC polarography SSP	1.5 mg/L (for DCP) 150 μg/L (for SSP)	[15]
Atrazine Ametrine	SSP	300 μg/L 200 μg/L	[16]
Atrazine Simazine Prometrine	DPP	15 μg/L	[17]
Atrazine Ametrine Simazine	DPP	–	[18]
Ametrine Prometrine	AdSV	0.2 μg/L 1 μg/L	[28]
Simetrine	AdSV DC polarography	0.5 μg/L 1000 μg/L	[27]
Simazine	DC voltammetry DPV	40 μg/L 20 μg/L	[29]
Simazine	DPP	40 μg/L	[30]

DPP: Differential pulse polarography
DPV: Differential pulse voltammetry
SSP: Single sweep polarography
AdSV: Adsorptive stripping voltammetry

EXPERIMENTAL

Instrumentation

Electrochemical analyses were carried out using a model 348B Polarographic Analyzer from EG&G PARC (Princeton, N.J.) connected with the model 303A EG&G PARC (Princeton, N.J.) mercury electrode. A saturated Ag/AgCl electrode was used as reference while a Pt wire served as counter electrode. A commercial 15 ml EG&G PARC (Princeton, N.J.) polarographic cell was also used.

Differential pulse voltammograms were obtained using the hanging mercury drop electrode mode with a medium drop size at either 2 or 10 mV/s and a pulse height of 50 mV. The voltammograms were recorded without performing any accumulation step. All voltammetric experiments, including the blanks, were normally performed in triplicate and the standard addition curves were constructed by subtraction of the blank from the experimental results. Some experiments (see later) were repeated ten times to check reproducibility.

Ultraviolet absorption spectra were recorded on a Shimadzu Inc. (Tokyo, Japan) model UV-180 spectrophotometer and the pH measured in an Analion (Ribeirão Preto, Brazil) model PM606F pH-meter. Ultra-violet irradiation tests were performed using a 100 W Hg bulb with the solution contained in a 5 ml quartz flask.

Chemicals and solutions

Analytical supra-pure grade Sulphuric acid (Merck, Darmstadt, Germany) was used to adjust the final pH of the samples and served as the supporting electrolyte. Atrazine herbicide, furnished by Ciba-Geigy (Brazil), was either 99% pure or in the form of the commercial formulation Gesaprim 500, which contains 500 g/L of the active ingredient. Due to the low solubility in water of pure atrazine, a 3 mM stock solution in methanol (Merck, spectroscopic grade, Rio de Janeiro, Brazil) was used in the standard addition procedures. The stock solutions were kept under refrigeration. The concentration of methanol in the electrolyte was always less than 1% v/v. All samples were prepared with water purified in a Milli-Q filtration system (Millipore, Bedford, MA) and deareated by bubbling high purity N_2 (White Martins, Sertãozinho, Brazil) for 15 minutes prior to the analytical determinations.

Natural water samples were collected, from Broa dam and Monjolinho creek at São Carlos county (SP, Brazil) and soil solutions were extracted by vacuum through a porous ceramic cup sampler (Figure 1) at the end of the rainy season. The water samples were collected in 1 L Pyrex glass flasks and soil solutions in Pyrex test tubes. All samples were kept under refrigeration and used within one week. Broa is a clean water dam used for domestic supplies in São Carlos city and Monjolinho a polluted creek that crosses the town. The collected samples were subjected only to paper filtration (Whatman 114, Maidstone, England) and the experimental solutions were prepared through the addition of known quantities of pure atrazine to the water samples. The final pH values were adjusted using a 1 N sulphuric acid solution. The atrazine concentration in the samples varied from 100 to 600 μg/L for the natural waters and from 0.1 to 3 mg/L for the soil solution analysis. Similar samples were prepared using pure water. Blank solutions were also prepared using the different water samples and the sulphuric acid solution.

