



Multivariate cathodic square wave stripping voltammetry optimization for nitro group compounds determination using antimony film electrodes

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ARTICLE INFO

Article history:

Received 21 December 2017
Received in revised form 20 February 2018
Accepted 21 February 2018
Available online 24 February 2018

Keywords:

Antimony film electrode
Response surface methodology
Desirability function
4,6-Dinitro-o-cresol

ABSTRACT

The main goal of this paper is the optimization of the square wave voltammetric response of antimony film electrode (SbFE) to determine reducible nitro groups using response surface methodology (RSM). The SbFE was prepared on a glassy carbon electrode (GCE) while cathodic stripping square wave voltammetry (CSSWV) was used as detection technique. In this study, the optimization process of solution pH and 4,6-dinitro-o-cresol (DNOC) accumulation time was carried out using a Central Composite Design (CCD) while a Box-Behnken Design for SWV instrumental variables optimization. The two reduction current peaks were used as dependent variable to evaluate the performance of the system. For solution pH and DNOC accumulation time the optimization process considered only reduction current peak, while for SWV instrumental parameters (step, amplitude and frequency) both the relationship between current peak and standard deviation with the different factors were analysed, finally both designs were quantitatively described by a multivariate regression model through the RSM. Furthermore, the optimal parameter combinations were obtained by maximizing the reduction current peak and minimizing standard deviation within the studied experimental range. Under the optimal parameter combination, a linear calibration curve ranged from $(1.0 \text{ to } 15) \times 10^{-6} \text{ mol L}^{-1}$ with a detection limit of $1.12 \times 10^{-6} \text{ mol L}^{-1}$ was obtained. The proposed analytical procedure was further applied to detect DNOC in natural water samples with satisfactory results.

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1. Introduction

Among different electrochemical techniques, stripping voltammetry plays an important role and has long been recognized as one of the most powerful tool in trace and ultratrace analysis of heavy metals and some organic compounds, due to its exceptional sensitivity in conjunction with different electrode materials [1]. Moreover, electrochemical methods are known for their relative simplicity, low-cost instrumentation and possibility of system integration and miniaturization. Therefore, on-site testing can be carried out, such as environmental monitoring, industrial control and measurements in specific and more challenging environments, e.g. in vivo studies. It is well known that a proper choice of the electrode materials is a crucial factor in assuring a favourable performance of a stripping voltammetric procedure.

The search for new electrode materials and sensors surfaces is systematically pursued in modern electroanalytical chemistry. For decades mercury electrodes has been providing the best characteristics for application in electrochemical analysis of metals and some reducible organic compounds. In recent years the use of mercury-based electrodes has

been decreasing due to their toxicity and handling problems. Search for new electrode materials or modifications of currently used materials possibly replacing mercury electrodes and applicable for metallic and organic analytes resulted in the introduction of antimony film electrodes (SbFEs) [2]. In a relatively short time, these electrodes have attracted much attention, which is reflected in the growing number of special studies focused on the SbFEs [3]. This electrode was employed successfully in electrochemical stripping analysis to determine metals [4–21]. However, as far as we know there were only a few works that use it for organic compounds i.e. sulfasalazine [22], pantoprazole [23], food dyes allura red with tartrazine [24], tetracyclines [25], and trifluralin [26]. Trifluralin belongs to the class of so called dinitroaniline herbicides and as the name suggests, it contains two nitro groups on a benzene moiety. Both these groups are electrochemically reducible via simultaneous 8-electron reduction to hydroxylamine groups in acidic medium [27–29]. In these studies, authors focused on the characterization and the comparison of different substrate electrode materials used for the preparation of antimony film electrodes and concluded that the antimony film glassy carbon electrode provide the best results. Nevertheless, the field of analytical optimization of nitro groups electroanalysis based on the antimony electrode has still remained completely unexplored and certainly needs a particular attention. Therefore, further

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investigation of SbFEs for the determination of organic compounds using another pesticide with two nitro groups (4,6-dinitro-*o*-cresol) as a model compound is presented in this paper.

4,6-dinitro-*o*-cresol (DNOC) is used agriculturally as a larvicide, ovicide and insecticide (against locusts and other insects) as well as a potato haulm desiccant. It is also used as a polymerization inhibitor and as an intermediate in the chemical industry. For agricultural uses, DNOC is mainly formulated as emulsifiable concentrate, either aqueous or oily [30]. The main sources of human exposure are from contact during manufacturing, and from use in agriculture and in the plastics industry. Because of the known acute toxicity and the strong yellow staining of the skin, agricultural workers are careful to use adequate protective clothing in order to reduce dermal exposure. In the plastics industry, DNOC is made and transported as a powder often dampened with water (12% by weight) to reduce the risk of workers' exposure to dusts. DNOC has caused acute poisoning in humans with several symptoms. Effects are enhanced at high environmental temperature. These effects are consistent with the proposed mechanism of action of DNOC. For these reasons it is important to have fast and sensitive methods for DNOC determination.

