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

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A B S T R A C T

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^{-1} Britton-Robinson buffer), pulse potential frequency of 20 s^{-1}, 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^{-7} to 1.70×10^{-5} mol L^{-1} FMT with a limit of detection of 3.7×10^{-7} mol L^{-1}. 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.

Keywords:
Boron-dopeddiamondelectrode
Square-wavevoltammetry
Carbamatepesticide
Formetanate
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 sp3 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_2 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

[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 (≥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 mol·L^{-1}) was prepared by mixing 0.04 mol·L^{-1} of phosphoric, acetic and boric acid. All other reagents were of analytical grade. The ultrapure water (18.2 MΩ·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/galvalnostat controlled by NOVA 1.10 software. A three-electrode system was prepared with a BDDE (8000 ppm; 0.265 cm^2, *Centre Suisse de Electronique et de Microtechinique S.A.*, Neuchâtel, Switzerland) (Metrohm) as working electrode, a platinum plate counter electrode (1.03 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 V for 30 s and −3.0 V for 60 s in 0.5 mol L^{-1} H_2SO_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 (ΔE_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 ± 1 °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 mol L^{-1}) at pH 7.0. Mango and grape recovery experiments were realized at four fortification levels (0.31–1.70 mg 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 1.0×10^{-3} mol L^{-1} of the electrochemical indicator $[Fe(CN)_6]^{3-/4-}$ in 0.1 mol 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 $[Fe(CN)_6]^{3-/4-}$ 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.

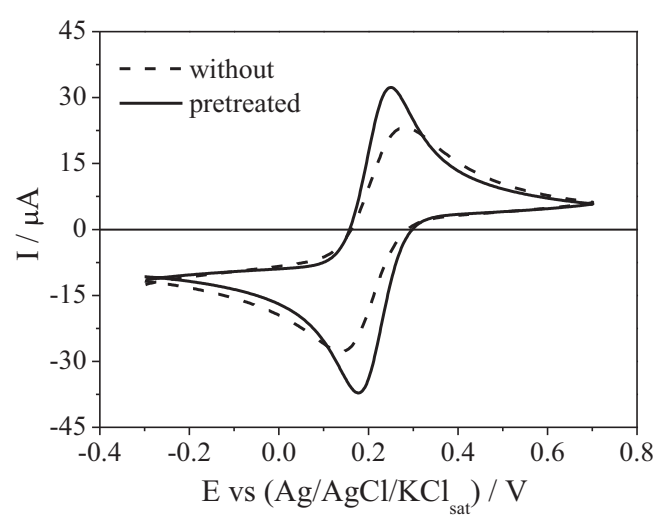


Fig. 1. (A) Cyclic voltammograms of 1.0×10^{-3} mol L^{-1} $[Fe(CN)_6]^{3-/4-}$ in 0.1 mol L^{-1} KCl on the DBBE with (solid line) and without (dashed line) electrochemical activation at 50 mV s^{-1}.