RESULTS AND DISCUSSION

Variation of peak current and potential with pH

Solutions containing 2×10^{-5} M (4.3 mg/L) of pure atrazine and with the pH varying between 0.5 and 4 were prepared and analyzed by DPV to establish the effect of pH on the cathodic process. Figure 2 shows a selection of voltammograms recorded at 2 mV/s. The two observed peaks (better defined for lower pH) can be attributed to the reduction of the mono and diprotonated forms of the atrazine molecule in acidic solutions, being the main one related to the first species[21].

In Figure 3 the variation of the recorded values of the main peak current and peak potential as a function of pH is presented for the complete set of experiments. It can be observed that the peak current shows a maximum for pH 2.3. On the basis of these results, which are in agreement with those published previously by Lippolis and Concialini[17], all the following determinations were carried out in solutions with pH adjusted to 2.3. The measured displacement of the peak potential is about 60 mV per unit of pH suggesting the involvement of one proton in the rate determining step.

The effect of hydroxyatrazine

It has already been suggested that hydroxyatrazine is the main product of atrazine photodegradation when irradiated with light of a wavelength close to 300 nm[7]. To

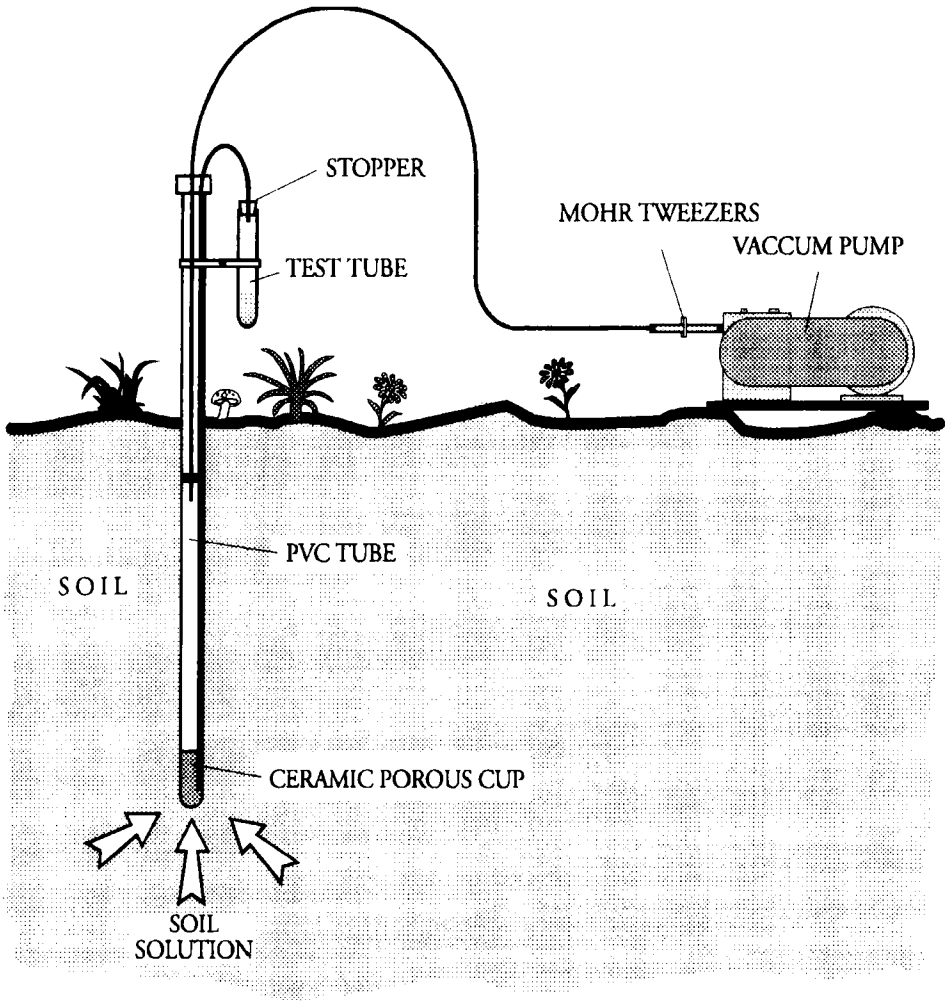

Figure 1 Soil solution sampler by vaccum through a porous ceramic cup.

