



Simultaneous Differential Pulse Voltammetric Determination of Omnipaque, Paracetamol and Ceftriaxone on boron-doped diamond electrode : Application to natural carrot, cucumber juice and wastewater

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Abstract: An electroanalytical method has been developed to individually and simultaneously evaluate omnipaque (OMP), paracetamol (PCM) and ceftriaxone (CTX) using differential pulse voltammetry (DPV) and a boron-doped diamond electrode pretreated anodically and then cathodically. The method offers linear results for measuring OMP, PCM and CTX in the concentrations 0 to 52.43 μM , 0 to 13.87 μM and 0 to 87.95 μM , respectively, with detection limits of 0.77 μM , 0.167 μM and 1.4 μM , respectively, in 0.1 HClO_4 medium respectively. The suggested method was effectively implemented to simultaneously assess these analytes in real matrices such as vegetable juice and wastewater from Treichville University Hospital, with recovery rates ranging from (75.8 \pm 0.2; 101.9 \pm 0.1%) in tomato juice, (80.5 \pm 0.3; 100.3 \pm 0.6%) in cucumber juice and (87.5 \pm 0.1; 101.4 \pm 0.1%) in Treichville University Hospital wastewater.

Keywords : Omnipaque, Paracetamol, Ceftriaxone, Differential pulse voltammetry, Boron-doped diamond electrode

1. Introduction

Marketed under the brand name Omnipaque, iohexol is an iodinated contrast medium used in coronary angiography and radiography (scanner). It must provide data of sufficient quality for diagnosis, and be biologically and physiologically inert (Roriz *et al.* 1999).

Paracetamol plays an essential role in many medicines, being the most commonly used active substance worldwide (Bannwarth. 2006; Carlos *et al.* 2015). It is an analgesic substance that relieves mild pain, but is also an antipyretic (Chen. 2012; Abdul *et al.* 2022). Its efficacy, tolerability, pharmacokinetics, cost and acceptability make it one of the most widely used drugs worldwide.

Although paracetamol has been the subject of a great deal of research, its stability is still little studied in the literature (Serge 2017).

Ceftriaxone is one of a vast family of antibiotics that play a crucial role in contemporary human and veterinary medicine, and have a significant influence on our well-being (Majdi *et al.* 2009). However, their evolution in the environment remains unknown. According to research, they were not fully eliminated in sewage treatment plants, and were present in effluent and sludge from STEP (Benito-Pena 2006).

As they spread, all these organic pharmaceuticals will contaminate surface waters and soils near pollution centers which will be used as market-gardening field (Galit Akerman *et al.* 2023; El Abdouni *et al.* 2021; Minh-Ky *et al.* 2023;). These emerging pollutants can contaminate market garden produce such as tomatoes, carrots, cucumbers, cabbage, onions, etc. As the most commonly consumed foodstuffs, these vegetables are present in every household after they have been bought at public markets, which means a risk of poisoning for Humans (Alaqarbeh, *et al.*, 2022). Analytical methods such as atomic emission spectrometry (Whiting *et al.*, 2022), inductively coupled plasma mass spectrometry (ICP-MS) (Sun *et al.*, 2024; Zhang *et al.* 2024), liquid chromatography (LC) (Xu, *et al.*, 2023), colorimetric methods, etc., have been developed to assess water pollution by these micropollutants (Bosch. 2006) However, most of these methods are still not widely used in laboratories, due to the complexity of their implementation, their high cost and the specialized personnel they require. In this situation, electrochemical methods present an interesting option, as they are affordable and can achieve low concentrations, high sensitivities and selectivities.