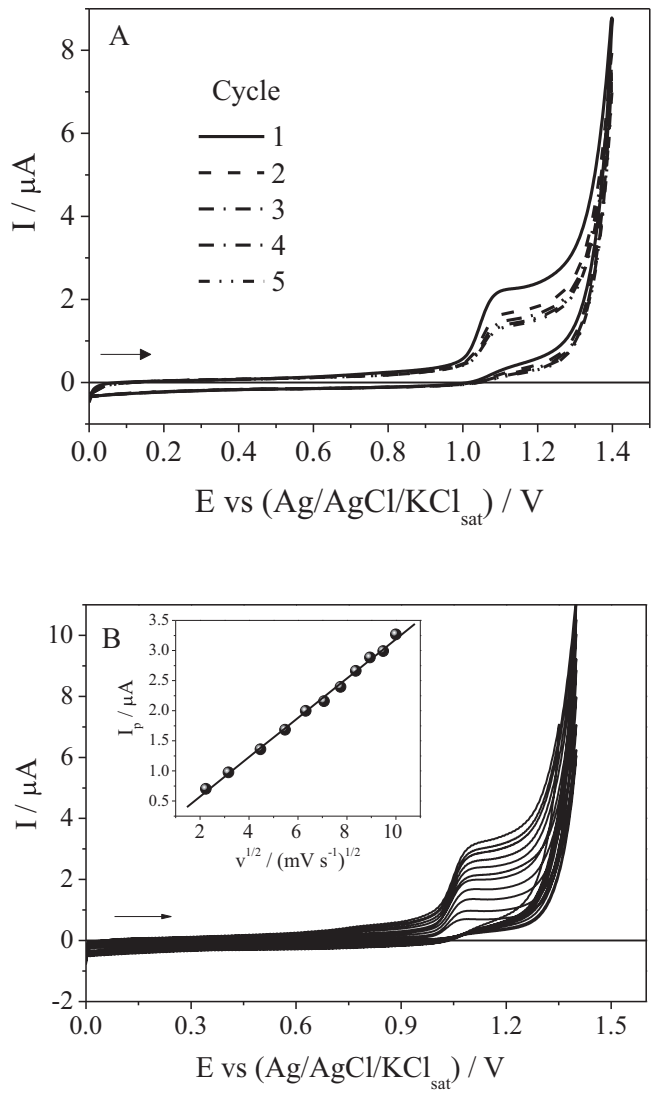


Fig. 2. Cyclic voltammograms of 1.0×10^{-5} mol L^{-1} FMT in Britton-Robinson buffer at pH 7.0 on the BDDE (A) for five subsequent scans at 50 mV s^{-1} and (B) at different scan rates in the range from 5 to 100 mV s^{-1} (the insert corresponds to the relationship between peak current and square root of the scan rate in the range).

Representative voltammograms with an anodic peak at ca. 1.1 V at pH 7.0 are displayed in Fig. 2. The intensity of the peak oxidation current stabilized after the third scan; afterwards no significant changes were observed. This pattern of variation can be associated with the weak interaction between the product of FMT reaction and the BDDE surface. According to the literature, inertness to the adsorption of the reaction electrochemical products and, consequently, facile surface cleaning are inherent characteristics of the BDDE [20, 21]. Moreover, it is reported that the cathodic pretreatment promotes an enhanced resistance to fouling, while simultaneously increasing the electrochemical signal [47, 48].

Based on the diagnostic criteria of CV for irreversible processes, the electron number was calculated by the following equation [49]:

$$|E_p - E_{p/2}| = \frac{1.857RT}{\alpha nF} \quad (1)$$

where $E_{p/2}$ is the half peak potential, R is the gas constant, T is the temperature, α is the electron transfer coefficient, n is the number of electrons, and F is the Faraday constant. Using the attained $|E_p - E_{p/2}|$ value for the first cyclic voltammogram at 50 mV s^{-1}, 84 mV, and

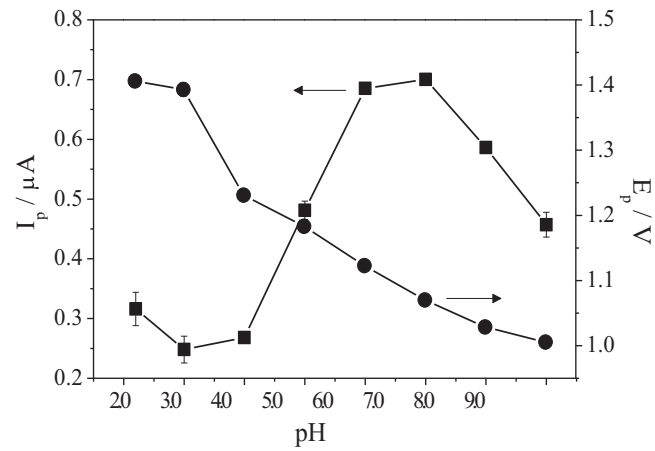


Fig. 3. Effect of the pH on the FMT peak potential (right y-axis) and current (left y-axis) for 1.0×10^{-5} mol L^{-1} FMT in Britton-Robinson buffer on the BDDE with $f = 10$ s^{-1}, a = 25 mV, $\Delta E_s = 2$ mV.

considering α = 0.5, αn was determined as being equal to 0.57 and the electron number equal to 1, being the rate-limiting step of the reaction. It has been reported that other carbamate pesticides, as methomyl [13], pirimicarb [27], propoxur [33] and methiocarb [34], exhibited oxidation processes with the participation of only one electron in the nitrogen atom in the conjugated system [50].

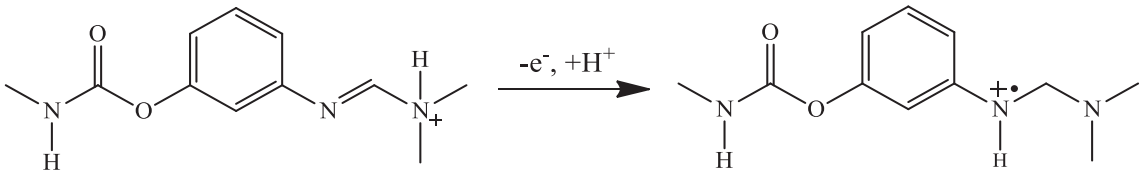
The effect of the scan rate (v) on oxidation peak current was also assessed from 5 to 100 mV s^{-1} (Fig. 2B). I_p value increases with increasing v values. The reached linear relationship between I_p and the square root of the scan rates ($v^{1/2}$) (I_p / A) = $-7.51 \times 10^{-8} + 3.26 \times 10^{-7}\ v^{1/2}/(\text{mV s}^{-1})^{1/2}$ with a correlation coefficient of 0.9985 and $n = 11$) indicates a diffusion-controlled redox process. This conclusion was further validated by the obtained linear dependence between log (I_p) and log (v) [log (I_p / A) = $-6.52 + 0.541$ log (v/mV s^{-1}) with a correlation coefficient of 0.9991 and n = 11].