confirm this degradation pathway under the present experimental conditions a 2×10^{-5} M atrazine solutions (pH 2.3) were irradiated for periods up to 60 minutes. The resulting solutions were analyzed by ultraviolet absorption spectrophotometry showing that the atrazine peak (223 nm) decreases with irradiation time, while the one corresponding to hydroxyatrazine (240 nm) increases as expected[22,23]. These measurements confirm that the photodegradation process takes place under such conditions, generating hydroxyatrazine as the main metabolite. The complete reaction is achieved only for periods larger than 90 minutes.

Similar irradiated solutions were analyzed by DPV to verify the selectivity of the technique towards atrazine. This kind of information is extremely important since any interference caused by hydroxyatrazine in the main reduction peak of atrazine should

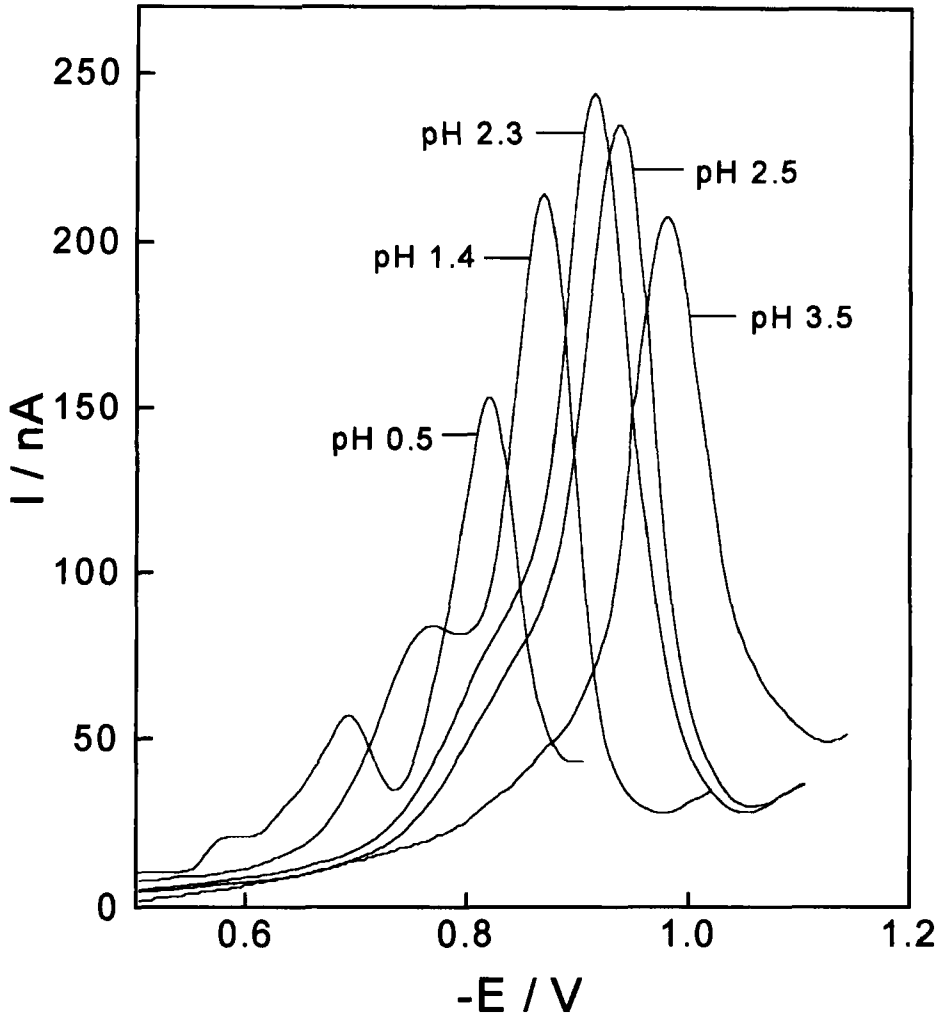

Figure 2 Differential pulse voltammograms of 2×10^{-5} M atrazine solutions recorded at various pH values. Scan rate: 2 mV/s. Pulse height: 50 mV.