In our contemporary society, analytical electrochemistry is particularly in demand, eager to provide tools for controlling the quality of chemicals, agri-food products and monitoring environmental parameters (Ferre-Aracil. 2016; Waleed Alahmad *et al.*, 2023). One of the benefits of this method is that it does not require the addition of chemicals. Their main disadvantages are electrode surface passivation, low selectivity and the stability of some common electrode materials (glassy carbon, gold, silver, carbon paste, etc.). To overcome these problems, boron-doped diamond (BDD), which is used as the anode electrode material in this study, represents an excellent option due to its exceptional physical and electrochemical properties. BDD electrodes have electrochemical features, playing the role of wide working potential due to its remarkably low capacitance in aqueous solutions as well as its chemical inertness generally explained by the mechanical durability due to the sp^3 diamond structure. Therefore, BDD have been developed as a superior electrode material for many applications, such as electrochemical sensor, wastewater treatment and electrosynthesis including CO_2 , antibiotics, chemical oxygen demand (COD), biochemical oxygen demand (BOD), glucose, Bupirimate, drugs, influenza virus, and so on reduction (Joshi *et al.*, 2010; Errami *et al.*, 2011; Errami *et al.*, 2013; Salem *et al.*, 2015; Einaga, 2018; Triana *et al.*, 2022; Vernasqui *et al.*, 2024). In some analytical electrochemical methods such as cyclic voltammetry (CV), square-wave voltammetry (SWV) or differential pulse voltammetry (DPV) (Koffi Konan Sylvestre *et al.* 2021), the use of a DDB electrode has enabled detection limits of $0.85\mu M$ (Radovan *et al.* 2008), $1.0\mu M$ (Santos. 2013) and $0.9\mu M$ (Sartori. 2013) respectively to be determined.

In this work, using a BDD electrode, the aim is to detect OMP, PCM and CTX individually and simultaneously in synthetic media ($0.1 M HClO_4$), and to demonstrate the effectiveness of the method by simultaneously detecting the same drugs in real media such as vegetable juices and wastewater.

2. Experimental Method

2.1. Reagents and Solutions

Perchloric acid solution (HClO_4 , 60%) and sulfuric acid (H_2SO_4 , 95-98%) were purchased from Panreac, GERMANY and SIGMA-ALDRICH, USA respectively. Paracetamol 500 mg, Omnipaque 300 mg I/mL and Ceftriaxone 1 g were supplied by BAILY-CREAT (France) and GE Healthcare (France). Omnipaque, paracetamol and ceftriaxone stock solutions were prepared separately by dissolving a precise quantity of omnipak, paracetamol and ceftriaxone in a certain volume of volume of perchloric acid (HClO_4 0.1 M). These different stock solutions were homogenized by shaking for 30 minutes. Working solutions for voltammetric studies were prepared by diluting the stock solutions. All solutions were protected from light and used within 24 hours to avoid decomposition. Distilled water was used to prepare the 0.1 M HClO_4 supporting electrolyte. The vegetable juices used in this work were obtained after a certain process.

First of all, these vegetables, purchased on the market, were each first rinsed abundantly with tap water and then with distilled water. Each of the vegetables was then ground in turn in a very clean blender with a well-defined quantity of perchloric acid (HClO_4 0.1M). The juice obtained was then filtered several times on ordinary filter paper (Filter-LaB) to obtain a homogeneous juice. Finally, 1 ml of this filtrate was dissolved in a volumetric flask containing 0.1M HClO_4 to obtain the 100 ml stock of juice used as a supporting electrolyte.

2.2. Equipment and Electrodes

An AUTOLAB PGSTAT 20 (Ecochemie) coupled to a potentiostat with a USB electrochemical interface was used to conduct the voltammetric measurements. A three-electrode, single-compartment glass cell and a computer are attached to this system in order to store and process data. The voltammograms were obtained using the GPES 4 program. Platinum wire served as the reference electrode and saturated calomel electrode (SCE) as the counter electrode in the glass electrochemical cell. The working electrode was a BDD electrode. The BDD has a 1 cm^2 surface area that comes into touch with the electrolyte. A pH meter was used to measure each pH value. Every potential discussed in this work was measured at room temperature (25°C) against the SCE electrode.

