



## Sensing of formetanate pesticide in fruits with a boron-doped diamond electrode



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### ABSTRACT

This study describes the development of a simple and accurate methodology for carbamate pesticide formetanate (FMT) analysis in fruits based on the use of a boron-diamond doped electrode (BDDE) cathodically pretreated and on the forward component of the current of square-wave voltammetry (SWV). FMT exhibits a well-defined irreversible oxidation process, which reaction mechanism is diffusion-controlled, involves the participation of one electron and is influenced by the electrolyte pH. However, protonation does not participate in the rate-determining step in the redox process. The optimum experimental and voltammetric conditions were pH 7.0 (0.04 mol L<sup>-1</sup> Britton-Robinson buffer), pulse potential frequency of 20 s<sup>-1</sup>, amplitude of the pulse of 25 mV, and height of the potential step of 3 mV. Under the optimum conditions, calibration curve was linear from 4.98 × 10<sup>-7</sup> to 1.70 × 10<sup>-5</sup> mol L<sup>-1</sup> FMT with a limit of detection of 3.7 × 10<sup>-7</sup> mol L<sup>-1</sup>. FMT sensing was performed in different fruits (mango and grape). Recoveries ranged from 95.2 ± 2.8 to 104.0 ± 3.5% for mango and 96.5 ± 2.5 to 105.2 ± 3.5% for grape proving the accuracy and precision of the electroanalytical methodology. The attained data validated the applicability of the developed approach for FMT quantification in fruits.

### 1. Introduction

In the last years, contamination of food and water promoted by pesticide residues has been a growing concern for the general public and for governmental authorities [1–6]. Currently, there are several diseases associated with pesticide exposures [6–8]. Organochlorine pesticides have been traditionally considered as main representatives of this type of contaminants, but, more recently, two other classes of chemical compounds widely used in agricultural crops, i.e. organophosphates and carbamates, have been considered as hazardous because they can inhibit acetylcholinesterase activity and can act as endocrine disruptors [9–11]. Therefore, the development of simple, highly selective and accurate analytical methodologies for pesticide determination in environmental and food samples has become a key issue. In this context, electroanalytical approaches have been successfully applied for carbamate pesticide detection in several matrices due to the remarkable versatility of these methods [12–14]. Selection of the most appropriate sensing material is a crucial step. The boron-doped

diamond electrode (BDDE) has the widest usable potential range from all electrode materials (up to 3 V), quasi-metallic conductivity, low background current, mechanical strength, chemical stability in acidic and basic media, and high resistance to surface fouling due to the sp<sup>3</sup> character of diamond carbon [15–22]. Thus, it is an excellent material with unicast properties, which has allowed several applications in electrochemical science [20, 23, 24], such as degradation of organic pollutants (due to its high capacity of generated hydroxyl radical in situ) [25], photoelectrochemical CO<sub>2</sub> reduction [26], electrochemical sensor [15, 16, 19, 27–29] and electro-organic synthesis [30]. Furthermore, the electrochemical performance of BDDE can be modified by a cathodic or anodic pre-treatment in sulphuric acid solution, due to the possibility of changing the surface termination of BDDE; H-termination and O-termination are obtained by cathodic and anodic pretreatment, respectively [31, 32].

The versatility of BDDE for pesticide determination has been demonstrated in few studies [13, 27, 33–36], which included five carbamates (methomyl in river and tap water and commercial formulations

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[13], pirimicarb in tap and weir water [27], propoxur in tap and weir water and a pesticide formulation [33], methiocarb in commercial pesticide [34], and carbaryl in natural water [35] and in natural water and pineapple juice [36]). To the best of our knowledge, there is no study regarding the exploitation of BDDE as sensor for formetanate hydrochloride (3-dimethyl amino methylene aminophenyl methylcarbamate hydrochloride, FMT) nor the determination of this pesticide with an unmodified solid electrode. FMT is a carbamate pesticide miticide/insecticide authorized to be used on several fruits and non-agricultural uncultivated areas/soils [37, 38]. Its quantification was rarely performed by electrochemical techniques, being only made by the conventional hanging mercury drop electrode [39], and more recently with the glassy carbon modified with cobalt phthalocyanine and functionalized multiwalled carbon nanotubes [40], and also by three different laccase-based biosensors electrochemical biosensor [14, 41, 42]. Thus, the main goal of this study was to characterize the electrochemical behavior of FMT on BDDE (cathodically pretreated) and subsequently optimize a simple, sensitive, accurate and inexpensive electroanalytical procedure for FMT sensing in fruits.

## 2. Materials and methods

### 2.1. Reagents

Formetanate hydrochloride ( $\geq 99.6\%$ ) was acquired from Sigma-Aldrich (Steinheim, Germany). FMT standards were made every day by dissolving an accurate quantity in ultrapure water. Britton-Robinson buffer (BR,  $0.04 \text{ mol}\cdot\text{L}^{-1}$ ) was prepared by mixing  $0.04 \text{ mol}\cdot\text{L}^{-1}$  of phosphoric, acetic and boric acid. All other reagents were of analytical grade. The ultrapure water ( $18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$ ) was obtained by a Milli-Q system (Millipore, Molsheim, France).

