



Voltammetric determination of insecticide thiodicarb through its electrochemical reduction using novel solid amalgam electrode fabricated with silver nanoparticles



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ABSTRACT

In this work we investigated the electrochemical behavior of insecticide thiodicarb and carried out its electroanalytical determination using novel solid amalgam electrode fabricated with silver nanoparticles for the first time. Cyclic voltammetry (CV) and square-wave adsorptive stripping voltammetry (SWAdSV) were used to carry out the electrochemical and analytical studies. The best voltammetric response was achieved through the optimization of the experimental and instrumental parameters. Thiodicarb presented its optimum analytical signal in a medium composed of 0.02 mol L^{-1} Britton-Robinson buffer at pH 6.0. Two voltammetric peaks were observed, one oxidation peak at $E_p = -0.51 \text{ V}$ and one reduction peak at $E_p = -0.64 \text{ V}$ (vs. Ag/AgCl). The electrochemical process was characterized as an irreversible system. The cathodic signal was used for the quantitative studies performed with SWAdSV. Thiodicarb showed linear dependence over the surface of the amalgam electrode for the concentration range from 1.05×10^{-7} to $1.52 \times 10^{-6} \text{ mol L}^{-1}$ and the limit of detection achieved was $2.03 \times 10^{-8} \text{ mol L}^{-1}$. Good repeatability (RSD = 3.8%) and reproducibility (RSD = 6.1%) were found. The voltammetric method developed here allowed the determination of thiodicarb in soymilk samples at levels below those determined by European Union and Brazil with good accuracy. The results were validated using high-performance liquid chromatography and indicated satisfactory concordance. Based on the data described here, the novel silver solid amalgam electrode presented enhanced analytical performance and showed itself as promising to be used on the routine analysis of thiodicarb in food samples.

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1. Introduction

Pesticides are a group of substances that have been extensively used in agriculture to control diseases and obtain high yields. Nevertheless, residues of these compounds may contaminate the air, water, soil, food chains and cause several problems to the humans and ecosystems [1]. Therefore, the presence of residues of pesticides in natural waters and food is considered a public health concern [2]. Carbamate compounds are used as pesticides worldwide due to their broad biological activity. This class of substances includes several insecticides that are employed as acaricides, molluscicides and nematocides [3].

Thiodicarb (3,7,9,13-tetramethyl-5,11-dioxa-2,8,14-trithia-4,7,9,12-tetraazapentadeca-3,12-diene-6,10-dione) is a non-systemic carbamate insecticide used to control worn pests on sweet corn, cotton and soybean. It has relatively narrow spectrum of activity, closely related to its main degradation product methomyl [4]. Thiodicarb molecule consists of two methomyl groups joined by their amino nitrogen through one sulfur atom [5]. As a carbamate derivative, thiodicarb inhibits the acetylcholinesterase and causes an accumulation of acetylcholine at synapses that stimulates parasympathetic postganglionic fibers and somatic motor nerve fibers. The inactivation of cholinesterase produces symptoms of intoxication that include excessive salivation, sweating, blurred vision, nausea and excitation of the central nervous system [6]. The chemical structure of thiodicarb is presented in Fig. 1.

Among the techniques that are frequently employed for the determination of thiodicarb, the most used is high-performance liquid chromatography (HPLC) coupled to fluorescence or mass

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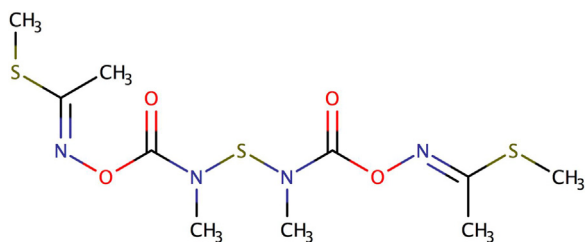


Fig. 1. Graphical representation of thiodicarb molecule.

spectrometry [7–10]. However, the chromatographic methods need expensive instrumentation and require long analysis times. On the other hand, the electrochemical methods are an interesting alternative for the determination of pesticides and may offer advantages such as easier sample preparation steps, shorter analysis times, satisfactory selectivity and sensitivity that may be compared to the chromatographic techniques [11]. Furthermore, electroanalytical approaches are interesting for environmental monitoring due to the possibility of miniaturization of the instrumentation. It allows the construction of compact and portable devices to be used for in-field analysis [12].

In the area of electroanalytical chemistry, the hanging mercury drop electrode (HMDE) is considered the most powerful analytical tool for determination of compounds through their electrochemical reduction. It is due to characteristics such as the high overpotential of the HMDE for the hydrogen evolution reaction [13–15]. Nevertheless, over the past decade, the use of liquid mercury as electroactive surface has been inhibited due to its well-known toxicity for the humans and environment [16]. This way, a challenge in electroanalytical science is to find environmentally friendly electroactive materials to replace the HMDE.