The influence of the pH from 2.0 to 9.0 of the BR buffer on the FMT SWV responses was characterized by BDDE measurements with $f = 10$ s^{-1}, $a = 25$ mV and $\Delta E_s = 2$ mV (Fig. 3). pH increase promoted the displacement of the E_p to less positive potential values. However, the relationship between Ep and pH was non-linear, suggesting the non-involvement of protonation in the rate-limiting step. In addition, the peak current (I_p) presented a maximum at pH 7.0, while decreasing for higher pH values. This profile can be associated with FMT hydrolysis reaction in basic media [51], which can cause a significant diminution of the concentration of electroactive species at the neighborhood of the BDDE surface. Thus, pH 7.0 was considered the optimum value.

The electrochemical FMT process exhibited on the electrode surface is dependent on the electrode type of carbonaceous materials. According to data previously published [40], FMT exhibits various process of oxidation and reduction on the glassy carbon electrode modified with cobalt phthalocyanine and functionalized multiwalled carbon nanotubes (MWCNT-CoPc/GCE), but in the present study, only one irreversible oxidation was observed on the BDDE. The corresponding mechanism of FMT oxidation on the BDDE is represented by in Scheme 1.

3.3. Optimization of the electroanalytical parameters

The impact of the SWV parameters on the peak current of 1.0×10^{-5} mol L^{-1} FMT on the BDDE in BR buffer at pH 7.0 was evaluated by varying the f, a and ΔE_s from 5 to 60 s^{-1}, 10 to 50 mV, and 1 to 8 mV, respectively. A linear correlation between I_p and f was detected from 5 to 20 s^{-1} followed by stabilization of current intensity around 40 s^{-1}, which can be attributed to the slow charge transfer



Scheme 1. Mechanism of FMT oxidation on the BDDE.

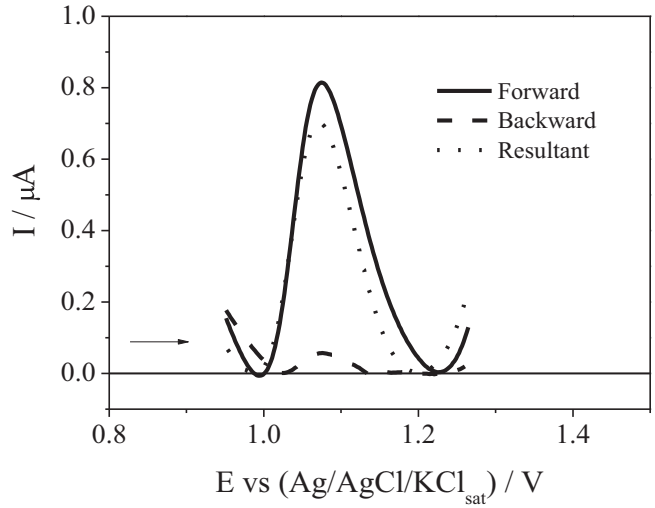


Fig. 4. Square-wave voltammograms showing forward, backward and resultant component of currents for 1.0×10^{-5} mol L^{-1} FMT in Britton-Robinson buffer at pH 7.0 on the BDDE performed with $f = 20\ s^{-1}$, a = 25 mV, $\Delta E_s = 3$ mV.

kinetics between FMT and the selected BDDE (doped with 8000 ppm boron). Furthermore, there was no linear dependence between E_p and log f, which is in agreement with SWV diagnostic criteria for irreversible processes without adsorption of reagent and/or product [52]. The linear relationships for a and ΔE_s were observed until 25 mV and 3 mV, respectively. For electroanalytical purposes, the SWV parameters considered as optimum were $f = 20\ s^{-1}$, $a = 25$ mV and $\Delta E_s = 3$ mV.

The components of the SWV signal, obtained under optimum conditions, can be observed in the Fig. 4.

Interestingly, both forward and backward components appear at the same direction, in other words, both refer to the oxidation process, resulting in a lower intensity for the resulting current. According to the theoretical SWV model for not electrochemically reversible reactions controlled by electrode kinetics [52], the response depends on the transfer coefficient and the dimensionless kinetic parameter (κ) is expressed by:

$$\kappa = \frac{k_s}{\sqrt{Df}} \tag{2}$$

where k_s is the standard rate constant, D is the diffusion coefficient, and f is the frequency [52]. The theoretical model also predicts that for irreversible reactions κ is lower than 0.01 and the current intensity of the resultant component is less than the forward component [53]. Thus, these results regarding FMT on the BDDE are consistent with the SWV theory for irreversible electrode reactions. In this study, the forward component, due to its higher sensitivity, was used for electroanalysis.