hinder the method for practical applications. The DPV results obtained for different irradiation times clearly show that the peak current at –0.91 V vs Ag/AgCl (see Figure 2) has a maximum value for the non-irradiated solution that decreases progressively with irradiation time. As the peak potential remained practically unchanged and no other reduction peaks were observed, it can be concluded that hydroxyatrazine does not interfere with the determination of atrazine. Similar determinations of atrazine contained in irradiated solutions that were prepared using Gesaprin showed analogous results.

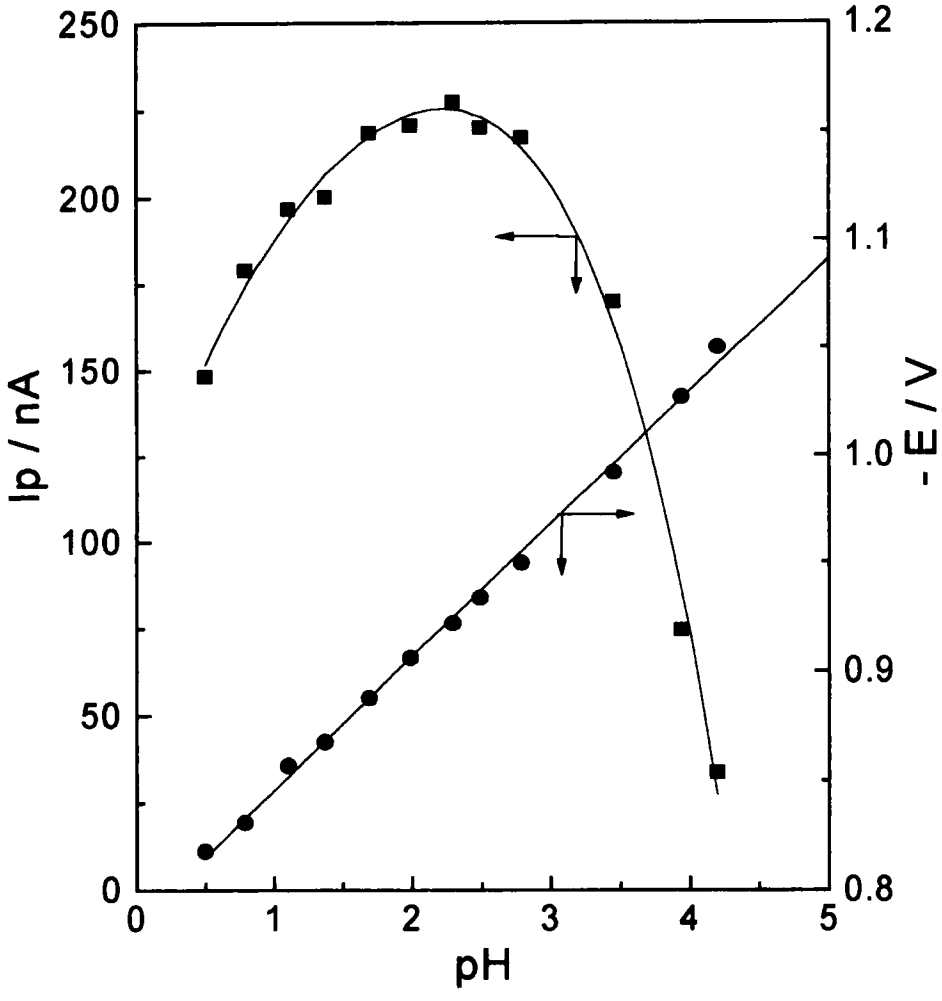

Figure 3 Variation of peak current (■) and peak potential (●) for atrazine reduction as a function of pH for DPV experiments.

