



Electrochemical quantification of propoxur using a boron-doped diamond electrode



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ABSTRACT

The present paper presents the results of an electrochemical study and proposes an electrochemical method to quantify the carbamate pesticide, propoxur, using a cathodically pre-treated boron-doped diamond electrode without any derivatization processes, which are commonly used for the electrochemical detection of this pesticide class. Propoxur undergoes an irreversible oxidation process with a well-defined peak in aqueous solutions with single electron transfer and no proton under the pH range studied. Using a differential pulse voltammetry technique under the optimized conditions, the analytical curve was obtained from 1.66 to 155 $\mu\text{mol L}^{-1}$ with a limit of detection of 0.50 $\mu\text{mol L}^{-1}$ and a low relative standard deviation of 0.88%. The accuracy of the proposed method was tested using various water samples and a propoxur-containing commercial product by spiking a known quantity of the pesticide. The recoveries ranged from 86.7 to 103%. Overall, the suggested method is simple, reliable and well suited for both routine analysis in the laboratory and in-field analysis.

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1. Introduction

Carbamate pesticides are one of the three major class of pesticides that are used as insecticides or fungicides for agricultural purposes [1,2] and their use has increased with demand for food [3,4].

Propoxur (2-isopropoxyphenyl-*N*-methylcarbamate, PPX, Fig. 1), also known as Baygon®, was introduced in 1959 and is one of the more common carbamate pesticides currently in use [5]. It has been used to control numerous species of household and public health pests [6,7], such as flies and mosquitoes, which affect humans and animals [8]. On the other hand, studies conducted on rats showed that PPX is a carcinogen [5,9] and exposure to carbamate pesticides during the prenatal period has been associated with leukaemia [10]. PPX may also be found on cereal grains and pasture crops due to the steps taken to prevent pest infestations. Consequently, it is inserted in the food chain of grazing animals, which can contaminate their milk [8,11,12]. PPX acts on the central and peripheral nervous system by inhibiting the acetylcholinesterase (AChE) enzyme, reducing its biological activity and leading to a range of health problems [13,14] because AChE removes the excess neurotransmitter, acetylcholine, which interrupts the nerve synapse [15].

Because of the widespread use of PPX as an insecticide, the development of sensitive and reliable methods to monitor it in different kinds of

samples is very important. The methods highlighted for the detection and quantification of PPX are coupled mainly to separation techniques, such as liquid chromatography–mass spectrometry (LC-MS) [16–19], high-performance liquid chromatography (HPLC) using different detection techniques [1,20–25], and gas chromatography–mass spectrometry (GC-MS) [25–32]. Spectrophotometric [33–35] and fluorescence [36] methods have also been proposed, and optical [37,38] and electrochemical [39,40] biosensors have been used to quantify PPX.

Some of the methods mentioned are remarkable and quite sensitive; however, they use very expensive instrumentation or chemicals (biological materials), lack portability, require well-trained staff, and are laborious. Electroanalytical techniques are an alternative that can overcome these problems because they offer some advantages over non-electrochemical methods, such as portability, high sensitivity, and are relatively inexpensive. These characteristics make electrochemical methods an excellent tool for environmental in-field monitoring [14,41].

Carbamate pesticides often require a large oxidation potential, which is difficult to achieve when using conventional electrodes (glassy carbon, gold, and platinum) to develop methods for quantification; hence, a derivatization process is commonly required [41–43]. In contrast, the boron-doped diamond (BDD) electrode has a large anodic potential range (>2 V), which makes it an excellent alternative to overcome this limitation of conventional electrodes [44–46]. To the best of our knowledge, PPX has never been quantified electrochemically without the use of a biosensor or a chemical derivatization process.

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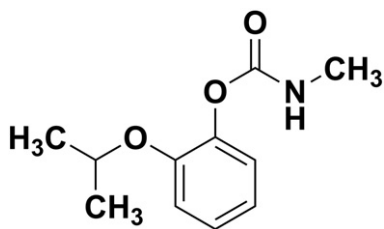


Fig. 1. Chemical structure of propoxur (PPX).

This paper proposes an accurate, sensitive, and useful electroanalytical method involving a differential pulse voltammetry (DPV) technique using a BDD, polarized cathodically, as the working electrode to quantify propoxur without the need for any derivatization process. The method was applied to a range of water samples as well as to a commercial pesticide formulation sample.

2. Experimental

2.1. Reagents and solutions

All chemicals were used as received. Propoxur was acquired from Sigma-Aldrich® (St. Louis, MO, USA, catalogue number 45644). All other chemicals were of analytical-grade and used as received.

The de-ionized water used to prepare the solutions was obtained using a water purification system (Direct-Q® 5 Ultrapure Water Systems, Millipore, MA, USA); the resistivity was greater than 18.1 MΩ cm. A PPX stock solution (10 mmol L⁻¹) in acetonitrile (Merck®, Darmstadt, Germany) was prepared for the cyclic voltammetry (CV) and linear sweep voltammetry (LSV) experiments, whereas a 1.00 mmol L⁻¹ (in acetonitrile (20%)/acetate buffer solution (80%)) solution was prepared for the DPV experiments. A solution of 1 mol L⁻¹ nitric acid was used to pre-treat cathodically or anodically the surface of the boron-doped diamond electrode. Nitric acid is a strong oxidizing agent, which can help to clean the BDD surface by species that could be adsorbed on it. Table 1 lists the composition and pH of the buffer solutions used as the supporting electrolyte for the pH study. The ionic strength (*I*) of the buffers was controlled to be at least 0.1 mol L⁻¹ with sodium sulphate.