### 2.2. Instrumentation and electrochemical activation

The electrochemical measurements were performed with an Autolab PGSTAT 128 N (EcoChemie, Netherlands) potentiostat/galvanostat controlled by NOVA 1.10 software. A three-electrode system was prepared with a BDDE (8000 ppm;  $0.265 \text{ cm}^2$ , Centre Suisse de Electronique et de Microtechnique S.A., Neuchâtel, Switzerland) (Metrohm) as working electrode, a platinum plate counter electrode ( $1.03 \text{ cm}^2$ ) and an Ag/AgCl/KCl (saturated) reference electrode. A Micronal B474 pH meter was utilized to adjust solutions pH. The BDDE was activated applying  $+3.0 \text{ V}$  for 30 s and  $-3.0 \text{ V}$  for 60 s in  $0.5 \text{ mol}\cdot\text{L}^{-1} \text{ H}_2\text{SO}_4$  [43].

### 2.3. Electrochemical investigation

A cell with 10.0 mL of supporting electrolyte was used for electrochemical experiments. Before each assay, the solution was agitated using a magnetic stirrer for 30 s.

Cyclic voltammetry (CV) was used to study the FMT electrochemical behaviour on the BDDE. SWV was the electrochemical technique performed to detect and to quantify the FMT. The voltammetric parameters were optimized based on a systematic study of the experimental parameters, such as the potential pulse frequency ( $f$ ), the amplitude of the pulse ( $a$ ) and the height of the potential step ( $\Delta E_s$ ) or scan increment. Furthermore, the pH of the medium was optimized. The only procedure performed between the electrochemical measurements with FMT was the magnetic stirring for 30 s to remove any possible residues adsorbed on the electrode surface, thus ensuring the reproducibility of the all experiments. All measurements were performed at  $26 \pm 1^\circ\text{C}$ .

### 2.4. Electroanalytical methodology

After the optimization of the voltammetric parameters, analytical curves were obtained using the standard addition method. The

detection limit (DL) and quantification limit (QL) were obtained using methodology described in the literature [44]. The precision and accuracy of the method were evaluated by the relative standard deviations (RSD).

The methodology for FMT analysis was applied to grapes and mangoes purchased from local stores at Fortaleza (Brazil). Samples of mango and grape were prepared according to the guidelines of the European Council Directive [45] and 15 g of homogenized sample were extracted by the QuEChERS “Quick, Easy, Cheap, Effective, Rugged and Safe” [40, 41, 46]. The supernatant was thereafter evaporated to dryness with nitrogen and just before electroanalysis, the residue was redissolved with Britton-Robinson buffer (BR,  $0.04 \text{ mol}\cdot\text{L}^{-1}$ ) at pH 7.0. Mango and grape recovery experiments were realized at four fortification levels ( $0.31\text{--}1.70 \text{ mg}\cdot\text{kg}^{-1}$  ( $w/w$ )). Triplicate samples were analyzed by the standard addition method.

## 3. Results and discussion

### 3.1. Characterization of the BDDE

Since electrochemical pretreatments can improve the charge transfer reaction on the BDDE surface [32], a simple, fast and efficient step consisting in the application of sequential anodic and cathodic potentials (as described in the experimental section) was selected. The effect of the applied pretreatment on the BDDE surface was studied by CV using  $1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$  of the electrochemical indicator  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  in  $0.1 \text{ mol}\cdot\text{L}^{-1}$  KCl (Fig. 1).

The attained voltammogram without electrochemical pretreatment (dashed line; Fig. 1) showed higher separation between the cathodic ( $E_{pc}$ ) and anodic ( $E_{pa}$ ) peak potentials and lower peak current compared with the pretreated BDDE response (solid line; Fig. 1). The differences among anodic and cathodic peak potentials ( $\Delta E_p = E_{pa} - E_{pc}$ ) were 140.8 mV and 73.4 mV for BDDE before and after electrochemical pretreatment, respectively. Thus, the polarization improved the BDDE conductivity and the reversibility of the  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  redox couple.

### 3.2. Electrochemical behavior of FMT on the pretreated BDDE

The voltammetric behavior of FMT on the BDDE was studied by performing five subsequent CV scans in the range from 0.0 V to 1.4 V in BR buffer with different pH values (2.0 to 9.0). A well-defined irreversible oxidation process with both peak potential ( $E_p$ ) and peak current ( $I_p$ ) dependent on electrolyte pH was detected.

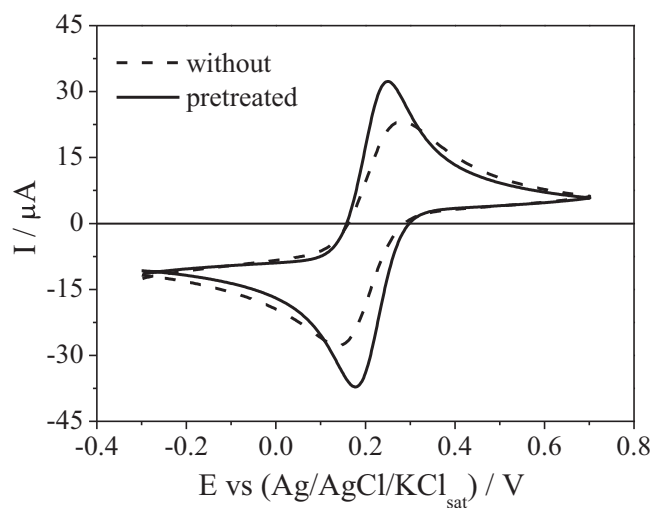


Fig. 1. (A) Cyclic voltammograms of  $1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1} [\text{Fe}(\text{CN})_6]^{3-/4-}$  in  $0.1 \text{ mol}\cdot\text{L}^{-1}$  KCl on the DBBE with (solid line) and without (dashed line) electrochemical activation at  $50 \text{ mV}\cdot\text{s}^{-1}$ .

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