3.4. Electroanalytical curves

The figures of merit were calculated based on the achieved FMT calibration curve on the BDDE using the optimum pH and SWV experimental conditions (Table 1). Calibration curve was performed in a wide linear range from 4.98×10^{-7} to 1.70×10^{-5} mol L^{-1} FMT in BR buffer at pH 7.0 with $f = 20\ s^{-1}$, $a = 25$ mV and $\Delta E_s = 3$ mV

Table 1
Electroanalytical parameters obtained for the determination of FMT at BDDE using SWV.

Parameter	BDDE
Linearity range (mol L^{-1})	4.98×10^{-7} to 1.70×10^{-5}
Intercept (A)	-7.79×10^{-8}
Slope (A mol^{-1} L)	0.103
$t_{calculated}$ [a]	2.26
Confidence interval of intercept	$\pm 1.56 \times 10^{-7}$
Confidence interval of the slope	± 0.020
Correlation coefficient (R)	0.9997
Standard Deviation of the intercept (A)	6.3×10^{-8}
Standard Deviation of the slope (A mol^{-1} L)	8.1×10^{-3}
Detection Limit (mol L^{-1})	3.7×10^{-7}
Detection Limit (mg kg^{-1})	0.09
Quantification Limit (mol L^{-1})	1.2×10^{-6}
Quantification Limit (mg kg^{-1})	0.31

[a] t — coefficient of the Student's t distribution at the 95% confidence level.

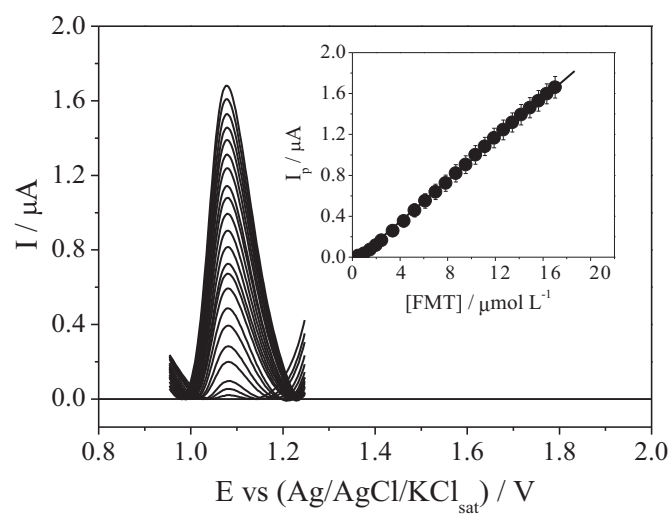


Fig. 5. Square-wave voltammograms for FMT concentrations from 4.98×10^{-7} to 1.70×10^{-5} mol L^{-1} in Britton-Robinson buffer at pH 7.0 on the BDDE with $f = 20\ s^{-1}$, a = 25 mV, $\Delta E_s = 3$ mV. The insert shows the mean calibration curve of three independent assays.

(Fig. 5). The mean of three independent electroanalytical curves is described by the following equation $I_p/A = -7.79 \times 10^{-8}$ ($\pm 6.3 \times 10^{-8}$) + 0.103 ($\pm 8.1 \times 10^{-3}$) [FMT]/A mol^{-1} L with a high correlation coefficient of 0.9997 and $n = 20$. The well-shaped voltammograms exhibited a peak at 1.08 $\pm$ 2.21×10^{-3} V with a RSD equal to 0.20%, indicating that no significant electrode fouling occurred allowing to reach high reproducibility. The t-test of significance was applied to the negative intercept and the calculated value of t was equal to 2.26, being lower than the critical value (4.30 at 95% level [44]), suggesting the absence of systematic errors. The DL and QL were calculated using the standard deviation of y-residuals ($S_{y/x}$) [44], as 3.7×10^{-7} mol L^{-1} (0.09 mg kg^{-1}) and 1.2×10^{-6} mol L^{-1} (0.31 mg kg^{-1}), respectively. It is important to note that the reached sensitivity is adequate for food safety control considering the set Brazilian [38] and European [37] Union Maximum Residue Levels of

Table 2
Recovery of FMT from spiked mango and grape samples ($n = 3$) using the BDDE.

