



Boron-doped diamond electrode acting as a voltammetric sensor for the detection of methomyl pesticide



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ABSTRACT

Standard methods for the detection of carbamate pesticides are expensive, time-consuming, and require highly trained employees. Thus, electroanalytical methods are considered to be rapid, simple and low-cost alternatives. Here, we develop sensitive voltammetric methods for the determination of methomyl (a carbamate pesticide) using a bare boron-doped diamond electrode, square wave voltammetry (SWV), differential pulse voltammetry (DPV) and Britton–Robinson buffer (pH 2.0) as supporting electrolyte. Methomyl has three oxidation processes: meantime process P₁ was chosen for the analytical determination due to its higher sensitivity in comparison with other processes. The detection limits and concentration ranges of the SWV and DPV methods were 1.9×10^{-5} and 1.2×10^{-6} mol L⁻¹, and 6.6–42.0 $\times 10^{-5}$ to 5.0–410.0 $\times 10^{-6}$ mol L⁻¹, respectively. The proposed methods were successfully applied in river water, tap water and commercial formulations showing >80% mean recoveries. Comparing the two techniques, DPV was seen as the most sensitive method.

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1. Introduction

Carbamate pesticides are commercialized worldwide and are used in agriculture, households or gardens, and parks. Methomyl, *S*-methyl *N*-(methylcarbamoyloxy)thioacetimidate (molecular formula: C₅H₁₀O₂N₂S, Fig. 1) is a carbamate pesticide (as well as aldicarb, carbaryl, carbofuran, and furadan) it was originally manufactured by DuPont®. It can be used as a contact insecticide (killing the target insects through direct contact) or as a systemic insecticide [1,2].

Methomyl is an inhibitor of the enzyme acetylcholinesterase and, depending on dosage and exposure time, it can be potentially lethal to mammals [3,4]. According to the World Health Organization, methomyl is considered extremely toxic, in toxicity class I [5,6]. It is commonly applied by liquid route (diluted in water). Due to its high solubility in water (57.9 g L⁻¹ at 25 °C), transport by rain water can easily occur reaching streams, rivers, ponds and lakes, and potentially contaminating the affected ecosystem [7,8]. The number of the cases of aquatic environment pesticide contaminations has grown in recent years [9]. Garcia et al. [10] states that these contaminants break down or integrate into natural aquatic systems, resulting in changes to aquatic animal

ecosystems affecting as well, as other mammals that use the untreated water.

Currently, in Brazil methomyl is widely used in agriculture for pest control, mainly in the culture of grains and vegetables such as: soybean, wheat, cotton, corn, potatoes, broccoli, cabbage and tomatoes. The Brazilian Health Surveillance Agency (ANVISA) establishes that the upper limit of methomyl residues allowed is 0.1 mg kg⁻¹ for soybean and corn, as well as 1.0 and 3.0 mg kg⁻¹ respectively for tomato and cabbage crops, [11,12]. Moreover the Brazilian Law provides regiments concerning research, production, waste disposal, and packaging, control, inspection, and monitoring of pesticides and their components (Brazilian Law 7802) [13]. However, many of the problems related to use of agrochemicals are the result of disregard for handling and application safety standards of these substances. As a result, both foods and the environment may receive levels of residues far above the levels recommended by law. Traditionally, chromatographic techniques are the most frequently used for investigation of pesticide residues [14,15]. Alternatively, electroanalytical techniques have been gaining attention for investigations and quantifications of pesticides.

Differing amperometric biosensors have been developed using the enzyme cholinesterase for determining carbamates including methomyl in environmental samples, using amperometric sensor responses while monitoring at +350 mV versus E_{Ag/AgI} [16,17], and

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+370 mV versus $E_{\text{Ag}/\text{AgCl}}$ [18]. Fernandes et al. [19] determined methomyl through laccase inhibition, carbon ceramic biosensor, and square wave voltammetry (SWV) technique with results comparable to those obtained with high performance liquid chromatography (HPLC) at 95% confidence. Tomašević et al. [2] investigated the electrochemical behavior of methomyl in neutral electrolyte using a gold electrode, and cyclic voltammetry (CV). The voltammetric response was monitored in the concentration range of 4–16 mg L⁻¹. The authors emphasized in their literature review that voltammetric studies for methomyl reduction have been developed using differential pulse voltammetry (DPV), with mercury electrode, and differential pulse polarography (with direct and alternating current), and with cyclic voltammetry. They noted an irreversible process with the transfer of four electrons.

Associated with the versatility of electroanalytical techniques, electrical conductivity is a determining factor in the choice of electrode material. For more than a decade, the use of boron-doped diamond (BDD) electrodes has been reported as a good alternative when compared to other conventional working electrodes (Glassy carbon – GC, gold – Au, and platinum – Pt) for electro-analyses of both organic and inorganic substances [20,21]. Pesticides and their metabolites, represent a group of organic compounds already studied using BDD, e.g. in analyses of the: insecticide methyl parathion [22], fungicide kresoxim-methyl [23], herbicides paraquat and atrazine [24,25], pesticide carbaryl [26] and other carbamates [27]. Further applications in pharmaceuticals [28,29], food [30], personal hygiene products [31], and water analysis [32] also demonstrate the widespread use of BDD electrode. An interesting study by Selva and Paixão [33] is worth highlighting that showed for the first time the use BDD electrode as a sensor to extract voltammetric information on oxidations of different carbamate pesticides (aldicarb, carbaryl, carbofuran, methomyl, and propoxur), for the purpose of discrimination and classification using a chemometric approach.