In this context, the amalgam electrodes are a promising option for replacement of the mercury electrodes. This family of electrodes has attractive characteristics such as wide negative potential window, low noise, easily renewable surface and mechanical robustness [17,18]. Solid amalgam electrodes can be obtained in different forms such as polished [19], paste [20], meniscus covered [21] and composite [22]. The amalgams can be prepared from different metals such as Au, Cu, Ag and Sb, [23]. Furthermore, amalgam electrodes are non-toxic and require minimal amounts of mercury for their fabrication. It makes them compatible with the idea of green chemistry [24].

The use of electrochemical methods for the voltammetric determination of thiodicarb is not too much explored in the literature. There are only three reports regarding this topic. Lima et al. developed a biosensor based on polyphenol oxidase enzyme extracted from pequi fruits for the voltammetric determination of thiodicarb. The method was based on the inhibition of the activity of polyphenol oxidase by thiodicarb. A limit of detection of $1.58 \times 10^{-7} \text{ mol L}^{-1}$ was achieved [25]. Moccelini et al. proposed a biosensor based on peroxidase enzyme obtained from alfalfa sprouts. This bioelectrode was employed for the determination of thiodicarb through its inhibitory effect on the peroxidase activity. The limit of detection obtained with this biosensor was $5.75 \times 10^{-7} \text{ mol L}^{-1}$ [1]. Lastly, Babu et al. investigated the electrochemical behavior and performed the voltammetric determination of some carbamate pesticides, including thiodicarb, using carbon nanotube paste electrode. The limit of detection obtained for thiodicarb was $1.07 \times 10^{-7} \text{ mol L}^{-1}$ [26]. The most of the electrochemical sensors used in these previous reports make use of complex procedures that involve the extraction of enzymes and their immobilization over supporting materials positioned on the electrode surface.

Solid amalgam electrodes present robustness, easier construction and simpler use when compared with these biosensors employed for thiodicarb quantification. Furthermore, the use of amalgam electrodes for this purpose has not been reported yet.

Thereby, we described here, for the first time, the voltammetric study and the electroanalytical determination of insecticide thiodicarb using novel solid amalgam electrode fabricated with silver nanoparticles. This electrode presented enhanced analytical performance when compared with conventional solid silver amalgam electrode. Cyclic voltammetry (CV) was employed for the investigation of the electrochemical behavior of thiodicarb and square-wave adsorptive stripping voltammetry (SWAdSV) was used for the quantitative measurements. The related experimental parameters were studied and optimized. The analytical suitability of the proposed electrochemical approach was demonstrated through the successful determination of thiodicarb in soymilk samples.

2. Experimental

2.1. Chemicals and solutions

The following chemicals were used as received: thiodicarb, silver powder (particle size $\geq 10 \mu\text{m}$, purity: 99%) and silver nanopowder (particle size: $< 100 \text{ nm}$, purity: 99%) were acquired from Sigma-Aldrich (St. Louis, MO, USA). Standard solutions of thiodicarb were prepared daily through solubilization of appropriate amounts of the reagent in ultrapure water.

Sodium hydroxide, acetic acid, boric acid and orthophosphoric acid were purchased from Acros Organics (Geel, Belgium). Potassium chloride and methanol HPLC grade were acquired from J.T. Baker (Phillipsburg, NJ, USA). All solutions used in the experiments were prepared using ultrapure water ($18.2 \text{ M}\Omega\cdot\text{cm}$) produced by a Millipore system (St. Charles, MO, USA).

2.2. Preparation and activation of the silver amalgam electrodes

The fabrication of the silver nanoparticles solid amalgam electrode (AgNP-SAE) was based on previous procedures published [27,28]. Firstly, the silver nanopowder was packed inside glass tube with inner diameter of 5 mm. The electric contact was established using a piece of platinum wire inserted through the nanopowder. This glass tube was immersed into a small volume of liquid mercury and kept for two days to allow the amalgamation process. After this period, the electrode was taken off from the liquid mercury and allowed to rest for four days to achieve the state of solid amalgam. The resulting silver solid amalgam disc was manually polished using soft emery paper and alumina powder (0.05 and $1 \mu\text{m}$ particle sizes).

The activation of the fresh electrodes was carried out through the application of -2.2 V for 300 s in 0.2 mol L^{-1} KCl solution continuously stirred. This activation process was repeated once a week or when some abrupt loss on the response of the electrode was observed [29]. Most frequent activation procedure was performed applying -2.2 V for 60 s at the same buffer solution in that the voltammetric experiments were performed. This shorter activation was repeated after each series of measurements, before starting the work and after pauses longer than one hour. The activation procedures are useful to remove oxides, reactants and other products that may be adsorbed on the electrode surface besides reduce the charge-transfer resistance and enhance the electrochemical performance of amalgam electrodes [30]. Some pictures of the AgNP-SAE are exhibited in Fig. S1 (ESI, Electronic Supporting Information).

Additionally, a silver solid amalgam electrode (Ag-SAE) was fabricated using conventional silver powder (particle size $\geq 10 \mu\text{m}$)

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