BDDE					
	$[FMT]_{added}$ (mg kg^{-1})	0.31	0.38	0.73	1.70
Mango	$[FMT]_{found}$ (mg kg^{-1})	0.32	0.36	0.73	1.71
	Confidence interval (mg kg^{-1})	± 0.03	± 0.02	± 0.09	± 0.14
	Recovery (%)	104.0	95.2	100.6	100.4
	RSD (%)	3.5	2.8	5.4	3.3
Grape	$[FMT]_{found}$ (mg kg^{-1})	0.24	0.37	0.75	1.79
	Confidence interval (mg kg^{-1})	± 0.02	± 0.04	± 0.04	± 0.14
	Recovery (%)	96.5	97.8	103.4	105.2
	RSD (%)	2.5	4.5	2.1	3.5

several fruit and vegetable crops. In addition, and if necessary, the LD can be further lowered by redissolving the extract in a lesser electrolyte volume or/and simply by augmenting the fruit amount to be extracted. Intraday ($n = 9$ at 2.44×10^{-6} mol L^{-1}) and inter-day ($n = 4$ at 2.44×10^{-6} mol L^{-1}) assays exhibited RSD lower than 5.0%, which demonstrated suitable repeatability as well as reproducibility.

In comparison with other electroanalytical methods for FMT sensing, the sensor proposed in this paper obtained comparable results to a sensor composed by cobalt phthalocyanine and funcionalized multi walled carbon nanotube modified glassy carbon electrode [40] which showed a wide linear range from 9.80×10^{-8} to 3.92×10^{-6} mol L^{-1} and DL value equal to 9.70×10^{-8} mol L^{-1}, a bi-enzymatic biosensor composed for laccase, tyrosinase and AuNPs entrapped in a chitosan in a graphene doped carbon paste electrode s [41] with linear range from 9.99×10^{-7} to 3.21×10^{-5} mol L^{-1} with DL value equal to 2.15×10^{-7} mol L^{-1} and a enzymatic biosensor composed by laccase, glutaraldehyde onto a gold electrode s [42] with present a linear range from 9.43×10^{-7} to 1.13×10^{-5} mol L^{-1} with DL value equal to 9.5×10^{-8} mol L^{-1}. The proposed sensor presents a similar linear range with others described in the literature, and DL in the same order with a biosensor, described, which is one construction more expensive and complex. In addition, the developed biosensors have less selectivity and specificity since they respond to the presence of all carbamates and organophosphorus pesticides because they are based on inhibition of the enzymatic activity.

3.5. Application to fruit samples

With the goal of assessing the applicability of the developed methodology, the QuEChERS procedure was combined with the BDDE and SWV for FMT determination in different complex fruit matrices, i.e. mango and grapes. Samples were spiked at four different levels (0.31–1.79 mg kg^{-1} (*w/w*)) and the recovery percentage, confidence interval and RSD values are shown in Table 2. No interfering signals caused by the fruit matrices were perceived in the SWV voltammograms. Recovery values between 95.2 and 105.2% with RSD varying from 2.1 to 5.4% were reached, suggesting excellent accuracy and precision. In particular for each type of fruit, yields varied from 95.2 ± 2.8 to 104.0 ± 3.5% for mango, and 96.5 ± 2.5 to 105.2 ± 3.5% for grape indicating that the type of fruit matrix had no significant effect on the accuracy and precision of the proposed methodology. These data also validated the applicability of the developed approach for FMT quantification in fruits.

4. Conclusions

This is the first time that a procedure based on a solid electrode without modification has been optimized and applied for FMT sensing. FMT on the cathodically pretreated BDDE exhibited one well-defined irreversible oxidation process with one electron involved. FMT oxidation was affected by the medium pH (with maximum signal at 7.0), but the relationship between peak potential and pH was non-linear, suggesting that no protonation occurred in the rate-limiting step. The forward component of the SWV current was used for electroanalytical purposes due to its higher sensitivity. The achieved electroanalytical data showed satisfactory linearity, detection and quantification limits coupled to good sensitivity, repeatability, reproducibility and accuracy. In addition, the proposed procedure was successfully applied to FMT determination in mango and grape fruits samples. Therefore, it can be concluded that the cathodically pretreated BDDE allied with SWV is an interesting approach for FMT sensing in fruits, which can represent a reliable, cheap, fast and simple option that can be implemented in food safety protocols.

Acknowledgements

The authors wish to thank the Brazilian research funding institutions: CNPq-INCT (proc. 573925/2008-9 and 573548/2008-0), CAPES (Funcap — 2133/2012/proc. 23038.007973/2012-90), PRONEX/FUNCAP (proc. PR2-0101-00030.01.00/15), PRONEM/FUNCAP/CNPq (PNE-0112-00048.01.00/16). Adriana N. Correia (proc. 400223/2014-7 and 303596/2014-7) and Pedro de Lima-Neto (proc. 302801/2014-6) thank CNPq and CNPq-PVE 2014 for their grants. Camila P. Sousa thanks CAPES-PNPD for her grants. The authors also thank to Professor Paula Homem-de-Mello for helping with the drawings. The Fundação para a Ciência e a Tecnologia (FCT) and the FEDER, under Programme PT2020 (Project UID/QUI/50006/2013) and the project Qualidade e Segurança Alimentar–uma abordagem (nano)tecnológica (NORTE-01-0145-FEDER-000011) are also acknowledged for the financial funding.