The choice of this electrode in a wide range of applications is of fundamental importance: mainly because of a broad potential window in aqueous solutions (up to 3 V), low background current, low adsorption effects for organic molecules, low sensitivity to dissolved oxygen, high thermal conductivity, and chemical stability [34–40].

Here, a BDD electrode was employed in the determination of methomyl in river water, tap water, and a commercial formulation, using two voltammetric methods (SWV and DPV modes) as analytical techniques.

2. Experimental

2.1. Instrumentation and reagents

All voltammetric experiments were carried out using an EcoChemie, μ Autolab® Type II, potentiostat coupled to a Metrohm, 663 VA Stand®, three-electrode module and a 3 mL single-compartment electrochemical cell. A platinum wire and an Ag/AgCl (3 mol L⁻¹, KCl) electrode were employed as counter and reference electrode. A GCE ($\varnothing = 3$ mm), AuE ($\varnothing = 2$ mm) and BDDE (surface area of 0.36 cm²) were used as working electrodes.

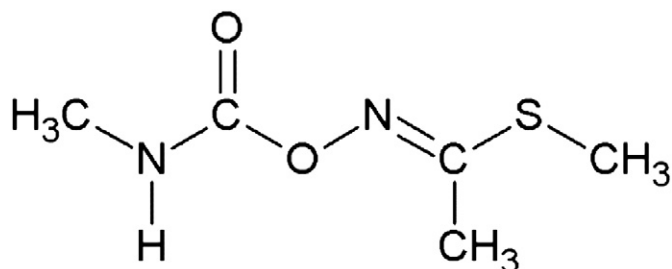


Fig. 1. Methomyl structural formula.

Table 1
Investigated parameters and their optimum values for methomyl determination.

| Techniques | Parameters | Studied ranges | Optimum values |
|------------------|----------------------------------|----------------|----------------|
| SWV | pH | 2.0–12.0 | 3.0 |
| | Frequency (s ⁻¹) | 10–150 | 35 |
| | Scan increment (mV) | 1–7 | 4 |
| | Pulse amplitude (mV) | 10–100 | 40 |
| | Deposition time ^a (s) | 0–120 | 10 |
| | Agitation speed (rpm) | 0–3000 | 1500 |
| DPV ^b | pH | 2.0–12.0 | 2.0 |
| | Interval of time (s) | 0.2–0.6 | 0.2 |
| | Scan increment (mV) | 1–7 | 4 |
| | Pulse amplitude (mV) | 10–100 | 50 |
| | Deposition time ^a (s) | 0–120 | 10 |
| | Agitation speed (rpm) | 0–3000 | 2000 |

^a In open circuit.

^b The modulation time was fixed in 70 ms.

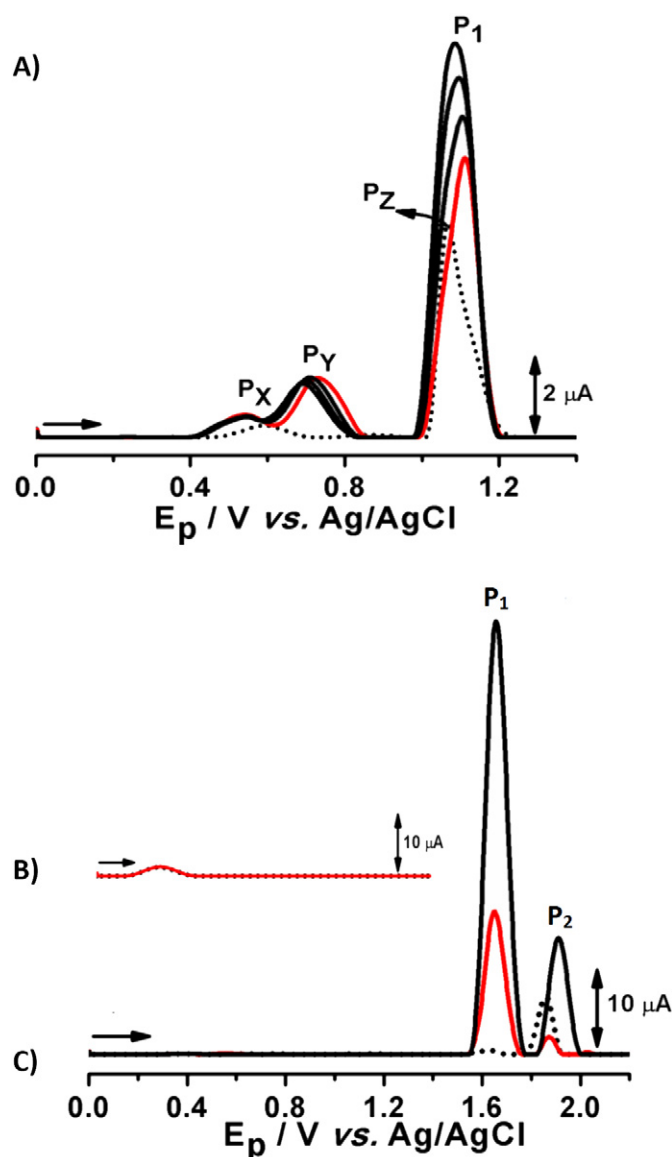


Fig. 2. Square wave voltammetry of methomyl in BR buffer 0.1 mol L⁻¹ (pH = 2.0) recorded in different working electrodes: A) Au – (...) blank, (—) in the presence of 1.0×10^{-4} mol L⁻¹ of methomyl, and (—) after successive additions (1.5, 2.0 and 2.4×10^{-4} mol L⁻¹ methomyl; B) GC and C) BDD – (...) blank, (—) in the presence of 1.0×10^{-4} mol L⁻¹ of methomyl and (—) addition of 2.3×10^{-4} mol L⁻¹ methomyl in BDD.

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