2.2. Electrochemical instrumentation and measurements

The pH of the buffer solutions was measured on a Metrohm pH meter (Herisau, Switzerland, model 827 pH lab) coupled to an Unitrode PT1000 glass electrode.

The electrochemical measurements were carried out using a potentiostat/galvanostat Autolab PGSTAT128N (Eco Chemie, Utrecht, The Netherlands) controlled using a laptop running NOVA 1.11 software with a three-electrode standard configuration. A BDD film, which was deposited on polycrystalline silicon wafer (8 × 8 mm²), with a doping level of approximately 8000 ppm was obtained from NeoCoat SA (La Chaux-de-Fonds, Switzerland). The BDD film was used as the working electrode coupled to an electrochemical cell, as published previously [47]. The counter and a home-made reference [48] electrodes were a

platinum wire (0.471 cm²) and Ag|AgCl_{sat.}|KCl(3 mol L⁻¹), respectively.

2.2.1. Cyclic and linear sweep voltammetry experiments

The BDD electrode was pre-treated cathodically before each measurement in 1 mol L⁻¹ nitric acid by applying +3 V for 5 s and -3 V for 60 s to ensure consistent conditions at the electrode surface. Exploratory CV was carried out over the potential range, 0 to 1.8 V, and a scan rate (*v*) of 100 mV s⁻¹. The nature of the limit step of the electrochemical process was evaluated by LSV and the potential window was the same that used for CV but with scan rates ranging from 5 to 300 mV s⁻¹. In these studies, the concentration of PPX was 500 μmol L⁻¹.

2.2.2. Differential pulse voltammetry experiments

Before all DPV experiments, the BDD electrode was polarized cathodically using the procedure described in the previous section, and two sets with five CV scans were recorded to obtain a stable background signal of the BDD electrode as well as better reproducibility of the signals recorded. The main parameters of DPV, i.e., scan rate, step, and amplitude potential, were optimized using the potential window from 0.8 to 1.6 V and a pre-conditioning potential of 0 V for 5 s. The step potential (ΔE_s) was examined over the range 1 to 10 mV, while the amplitude potential (ΔE_a) was verified from 20 to 100 mV and the scan rate was evaluated from 10 to 100 mV s⁻¹. This study was carried out using a 100 μmol L⁻¹ PPX solution in acetate buffer (pH 5, *I* = 0.1 mol L⁻¹).

The analytical curve was obtained under the optimized DPV conditions. In the electrochemical cell, 3.00 mL of the supporting electrolyte solution (pH 5) was added and ten DPV scans were recorded. Successive aliquots of the stock solution (1.00 mmol L⁻¹ PPX) were added to the cell. After each addition, three DPV scans were recorded and the solution was stirred between the runs for 10 s.

2.3. Sample preparation and analysis

Two tap water samples from various sites served by different dams were collected and analysed. A sample from a weir in São Paulo city, Brazil was also analysed. These three samples were filtered through a syringe filter with a 0.45 μm porous membrane (Whatman®).

Bolfo®, a grey solid fine powder, is a commercial pesticide formulation, where the main active component is PPX, and was acquired from an agricultural store. Bolfo® was weighed (0.0215 g), and 2 mL of acetonitrile was added to extract the PPX. The system was then filtered into a 50.0 mL volumetric flask. The extraction and filtration process was repeated three more times. Subsequently, 40 mL of de-ionized water was added and the volumetric flask was filled with acetonitrile.

The protocol analysis was performed using the standard addition approach curve. The DPV parameters were the same as those used for the analytical curve. In this step, 500 μL of 0.5 mol L⁻¹ acetate buffer (pH 5, *I* = 0.5 mol L⁻¹) was placed in the electrochemical cell, followed by the addition of 2.00 mL of the sample under analysis. First, the system was checked to determine if there was an oxidation signal in the region of the oxidation signal of PPX at approximately 1.4 V. The samples were then spiked with PPX to give a final concentration of 10.0 μmol L⁻¹ in the electrochemical cell. After recording the three DPV scans of the sample, three aliquots of a 1.00 mmol L⁻¹ PPX stock solution were added and for each addition, three DPV scans were performed. Between each DPV scan, the solution was stirred for 10 s.

2.4. Interference study

Experiments were performed to determine if some of the ions commonly present in the tap and natural water could interfere with the proposed method. K⁺, Na⁺, Mg²⁺, HCO₃⁻ and SO₄²⁻ ions were in 100-fold excess compared to PPX, whereas the concentration of Cl⁻ was in 300-fold excess. The following ions were in 10-fold excess compared to

Table 1

Buffer composition with an ionic strength (*I*) of at least 0.1 mol L⁻¹ corrected with sodium sulphate. Volume = 100 mL.

Buffer	pH	Composition	Na ₂ SO ₄ /g
H ₃ PO ₄ /H ₂ PO ₄ ⁻	2	0.0052 mol H ₃ PO ₄ + 0.0047 mol H ₂ PO ₄ ⁻	0.246
H ₃ PO ₄ /H ₂ PO ₄ ⁻	3	0.0009 mol H ₃ PO ₄ + 0.009 mol H ₂ PO ₄ ⁻	0.046
HAcO/AcO ⁻	5	0.003 mol HAcO + 0.0069 mol AcO ⁻	0.145
H ₂ PO ₄ ⁻ /HPO ₄ ²⁻	7	0.0037 mol H ₂ PO ₄ ⁻ + 0.0062 mol HPO ₄ ²⁻	-

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