References

[1] J.P. dos Anjos, J.B. de Andrade, Determination of nineteen pesticides residues (organophosphates, organochlorine, pyrethroids, carbamate, thiocarbamate and strobilurin) in coconut water by SDME/GC–MS, Microchem. J. 112 (2014) 119–126.

[2] L. Han, Y. Sapozhnikova, S.J. Lehotay, Method validation for 243 pesticides and environmental contaminants in meats and poultry by tandem mass spectrometry coupled to low-pressure gas chromatography and ultrahigh-performance liquid chromatography, Food Control 66 (2016) 270–282.

[3] J. Kapelewska, U. Kotowska, J. Karpińska, D. Kowalczuk, A. Arciszewska, A. Świrydo, Occurrence, removal, mass loading and environmental risk assessment of emerging organic contaminants in leachates, groundwaters and wastewaters, Microchem. J. 137 (2018) 292–301.

[4] H.S. Rathore, L.M. Nollet, Pesticides: Evaluation of Environmental Pollution, CRC Press, 2012.

[5] I. Tongo, L. Ezemonye, Human health risks associated with residual pesticide levels in edible tissues of slaughtered cattle in Benin City, Southern Nigeria, Toxicol. Rep. 2 (2015) 1117–1135.

[6] ÿ. Campos, V. dos Santos Pinto da Silva, M. Sarpa Campos de Mello, U. Barros Otero, Exposure to pesticides and mental disorders in a rural population of Southern Brazil, Neurotoxicology 56 (2016) 7–16.

[7] M.C.R. Alavanja, M.K. Ross, M.R. Bonner, Increased cancer burden among pesticide applicators and others due to pesticide exposure, CA Cancer J. Clin. 63 (2013) 120–142.

[8] W. Mnif, A.I.H. Hassine, A. Bouaziz, A. Bartegi, O. Thomas, B. Roig, Effect of endocrine disruptor pesticides: a review, Int. J. Environ. Res. Public Health 8 (2011) 2265–2303.

[9] J.S. Van Dyk, B. Pletschke, Review on the use of enzymes for the detection of organochlorine, organophosphate and carbamate pesticides in the environment, Chemosphere 82 (2011) 291–307.

[10] T. Berman, T. Göen, L. Novack, L. Beacher, L. Grinshpan, D. Segev, K. Tordjman, Urinary concentrations of organophosphate and carbamate pesticides in residents of a vegetarian community, Environ. Int. 96 (2016) 34–40.

[11] U. EPA, Endocrine Disruptor Screening Program Universe of Chemicals and Validation Principles, https://www.epa.gov/sites/production/files/2015-07/documents/edsp_chemical_universe_and_general_validations_white_paper_11_12.pdf, (2012) , Accessed date: 18 April 2018.

[12] T.M.G. Selva, T.R.L.C.d. Paixao, Boron-doped diamond as a sensor for the classification of carbamate pesticides using a chemometric approach, New J. Chem. 40 (2016) 2514–2520.

[13] D.J.E. Costa, J.C.S. Santos, F.A.C. Sanches-Brandão, W.F. Ribeiro, G.R. Salazar-Banda, M.C.U. Araujo, Boron-doped diamond electrode acting as a voltammetric sensor for the detection of methomyl pesticide, J. Electroanal. Chem. 789 (2017) 100–107.

[14] T.M.B.F. Oliveira, M. Fatima Barroso, S. Morais, M. Araujo, C. Freire, P. de Lima-Neto, A.N. Correia, M.B.P.P. Oliveira, C. Delerue-Matos, Laccase-Prussian blue film-

