



Polished silver solid amalgam electrode and cationic surfactant as tool in electroanalytical determination of methomyl pesticide



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ABSTRACT

The polished silver solid amalgam electrode (p-AgSAE) combined with square wave voltammetry (SWV) was used in the development of an analytical procedure to Methomyl determination in natural water samples. The experimental and voltammetric parameters were optimized and the use of cationic surfactant cetyltrimethyl ammonium bromide promoted a considerable change in the kinetic and mechanism of the Methomyl reaction. Was observed the presence one-single reduction peak, related to a totally irreversible two-electrons transfer, followed by chemical reaction involving two protons. Analytical parameters (linearity range, analytical curve equations, correlation coefficient, detection and quantification limits, recovery efficiency, and relative standard deviation for intraday and interday experiments) were evaluated indicating that the proposed voltammetric procedure is suitable for determination of Methomyl. The application of the proposed procedure in natural water analysis indicated high robustness with only simple filtration, without pre-concentration steps, good stability and suitable sensitivity to determination of Methomyl in natural water samples.

1. Introduction

Carbamate pesticides represent one of the chemical classes that have attracted most interest in the development of analytical methods for the monitoring their residues and their metabolites in surface and groundwater samples, soil and food [1,2]. The contamination by carbamates promote a disrupt of thyroid functions by interaction of carbamates with thyroid hormone receptor or thyroid binding proteins [3,4]. Some carbamates pesticides present anti-estrogenic activity interfering in reproductivity capacity, and other some carbamates can participate in the development of some types of cancer [5,6].

Among them, the Methomyl {S-methyl-N-[(methylcarbamoyl)oxy]thioacetimidate}, called here as MT, is used in agricultural practices as insecticide and nematocide, and chemically belongs to the family of carbamic acids compounds. Furthermore, MT is a principal metabolite in degradation process of other carbamates, including Thiodicarb, Alanicarb and Aldicarb [7]. MT is an endocrine disrupt compound due to modify the estrogen production, interfering in reproductive capacity, for this, is highly toxic to animals and humans [8]. So, its quantification in drinking water has a high scientific importance.

According to Environmental Protection Agency (EPA) [9], the separation and measurement of the MT in natural water can be realized by high-performance liquid chromatography coupled to ultraviolet

detector (HPLC/UV-Vis), producing a limited sensitivity due considerable interference from complex samples and low wavelengths used in carbamates detection. For this, the use of HPLC coupled to mass spectrometry has (HPLC-MS) become a suitable tool in environmental analysis of MT and other carbamates pesticides [10,11]. Gas chromatography coupled to mass spectrometry (GC-MS) has been reported as highly sensitivity MT analysis in water samples promoting additional selectivity and sensitivity [12,13].

However, the use of chromatographic requires the solid phase extraction (SPE) to reach limits of detection sufficient low for trace analysis [14–16]. Nevertheless, SPE presents long time to analysis, are expensive due to consumption of organic solvents, and considerable volume of samples are necessary and mainly, only a small portion is injected onto the chromatographic column. For this, some non-chromatographic techniques, such as fluorescence spectroscopy [17] and electrochemical [18,19] techniques also have been used in MT determination.

The use of biosensor based on acetylcholinesterase enzyme has been reported to MT analysis, however, the sensitivity is usually lower than obtained with the traditional chromatographic techniques, due to the reversible behavior of inhibition reaction of the acetylcholinesterase to acetylcholine promoted by MT [20,21].

Zapp and co-workers [22] proposed the use of montmorillonite, a

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clay mineral, modified by platinum nanoparticles and ionic liquid, as a support to Lacasse immobilization. This biosensor was used in MT determination in carrot and tomato samples, but was not used in natural water samples. *Fernandes* and co-workers [23] shown a sol-gel derived carbon ceramic biosensor for the determination of MT in vegetable extracts samples. The substrate used was the esculetin, that resulted in a decrease in enzymatic activity when fresh vegetable samples containing MT were added to the reaction medium. In this research, natural water samples also were not analyzed.

In these works, the analytical results were dandified by Lacasse immobilization method and by pH of the samples, by ionic strength and by content of the samples employed. It's occurred due to biocatalytic processes are complex and some components in the samples also may inhibit the enzymatic activity. So, *Costa* and co-workers [24] employed a boron doped diamond electrode to determination of MT in river water, tap water, and commercial formulations. However, the oxidation potential of MT presented value greater than 1.5 V, promoting interference of other redox processes in complex samples.

According to our knowledge, until this moment, no work showing the use of others solid electrodes has been reported to electroanalytical determination of the MT. For this, the goal of this work was the development of reliable, fast, inexpensive and environmental friendly analytical procedure to MT determination in natural water using p-AgSAE allied to square wave voltammetry (SWV), an electroanalytical technique extremely sensitive in the pesticides detection [25,26].

2. Experimental

2.1. Reagents and equipments

In this work, all chemicals employed presented high analytical purity and the solutions employed were prepared with water purified by a Gehaka model OS20 LX system ($18.2 \text{ M}\Omega \text{ cm}^{-1}$ at 25°C). MT (99.50%) has obtained from Ouro Fino Agricultural Company, from Minas Gerais, Brazil, and used without purifications steps. The MT stock solutions were prepared by dissolving a suitable quantity of it in pure acetonitrile to obtain concentrations of $1.00 \times 10^{-3} \text{ mol L}^{-1}$ and $1.00 \times 10^{-4} \text{ mol L}^{-1}$. To prevent degradation process, these solutions were then stored in a dark flask and kept in a refrigerator.