The effect of electrode material

Besides the experiments with Hg electrodes, differential pulse voltammetries using a vitreous carbon electrode were also carried out. In this case, atrazine does not present electroactivity suggesting the participation of the electrode material (Hg) in the reduction process. Such characteristic has already been reported in the literature[17]. This fact, together with the observed blockage of the electrode surface at higher (> 1 mg/L) atrazine concentrations[24] as well as the measured variation in peak potential with pH, suggest that the protonated atrazine molecule should react with the Hg surface after the electroreduction of C-Cl bond. One possible explanation is that the neutral radical formed in the reduction step will remain attached to the Hg surface in a route analogous

to the production of organometallic compounds, as described in the organic electrochemistry literature[25]. Meanwhile, this effect does not interfere with the present determinations at low atrazine concentrations probably because the diffusion control is reached well before total coverage of the electrode surface occurs.

Evaluation of the sensitivity in pure solutions

Solutions containing pure atrazine with concentrations varying from 2 to 65 μg/L were analyzed by DPV. The resulting voltammograms subtracted from that registered for a blank solution of pH 2.3 containing only sulphuric acid are shown in Figure 4. The slope obtained for the linear relationship between I_p and concentration in the standard addition curve showed in the insert of Figure 4 points to a minimum detection limit of 5 μg/L for the method in the absence of interferences. This parameter was estimated as being three times the standard deviation of an average of ten voltammograms of blank solutions divided by the slope of the callibration curve[26]. The corresponding linear correlation coefficient (r^2) has a value of 0.997 indicating a high accuracy for the measurements.

For atrazine concentrations higher than 1 mg/L, the observed good linearity is lost probably due to poisoning of the surface. In such situations, it might be advisable to use differential pulse polarography (DPP), where the renewable Hg surface minimizes the blocking effect[24].

In addition, sample solutions prepared with the Gesaprin formulation were submitted to the same determination procedure showing very similar results regarding peak current and shape. This leads to the conclusion that the ingredients present in the commercial Atrazine formulation do not interfere with the method proposed in this paper.

Preliminary applications to environmental analysis

With the aim of testing the technique presented here for applications to the analysis of natural systems additional experiments were carried out using real water samples as well as soil solutions. In these cases, the standard addition curves were always run in triplicate while the blank samples were repeated ten times to improve the statistical reliability of the data.

The voltammetric behavior of real water samples is similar in shape to that of atrazine in pure water (Figure 4) but the standard addition curves obtained at 10 mV/s and presented in Figure 5 exhibit lower I_p values for comparable atrazine additions, slightly decreasing the sensitivity of the method for this kind of application. The relationship between I_p and atrazine concentration in pure, polluted creek and clean dam waters were linear in the whole concentration range studied. The slopes of the regression equations and the calculated detection limits obtained for the analyzed waters using the same criteria as before, are presented in Table 2. The values of the linear correlation coefficients (r^2) and the relative standard deviations (RSD) are also included in that Table.

For comparison the results obtained in pure water at 2 mV/s are also presented in Table 2. The higher scan rate used in those experiments (10 mV/s) was chosen in order to minimize interferences from dissolved contaminants present in natural waters, such as humic substances and other organic materials. As a consequence, the detection limit in pure water increases from 5 to 11 μg/L but it still remains sufficiently low for analytical applications.