graphene doped carbon paste modified electrode for carbamate pesticides quantification, Biosens. Bioelectron. 47 (2013) 292–299.
[15] E.H. Duarte, J. Casarin, E.R. Sartori, C.R.T. Tarley, Highly improved simultaneous herbicides determination in water samples by differential pulse voltammetry using boron-doped diamond electrode and solid phase extraction on cross-linked poly (vinylimidazole), Sens. Actuator B-Chem. 255 (2018) 166–175.
[16] N. Alpar, Y. Yardim, Z. Senturk, Selective and simultaneous determination of total chlorogenic acids, vanillin and caffeine in foods and beverages by adsorptive stripping voltammetry using a cathodically pretreated boron-doped diamond electrode, Sens. Actuator B-Chem. 257 (2018) 398–408.
[17] E. Mehmeti, D.M. Stankovic, A. Ortner, J. Zavasnik, K. Kalcher, Highly selective electrochemical determination of Phlorizin using square wave voltammetry at a boron-doped diamond electrode, Food Anal. Methods 10 (2017) 3747–3752.
[18] Y.R. Li, H.J. Li, M.J. Li, C.P. Li, D.Z. Sun, B.H. Yang, Porous boron-doped diamond electrode for detection of dopamine and pyridoxine in human serum, Electrochim. Acta 258 (2017) 744–753.
[19] K. Cinkova, K. Kianickova, D.M. Stankovic, M. Vojs, M. Marton, L. Sovrc, The doping level of boron-doped diamond electrodes affects the voltammetric sensing of uric acid, Anal. Methods 10 (2018) 991–996.
[20] A. Kraft, Doped diamond: a compact review on a new, versatile electrode material, Int. J. Electrochem. Sci. 2 (2007) 355–385.
[21] Ľ. Švorc, M. Rievaj, D. Bustin, Green electrochemical sensor for environmental monitoring of pesticides: determination of atrazine in river waters using a boron-doped diamond electrode, Sensors Actuators B Chem. 181 (2013) 294–300.
[22] Z. Lukáčová-Chomisteková, E. Culková, R. Bellová, D. Melicherčíková, J. Durdiak, E. Beinrohr, M. Rievaj, P. Tomčík, Voltammetric detection of antimony in natural water on cathodically pretreated microcrystalline boron doped diamond electrode: a possibility how to eliminate interference of arsenic without surface modification, Talanta 178 (2018) 943–948.
[23] J.V. Macpherson, A practical guide to using boron doped diamond in electrochemical research, PCCP 17 (2015) 2935–2949.
[24] Y. Zhou, J. Zhi, The application of boron-doped diamond electrodes in amperometric biosensors, Talanta 79 (2009) 1189–1196.
[25] F. Souza, S. Quijorna, M.R.V. Lanza, C. Sáez, P. Cañizares, M.A. Rodrigo, Applicability of electrochemical oxidation using diamond anodes to the treatment of a sulfonylurea herbicide, Catal. Today 280 (2017) 192–198.
[26] N. Roy, Y. Hirano, H. Kuriyama, P. Sudhagar, N. Suzuki, K.I. Katsumata, K. Nakata, T. Kondo, M. Yuasa, I. Serizawa, T. Takayama, A. Kudo, A. Fujishima, C. Terashima, Boron-doped diamond semiconductor electrodes: efficient photoelectrochemical CO2 reduction through surface modification, Sci. Rep. 6 (2016) 38010.
[27] T.M.G. Selva, W.R. de Araujo, R.P. Bacil, T.R.L.C. Paixão, Study of electrochemical oxidation and quantification of the pesticide pirimicarb using a boron-doped diamond electrode, Electrochim. Acta 246 (2017) 588–596.
[28] H.S. Ali, A.A. Abdullah, P.T. Pınar, Y. Yardım, Z. Şentürk, Simultaneous voltammetric determination of vanillin and caffeine in food products using an anodically pretreated boron-doped diamond electrode: its comparison with HPLC-DAD, Talanta 170 (2017) 384–391.
[29] K. Tyszczuk-Rotko, I. Bęczkowska, M. Wójciak-Kosior, I. Sowa, Simultaneous voltammetric determination of paracetamol and ascorbic acid using a boron-doped diamond electrode modified with Nafion and lead films, Talanta 129 (2014) 384–391.
[30] S.R. Waldvogel, B. Elsler, Electrochemical synthesis on boron-doped diamond, Electrochim. Acta 82 (2012) 434–443.
[31] J.T. Moraes, C.A.R. Salamanca-Neto, Ľ. Švorc, E.R. Sartori, Advanced sensing performance towards simultaneous determination of quaternary mixture of antihypertensives using boron-doped diamond electrode, Microchem. J. 134 (2017) 173–180.
[32] S.C.B. Oliveira, A.M. Oliveira-Brett, Voltammetric and electrochemical impedance spectroscopy characterization of a cathodic and anodic pre-treated boron doped diamond electrode, Electrochim. Acta 55 (2010) 4599–4605.