H_3PO_4 , H_3BO_3 and CH_3COOH , in a concentration of the 0.04 mol L^{-1} plus 0.1 mol L^{-1} NaClO_4 were used to prepare the Britton-Robinson (BR) buffer, which had the desired pH values adjusted by addition of the amounts of 1.0 mol L^{-1} NaOH solution. The surfactant cetyltrimethyl ammonium bromide (CTAB) was used in the concentration from $1.00 \times 10^{-5} \text{ mol L}^{-1}$ to $1.00 \times 10^{-3} \text{ mol L}^{-1}$, which corresponds to critical micellar concentration (c.m.c.) [27].

A potentiostat ($\mu\text{Autolab}$, from Metrohm-Eco Chemie) coupled to NOVA software version 2.1.2 was used in voltammetric experiments. The pH values of the solutions were measured using a pH meter (mPA 210, from Tecnopon) equipped with a 3.00 mol L^{-1} Ag/AgCl/KCl-glass combined electrode.

2.2. Electrochemical cell and working electrode

An electrochemical cell containing 10 mL of the BR buffer as supporting electrolyte, was used. A platinum wire and an Ag/AgCl 3.0 mol L^{-1} electrode were used as auxiliary and as reference electrode, respectively, and a home-made p-AgSAE was used as working electrode.

The p-AgSAE was constructed using a natural amalgamation process, according description presented in a previous works [28,29]. For this, 0.35 g analytical grade liquid mercury and 0.15 g of fine silver powder (particle size: 5–9 μm , purity: 99.90%, Sigma-Aldrich) were vigorously blended. The paste resulting was compacted inside a Pyrex® glass capillary tube with an inner diameter of about 0.30 mm. After 24 h, an electric contact was inserted by use a copper wire and silver adhesive. The resulting disks were polished with an emery paper (up to

2000 grit sandpaper, 3 M).

Subsequently, p-AgSAE was inserted in electrochemical cell containing 0.20 mol L^{-1} KCl and the potential of the -2.20 V was applied for 600 s under a stream of purified N_2 (White Martins). This procedure, called as electrochemical activation, allowed a considerable reduction in the resistance to charge transfer and a consequent increase in the analytical responses, and ever is necessary before each day of experiments or after every delay of longer than one hour without use of the electrode [30]. Besides, between each voltammetric scan is applied -2.2 V for 30 s to removal of the adsorbed product reaction from the p-AgSAE [31,32].

2.3. Voltammetric experiments

Preliminary experiments were performed using 10 mL of the BR buffer in pH values from 2.0 to 12.0, plus $3.00 \times 10^{-5} \text{ mol L}^{-1}$ of MT standard solutions in the electrochemical cell. Prior to each one, the solution was deaerated by bubbling in N_2 for 10 min. SWV experiments were realized using scan potential from 0.00 V to -1.50 V at $26 \pm 1^\circ\text{C}$, with the pulse potential frequency (f) of 100 s^{-1} , amplitude of the pulse (a) of 50 mV and the height of the potential step (ΔE_s) of 2 mV. These experiments were done with and without the use of CTAB surfactant to observe the effects of its addition in concentrations below, near and above its c.m.c [27].

The voltammetric parameters related do SWV (f , a and ΔE_s) were individually evaluated in relation to the maximum value of peak current (sensitivity) and the minimum half-peak width (selectivity) [25,26]. Besides, these parameters were used to evaluate the redox reaction mechanism of MT at p-AgSAE.

In this work, the experimental and voltammetric parameters were individually evaluated by analysis of resultant peak currents (I_p), the peak potentials (E_p) and the variation in the half-peak width ($\Delta E_{p/2}$), responsible by sensitivity and selectivity suitable in the voltammetric procedures.

After the experimental and voltammetric optimization, the analytical curves were constructed by the standard addition method. The detection and quantification limits (LOD and LOQ, respectively) were calculated according to guidelines recommended by IUPAC [33], using of the standard deviation of the mean current measured at the reduction potential of MT for 10 voltammograms of the blank solution in purified electrolyte (S_b) together with the slope of the straight line of the analytical curves (s).

The recovery experiments were done to attest the efficiency of the methodology. For this, a known amount of MT was added to the supporting electrolyte followed by the standard additions from the MT stock solution and plotting the resulting analytical curves. The recovery efficiencies (%R) were calculated considering the value of the perceptual of the relationships between $[\text{MT}]_{\text{added}}$ and $[\text{MT}]_{\text{recovered}}$, which refer to the concentration of MT intentionally added in the electrochemical cell, and the concentration obtained by extrapolating the analytical curves, respectively [34]. All measurements were performed in triplicate.

The precision of the proposed procedure was evaluated based on the reproducibility of experiments carried out using five different standard solutions of MT on five different days (interday). The accuracy was evaluated based on repeatability experiments that included ten replicated determinations in the same solution of MT (intraday). The relative standard deviations (RSD) were calculated for the reproducibility and repeatability measures, using the relationships between the standard deviation and the mean of the obtained peak current values [34].

2.4. Application of methodology

The proposed methodology was applied in natural water samples analysis. Three samples were used to evaluate the interfering effects

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