



Multivariate optimization of square wave voltammetry using bismuth film electrode to determine atrazine



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ABSTRACT

A rapid and simple square wave voltammetry method (SWV) for atrazine determination with bismuth film electrode using chemometrics was developed. Different variables such as buffer pH and SWV frequency, pulse height and step potential were screened in a 2^4 full factorial design. The significant variables were optimized by using a central composite design (CCD) combined with desirability function (DF). Optimum conditions were set as follow: buffer pH 2.3, frequency 300 Hz, pulse height 0.09 V and step potential -0.0024 V. Under these optimum conditions the method has a linear response over $(1.8\text{--}7.5) \times 10^{-6} \text{ mol L}^{-1}$ with detection and quantification limits of 5.9×10^{-7} and $1.8 \times 10^{-6} \text{ mol L}^{-1}$, respectively.

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1. Introduction

Environmental monitoring has become an increasingly demanding field in recent years, due to the fact that both, governments and consumers are becoming more aware of the damage that pollution can do, caused by industrial and agricultural practices. Therefore, guidelines have been set on the maximum permissible levels of certain pollutants, such as pesticides. Atrazine (ATZ) (2-chloro-4-ethylamino-6-isopropylamine-triazine) is a member of s-triazine family of herbicide and is one of the most commonly used herbicide [1], and its structure is presented in Scheme 1. Due to the widespread use of atrazine to control annual grasses and broad-leaved weeds in crops like sugar cane, maize, soybean, citrus fruits, etc. in the railways, roadside verges and golf courses, great attention has been given to its environmental impacts and monitoring [2–4]. Although the toxicological effects of atrazine and other triazines on humans is weaker than those reported for chlorinated and organophosphorus pesticides, severe environmental problems can result from their persistence in soils and sediments, as well as their run-off to surface and ground waters. Due to its low reactivity, water solubility and slow degradation, ATZ is reasonably stable, mobile and persistent in the environment for a long period of time (half-life varying among 20–100 days) [5]. In very small quantities, it may act as a

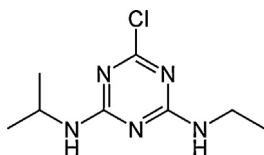
carcinogen of type C and an endocrine disruptor of the hormonal system [6].

A literature research shows many reports describing various analytical methods for the determination of ATZ and other triazine herbicides. These particularly involve spectrophotometric [7] and especially chromatographic methods such as high performance liquid chromatography (HPLC) [8,9] and gas chromatography (GC) [10]. The latter have become the most widely used for the determination of trace amounts of triazine herbicides, because of their absolute best sensitivity and selectivity. However, these techniques require the complicated sample preparation usually involving the pre-concentration step prior to the analysis. In addition, they are expensive, time consuming, and the solvent waste-production requires highly skilled personnel that often restricts their use in routine analytical practice.

The electrochemical methods are especially suitable for the environmental monitoring of heavy metals and electroactive organic pollutants. They are simple, inexpensive, sufficiently sensitive as well as they can represent an independent alternative to so far dominant spectrophotometric and chromatographic techniques [11]. Regarding the electrochemical determination of ATZ, enzyme biosensors and immunosensors have been used [12] or mercury electrodes, such as hanging mercury drop electrode (HMDE) [13–15], static mercury drop electrode (SMDE) [16] and mercury film electrode (MFE) [17,18] are mostly exploited. These methods are most sensitive due to the excellent electrochemical properties of mercury. On the other hand, the highly toxic nature of mercury insists on the search for alternative electrode materials. Therefore,

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Scheme 1. Atrazine structure.

the novel, simple and environmentally acceptable electrochemical tool for the sensitive environmental monitoring of pesticide residues is of great importance.

Recently, a significant step forward is the introduction and development of bismuth [19] and antimony-based electrodes [20,21]. Bismuth film electrodes (BiFEs) consist of an electrochemically generated thin bismuth film, deposited mainly on carbon-based substrates, such as glassy carbon [22], carbon fiber [23], or screen-printed carbon [24]. The bismuth film is mechanically stable, exhibiting high electroanalytical performance for trace metal analysis, well comparable to the mercury electrodes. Most of the articles presented in the literature are dedicated to the application of BiFE to determine metallic cations [25–29]. However, few papers described the use of BiFE for organic compounds, such as drugs [30,31] and pesticides [32–35] determination.