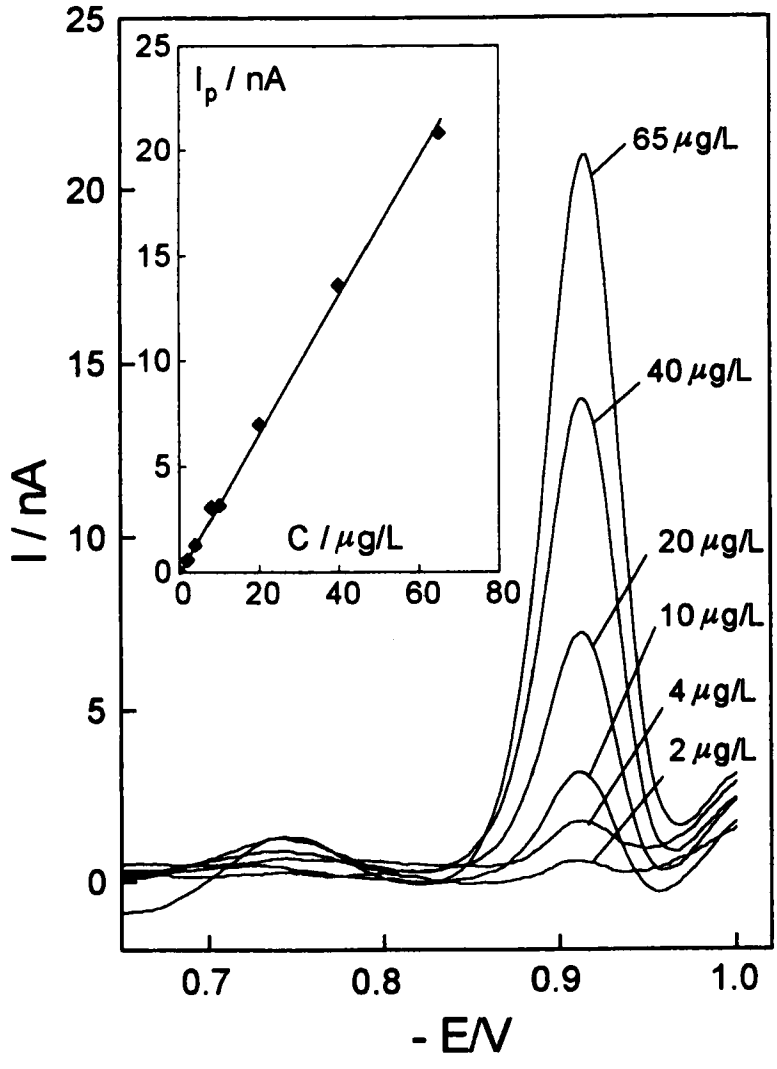

Figure 4 Differential pulse voltammograms (subtracted from the blank) of pure atrazine solutions at pH 2.3. Scan rate: 2 mV/s. Pulse height: 50 mV. The standard addition curve I_p vs atrazine concentration is shown in the insert.

The experimental conditions adopted here represent the best compromise between reproducibility and detection limit of the method concerning atrazine determination in the real water samples investigated. Thus, the results in Table 2 show that the detection limit remains fairly low for all water samples except those resulting from the soil. On the other hand, an increase in the contaminants level causes a slight decrease in the accuracy as revealed by the values of r^2 while the reproducibility remains high and almost independent of the purity of the water sample showing RSD of the order of 3%.