2.3. Analytical Procedures

A calibration curve was created by building analytical curves in the HClO_4 supporting electrolyte. Concurrent DPV measurements were performed for different OMP, PCM and CTX concentrations like follows: OMP concentrations varying alone up to $254.4 \mu\text{M}$ with that of fixed PCM and CTX; PCM concentrations varying alone up to $85.99 \mu\text{M}$ with that of fixed OMP and CTX; CTX concentrations varying alone up to $193 \mu\text{M}$ with that of fixed OMP and PCM. The BDD electrode was electrochemically prepped in a 0.5 mol/L H_2SO_4 solution before the tests began. This pre-treatment consists of a cathodic pretreatment (-2 V , 90 s) after an anodic pretreatment ($+2 \text{ V}$, 15 s). In this manner, all contaminants were removed from the BDD surface, which was subsequently mostly hydrogenated (Salazar-Banda *et al.*, 2006)

Adequate amounts of OMP, PCM and CTX were extracted from the stock solutions using the metered addition method, and then added to the measuring cell that held 100 milliliters of the carrier. DPV curves were recorded at each test after the fluid was homogenized by swirling with a magnetic bar. After that, the calibration curves for every species were displayed for every experiment series. Then, using the following formulas, the detection limits (LOD) and quantification limits (LOQ) of OMP,

PCM and CTX were determined: $LOD = 3 \cdot SD/b$ and $LOQ = 10 \cdot SD/b$, where SD is the standard deviation and b is the calibration curve's slope (Batista, *et al.*, 2010).

3. Results and Discussion

3.1 Electrochemical Behavior of OMP, PCM and CTX

In order to determine the best conditions for studying the electrochemical behavior of **OMP, PCM and CTX** on the boron-doped diamond electrode (BDDE), our previous work (Koffi *et al.*, 2019) enabled us to choose the perchloric acid solution with a concentration of 0.1M at pH = 0.217 as the support medium in which the best voltammetric responses are obtained.

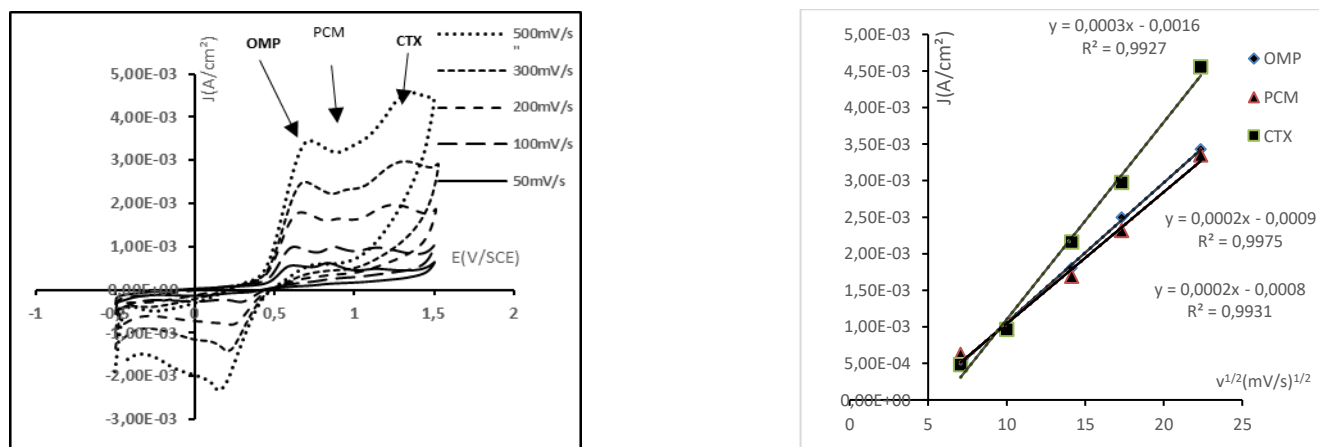


Figure 1: Cyclic voltammograms in a 0.1 M HClO₄ solution containing 4g/L of OMP, 2 g/L of PCM and 2g/L of CTX at different scans (A) ; evolution as a function of the square root of the scanning speed of the anodic peak currents (B)

The electrochemical behavior of OMP, PCM and CTX on BDDE was studied by cyclic voltammetry.