In order to identify the best variables operating conditions, the response surface methodology as Central Composite or Box–Behnken designs [31] is commonly and usefully used. These methods allow the simultaneous analysis of more than one factor at the same time and their statistical significance to reduce the number of experiments, minimize reagent consumption, and assess the interaction between the factors. A proper design matrix can lead to a regression equation which highlights effects of individual factors and their relative importance in a given operation process. The possibility of evaluating the interaction effects between the variables on the response can also be used, that is not possible in a classical method (one-factor at-a-time (OFAT)) [31]. 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). Until now, few reports of the voltammetric response optimization using response surface methodology (RSM) have been published [25,32–36]. Nevertheless, there is lack of articles on the voltammetric response optimization for modified electrode in DNOC determination using RSM.

This study has been focused on the multivariate optimization of chemical and cathodic stripping square wave voltammetry (CSSWV) instrumental variables by RSM to determine the pesticide DNOC as model of nitro group compounds. The SbFE has been prepared on a glassy carbon electrode and CSSWV has been used for DNOC determination in water samples. Applicability of this method has been verified by DNOC quantification in natural water samples.

2. Material and methods

2.1. Apparatus

Square wave voltammetry and potentiostatic measurements were all performed with Autolab (PGSTAT 101 Eco-Chemie) potentiostat controlled by NOVA software (Eco Chemie). 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, auxiliary, and reference electrodes, respectively. All potentials are referred to this reference electrode. All electrochemical experiments were carried on at room temperature. Test solutions were stirred during DNOC deposition and cleaning steps with a magnetic stirrer.

2.2. Reagents and solutions

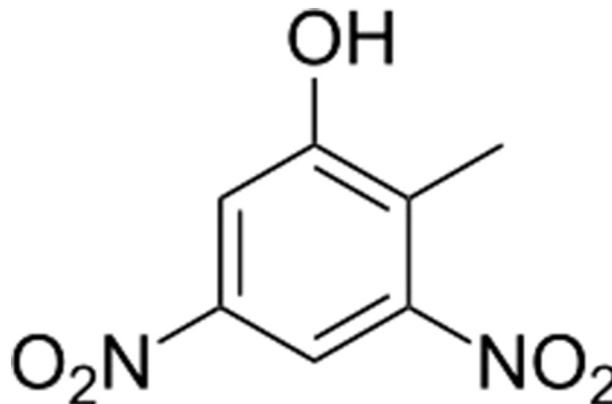
All reagents were obtained as analytical grade and used without further purification. Milli-Q water obtained from a purifying system (18 Mcm⁻¹) Millipore was used for all experiments. 4,6-Dinitro-*o*-cresol (DNOC) and SbCl₃ were purchased from Sigma–Aldrich (St. Louis, MS, USA). Phosphoric acid, acetic acid, sodium acetate, boric acid, hydrochloric acid, and potassium hydroxide were from J.T. Baker. Britton Robinson buffer solution (BRBS) with different pH values was prepared by mixing acetic acid, phosphoric acid, and boric acid to a final 0.12 mol L⁻¹ concentration of each component and the pH was adjusted to the required value by adding either 1.0 mol L⁻¹ hydrochloric acid (HCl) or potassium hydroxide (KOH) solution. The 1 × 10⁻³ mol L⁻¹ SbCl₃ stock solution was prepared by dissolving the appropriate amount of the solid salt in diluted 5% HCl solution. The electrodeposition solution (5 × 10⁻⁵ mol L⁻¹) was prepared in a 10 mL volumetric flask by adding 0.50 mL of stock solution and diluting to 10 mL with acetic buffer solution pH 4.50. To evaluate the accuracy and applicability of the proposed method, the optimized procedure for different water samples was performed. Water samples were taken from different sources, San Roque Lake, Rio Tercero River and drinking water from Córdoba city local net, all locations from Córdoba, Argentina. The collected water samples were filtered through a 0.45 μm Micropore membrane and maintained in glass containers, then stored at 4 °C until they were analysed. For each sample, a 2.0 mL aliquot was transferred to a 10 mL calibration flask, and then DNOC standard solution was added to a 5 × 10⁻⁶ mol L⁻¹ final concentration and filled with buffer solution.

2.3. Preparation of SbFE

The glassy carbon electrode was mechanically polished with 0.05 μm alumina/water slurry (Buehler, USA) on a polishing cloth to a mirror-like finish, followed by a sonication step, rinsed with distilled water, dried in air and inserted into the electrochemical cell. The antimony film electrodeposition was carried out at a constant potential in the electrodeposition solution by applying a -1.00 V deposition potential for 60 s. To remove the bismuth film, a potential step of +0.5 V for 60 s in BRBS was applied, after which a fresh film deposition was performed.

2.4. Experimental procedure

The determination of pesticides such as DNOC (Scheme 1) can be carried out by a cathodic electrochemical process, corresponding to the nitro group reduction as proposed in the literature [27–29]. In this work, DNOC determinations were done by cathodic stripping square wave voltammetry (CSSWV) with a previous accumulation step, and two peaks were obtained. The SWV parameters together with the



Scheme 1. 4,6-Dinitro-*o*-cresol (DNOC) structure.

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