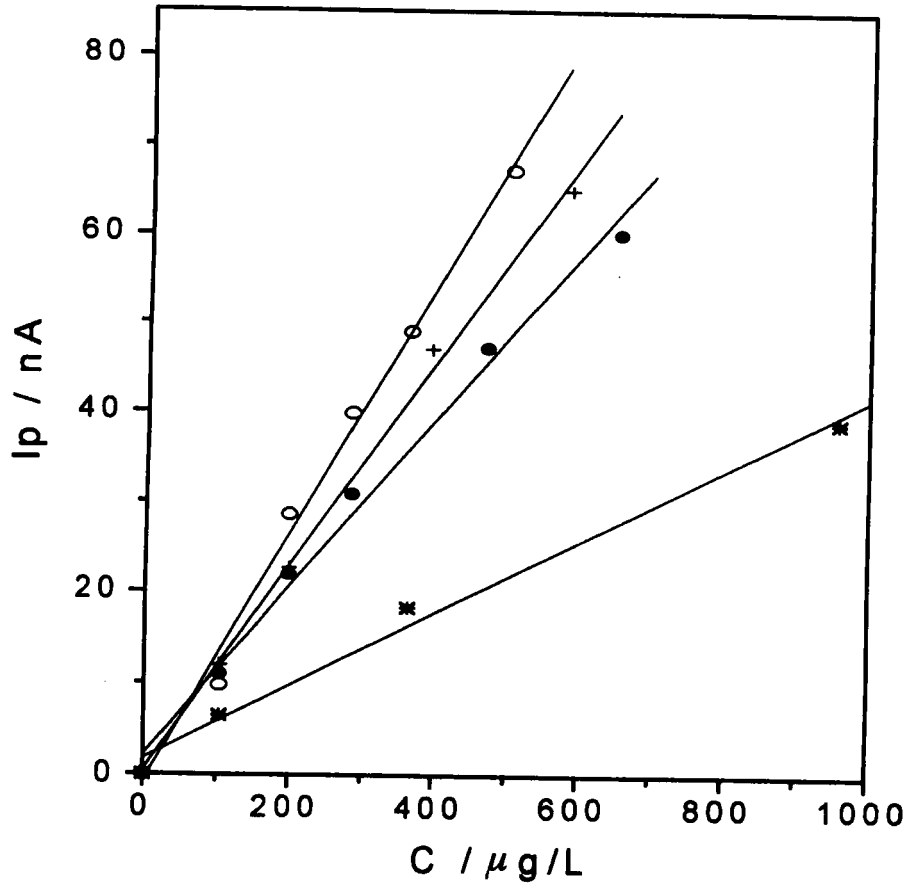

Figure 5 Standard addition curves obtained by DPV for: pure water (○), Broa dam (+) and Monjolinho creek (●) samples and for soil solution (*), at pH 2.3. Scan rate: 10 mV/s. Pulse height: 50 mV.

Table 2 Statistical parameters obtained from the experiments.

Sample	*Scan rate mV/s*	*Slope nA/(μg/L)*	r^2*	*Detection limit μg/L*	*Relative standard deviation (%)*
Pure H_2O	2	0.330	0.999	5	3.4
Pure H_2O	10	0.137	0.998	11	2.9
Broa dam	10	0.112	0.998	13	3.2
Monjolinho creek	10	0.092	0.995	16	2.9
Soil solution	10	0.040	0.987	38	3.1

*Linear correlation coeficient.

The results for soil solution samples that are also included in Figure 5 and Table 2 showed, as expected, a marked current inhibition, due to the greater concentration of contaminants in these environments. The inhibition mechanism can be explained by a competition of the contaminants through an adsorption process occurring at the mercury surface or more probably by a masking effect caused either by complexation or by colloidal occlusion of atrazine[27].

CONCLUSIONS

This work describes the successful application of an electroanalytical technique for the analysis of atrazine in natural waters and soil solutions. It also demonstrates that differential pulse voltammetry at the static drop mercury electrode can be conveniently used for the quantitative determination of that herbicide in those environments. By a proper choice of the experimental conditions such as pH, drop size, and scan rate, it is possible to minimize the effect of interferences and reach detection limits in the range 13–16 μg/L for contaminated samples.

The method shows good reproducibility and high accuracy, even for soil solutions where the detection limit rises to 38 μg/L but the former parameters still remain with acceptable values for practical applications.

An important advantage of the technique is that allows sample analysis without pre-treatments or extraction with solvents. Work is under progress to demonstrate the adequacy of this procedure for the study movement, adsorption and degradation of atrazine in soils.

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