Figure 1A shows the cyclic voltammetric profile of the simultaneous electrochemical oxidation of OMP with a concentration of 4g/L, PCM with a concentration of 2g/L and CTX with a concentration of 2g/L in 0.1 M HClO₄ solution. As can be seen, OMP, PCM and CTX show only one well-defined oxidation peak at 0.62V/SCE; 0.88V/SCE and 1.15V/SCE respectively, with the presence of a single cathodic peak related to OMP. Clearly, the electrochemical reactions of PCM and CTX at the BDDE surface are irreversible, except for those of OMP, which may be quasi-reversible. These curves were recorded under the pre-treatment conditions indicated above, in order to achieve better resolution of the oxidation peaks of the compounds studied.

The effect of sweep speed on the peak current of OMP, PCM and CTX was studied in the range 50 to 500 mV/s. The CV curves observed reveal a totally irreversible behavior of the PCM and CTX, while that of the OMP is quasi-reversible in nature. As the scan speed increases, the anodic current peaks of all three molecules increase as the potential shifts to a more positive value. However, the OMP reduction peak is shifted to a more negative value with the increase in scan speed and simultaneous increase in current. The anodic peak current density (J) of all three molecules is linearly proportional to scan speed (v) (**Figure 1B**), revealing that oxidation processes are controlled by adsorption at the BDDE. The good resolution and the good separation of these oxidation peaks clearly show that studies of detection and quantification of PCM and OMP can be carried out simultaneously in the reaction medium on the surface of our BDDE without interference.

3.2. Individual and simultaneous determination of OMP, PCM and CTX

Before recording the voltammograms with differential pulses for the individual or simultaneous determination of **OMP, PCM and CTX** using a BDDE pretreated anodially then cathodically, the

influence of the key parameters in DPV on the peak potential and the peak current were studied in the following ranges: pretreatment potential ($-2.5 \leq E_p \leq 3$ V/SCE); pretreatment time ($15 \leq t_{Ep} \leq 300$ s); modulation amplitude ($0.01 \leq MA \leq 0.5$ V/SCE); modulation time ($0.005 \leq t_M \leq 0.25$ s); step potential ($0.001 \leq \Delta E_p \leq 0.02$ V/SCE). The optimized parameters obtained and used in this work are therefore: $E_p = -2$ V/SCE, $t_{Ep} = 90$ s, $AM = 0.1$ V/SCE, $t_M = 0.05$ s and $\Delta E_p = 0.007$ V/SCE (Koffi et al. 2019).

3.3 Individual determination of OMP, PCM and CTX

In this figure 2A, the voltammograms recorded under the same optimum conditions show that the oxidation peaks of the OMP are all observed at the same potential ($E = 0.5$ V/SCE) for the concentrations varying from 0 to $52.43 \mu\text{M}$. An increase in the intensity of the oxidation peak current of the OMP with its concentration is observed in the figure 2B, giving a linear calibration curve of $R^2 = 0.9996$. Applying the same experimental conditions, the calculated limit of detection and quantification are $0.77 \mu\text{M}$ and $2.57 \mu\text{M}$ respectively with recovery rates ranging from 98.7 to 100.7% (Martin, et al., 2023)