[33] T.M.G. Selva, T.R.L.C. Paixão, Electrochemical quantification of propoxur using a boron-doped diamond electrode, Diam. Relat. Mater. 66 (2016) 113–118.
[34] J. Chylkova, M. Tomaskova, I. Svancara, L. Janikova, R. Selesovska, Determination of methiocarb pesticide using differential pulse voltammetry with a boron-doped diamond electrode, Anal. Methods 7 (2015) 4671–4677.
[35] L. Codognoto, S.T. Tanimoto, V.A. Pedrosa, H.B. Suffredini, S.A.S. Machado, L.A. Avaca, Electroanalytical determination of carbaryl in natural waters on boron doped diamond electrode, Electroanalysis 18 (2006) 253–258.
[36] G.S. Garbellini, L.A. Avaca, G.R. Salazar-Banda, Potencialidades do uso de ultrassom na determinação do pesticida carbaril empregando eletrodos de diamante, Quim Nova 33 (2010) 2261–2265.
[37] R.P. Keigwin, EPA-HQ-OPP-2010-0939: Formetanate HCl Final Work Plan for Registration Review June 2011, http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OPP-2010-0939-0012, (2011) , Accessed date: 18 April 2018.
[38] ANVISA, F40 – Formetanato, http://portal.anvisa.gov.br/documents/111215/117782/F40%2B%25E2%2580%2593%2BFormetanato.pdf/f155fc0c-ee6e-420c-880f-c4f0d09ff2ae, (2018) , Accessed date: 18 April 2018.
[39] M. Subbalakshmamma, S.J. Reddy, Electrochemical behavior of formetanate and chlordimeform pesticides, Electroanalysis 6 (1994) 612–615.
[40] F.W.P. Ribeiro, F.W. de Souza Lucas, L.H. Mascaro, S. Morais, P.N. da Silva Casciano, P. de Lima-Neto, A.N. Correia, Electroanalysis of formetanate hydrochloride by a cobalt phthalocyanine functionalized multiwalled carbon nanotubes modified electrode: characterization and application in fruits, Electrochim. Acta 194 (2016) 187–198.
[41] T.M.B.F. Oliveira, M.F. Barroso, S. Morais, M. Araújo, C. Freire, P. de Lima-Neto, A.N. Correia, M.B.P.P. Oliveira, C. Delerue-Matos, Sensitive bi-enzymatic biosensor based on polyphenoloxidases–gold nanoparticles–chitosan hybrid film–graphene doped carbon paste electrode for carbamates detection, Bioelectrochemistry 98 (2014) 20–29.
[42] F.W. Ribeiro, M.F. Barroso, S. Morais, S. Viswanathan, P. de Lima-Neto, A.N. Correia, M.B. Oliveira, C. Delerue-Matos, Simple laccase-based biosensor for formetanate hydrochloride quantification in fruits, Bioelectrochemistry 95 (2014) 7–14.
[43] G.R. Salazar-Banda, L.S. Andrade, P.A.P. Nascente, P.S. Pizani, R.C. Rocha-Filho, L.A. Avaca, On the changing electrochemical behaviour of boron-doped diamond surfaces with time after cathodic pre-treatments, Electrochim. Acta 51 (2006) 4612–4619.
[44] J.C. Miller, J.N. Miller, Statistics for Analytical Chemistry, Pearson Prentice Hall, United Kingdom, 2005.
[45] E. Commission, Commission Directive 2002/63/EC of 11 July 2002—Establishing Community Methods of sampLing for the Official Control of Pesticide Residues in and on Products of Plant and Animal Origin and Repealing Directive 79/700, EEC, DOI (2002).
[46] L.V. Podhorniak, A. Kamel, D.M. Rains, Determination of Formetanate hydrochloride in fruit samples using liquid chromatography − mass selective detection or − tandem mass spectrometry, J. Agric. Food Chem. 58 (2010) 5862–5867.
[47] R. Trouillon, Y. Einaga, M.A.M. Gijs, Cathodic pretreatment improves the resistance of boron-doped diamond electrodes to dopamine fouling, Electrochem. Commun. 47 (2014) 92–95.
[48] R.A. Medeiros, B.C. Lourencao, R.C. Rocha-Filho, O. Fatibello-Filho, Simultaneous voltammetric determination of synthetic colorants in food using a cathodically pretreated boron-doped diamond electrode, Talanta 97 (2012) 291–297.
[49] A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, Wiley, 2000.
[50] G.E. Batley, B.K. Afgan, Voltammetric analysis of some carbamate pesticides, J. Electroanal. Chem. Interfacial Electrochem. 125 (1981) 437–445.
[51] C.B. Divito, S. Davies, S. Masoudi, C.N. Muhoro, Relative stability of Formamidine and carbamate groups in the bifunctional pesticide Formetanate hydrochloride, J. Agric. Food Chem. 55 (2007) 5377–5382.
[52] V. Mirceski, S. Komorsky-Lovric, M. Lovric, Square-wave Voltammetry: Theory and Application, Springer Science & Business Media, Berlin Heidelberg, 2007.
[53] Š. Komorsky-Lovrić, M. Lovrić, Kinetic measurements of a surface confined redox reaction, Anal. Chim. Acta 305 (1995) 248–255.