The square wave voltammetry (SWV) is rapid, sensitive and consumed less analyte than the other pulsed techniques [36]. Most of the optimization of SWV also deal with the traditional one-factor-at-a-time (OFAT) approach, examine the SWV parameters such as frequency, step potential and pulse height [13,14,17]. If the factors are independent (which is rarely the situation), the most common practice is OFAT while holding all others parameters constant. However, the result of this univariate analysis shows inadequate optimization toward response(s). Moreover, OFAT approach is costly in sense of time and reagents. There is now increasing recognition that hereditary malpractice ought to be replaced by soundly based reliable methods, such as response surface methodology (RSM) based on statistical design of experiments (DOEs). Response surface methodology is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes [37] that is dedicated to the evaluation of relations existing between a group of controlled experimental factors and the observed results of one or more selected criteria. Such statistical analyses are more efficient, since they account for interaction effects between the studied variables and determine more accurately the combination of levels that produces the optimum of the process. The importance, theoretical concepts and application behind the optimization through experimental design, as well as RSM in research and development efforts have been thoroughly discussed in a number of informative articles [37–40]. Furthermore, a study has been done on the SWV optimization by using statistical experimental design [41]. Thus, RSM provides a predicted model, considering the response over the whole domain. By using this predicted model the optimum response can be determined.

In the present study, SWV using bismuth film electrode was employed for atrazine determination. Influence of important variables was investigated and optimized by experimental design. We focused on the enhancement of the intensity of atrazine current by using screening and response surface experimental designs as improved optimization methodology. Derringer's desirability function, was used for the evaluation the SWV parameters.

2. Experimental

2.1. Apparatus

Square wave voltammetry measurements were performed with Autolab (PGSTAT 101 Eco-Chemie) potentiostat. A conventional

three-electrode system was used where glassy carbon (GCE, 3 mm 75 diameter), a platinum wire, and a Ag/AgCl (3 M KCl) were used as working, counter, and reference electrodes, respectively. All potentials are referred to this reference electrode. All electrochemical experiments were performed at room temperature.

2.2. Data analysis

The STATISTICA statistical package software version 7.0 (Stat Soft Inc., Tulsa, USA) was used for experimental design analysis and data processing. The quality of the fit of the polynomial model equation was expressed by the coefficient of regression R^2 , and its statistical significance was checked by a Fisher F -test. The level of significance was given as values of the probability less than 0.05.

2.3. Reagents and solutions

All reagents were obtained as analytical grade and used without further purification. Purified water obtained from a Milli-Q water purifying system ($18 \text{ M}\Omega \text{ cm}^{-1}$) was used for all experiments. Atrazine and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were purchased from Sigma–Aldrich (St. Louis, MS, USA). K_2HPO_4 , KH_2PO_4 , acetic acid, sodium acetate, sulfuric acid and potassium hydroxide were J.T. Baker. 0.05 mol L^{-1} Phosphate buffer solution (PBS) was prepared by adjusting a mixture of 0.05 mol L^{-1} $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ to the required pH value by adding either 1.0 mol L^{-1} hydrochloric acid (HCl) or potassium hydroxide (KOH) solution.

The electrodeposition solution was prepared with $1 \times 10^{-3} \text{ mol L}^{-1}$ $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 0.1 mol L^{-1} H_2SO_4 .

To evaluate the accuracy and applicability of the proposed method, the optimized procedure for different water samples was performed. River water samples were taken from different field areas of the Los Espinillos River at Córdoba, Argentina (November 2012). The collected water samples were filtered through a $0.45 \mu\text{m}$ micropore membrane and were maintained in glass containers, then stored at a temperature of 4°C until their analysis time. For each sample, an aliquot of 2.5 mL was transferred to three different calibration flasks. After this, an aliquot of $3.8 \times 10^{-4} \text{ mol L}^{-1}$ ATZ standard solution was added to the samples and filled with buffer solution up to 10 mL and homogenized.

2.4. Preparation of BiFE

The glassy carbon electrode was mechanically polished with $0.05 \mu\text{m}$ alumina/water slurry (Buehler, USA) on a polishing cloth to a mirror-like finish followed by sonication, rinsed with distilled water, dried in air and inserted into the electrochemical cell. The bismuth film electrodeposition onto the GCE was carried out chronoamperometric by applying a deposition potential of -1.00 V for 360 s in the electrodeposition solution.

To remove the bismuth film, a potential step of $+0.5 \text{ V}$ for 60 s in a PBS buffer solution was applied, after which the deposition of a fresh film was performed.

2.5. Experimental procedure

The determination of pesticides such as ATZ (Scheme 1) can be obtained by electrochemical reduction which corresponds to the reduction of the carbon–chloride bond of the triazine ring with the previous protonation equilibrium of atrazine as proposed by De Souza et al. [42]. In this work, ATZ determinations were evaluated by square wave voltammetry (SWV), and a cathodic peak was obtained. The SWV parameters and the best chemical conditions (chemical buffer and pH) were evaluated. The following optimized SWV procedure was used: 10 mL of phosphate buffer 0.05 mol L^{-1}

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