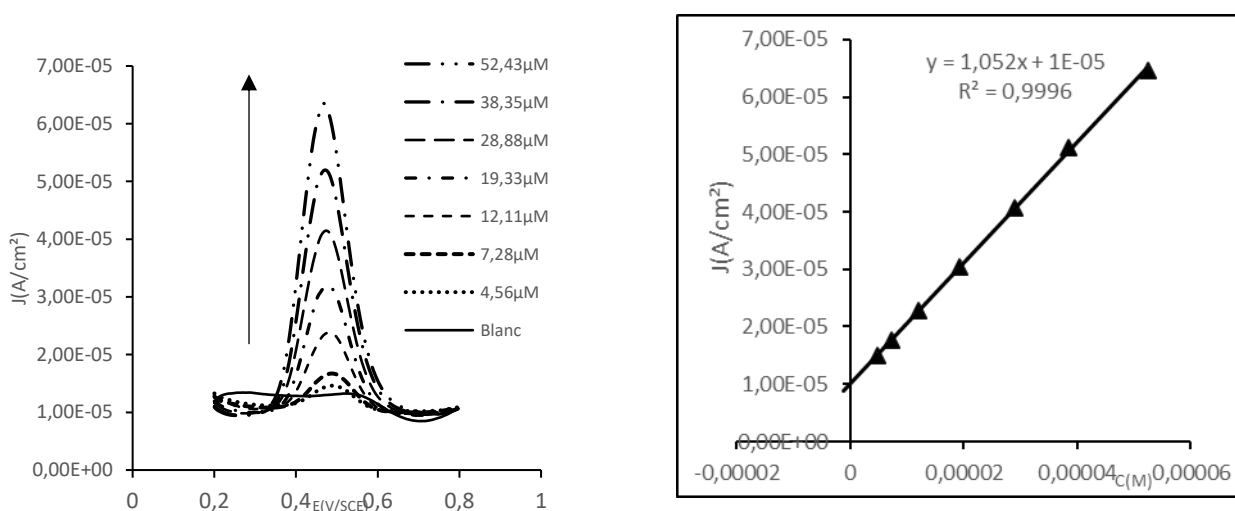


Figure 2 : Differential pulse voltammograms at different concentrations of omnipaque in HClO₄ solution on BDD electrode by DPV; the concentration varies from 0 μM to 52.43 μM, (B) Calibration curve of method.

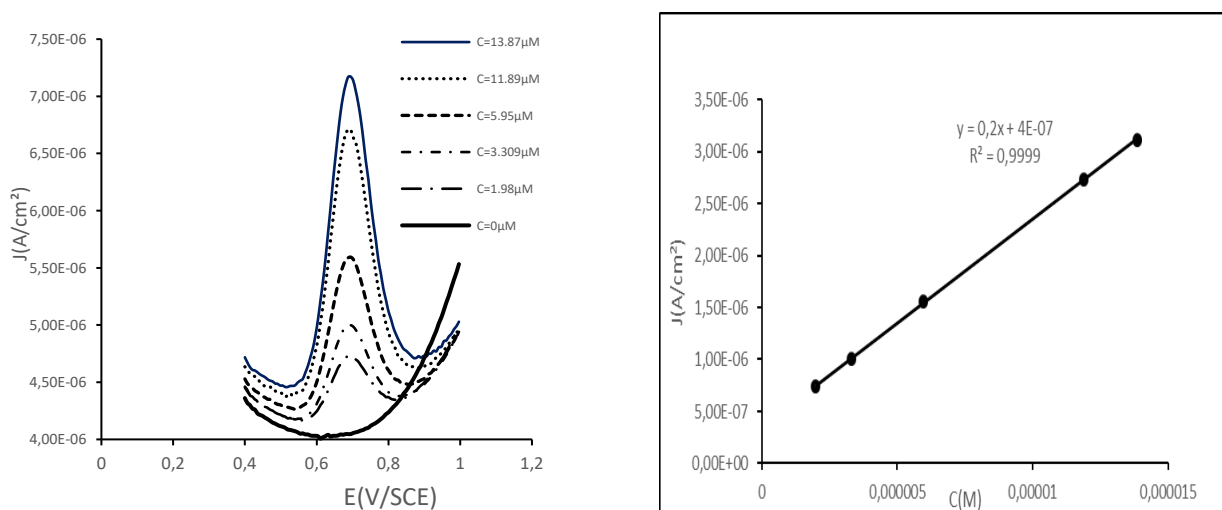


Figure 3 : (A) Differential pulse voltammograms at different concentrations of paracetamol in HClO₄ solution on BDD electrode by DPV ; the concentration varies from 0 μM to 19.8 μM, (B) Calibration curve of method.

Figure 3 A shows the voltammetric response of the oxidation peaks for each of the concentrations of PCM ranging from 0 μM to 13.87 μM . Voltammograms recorded under the optimum conditions obtained show that the oxidation peaks of the PCM are all observed at the same potential ($E = 0.7 \text{ V/SCE}$), whatever its concentrations. **Figure 3B** shows the intensity of the oxidation peak current of the PCM increases linearly with paracetamol concentration. The limit of detection and quantification are 0.167 μM and 0.559 μM , respectively. Three series of independent measurements, each with five (05) different concentrations of paracetamol, were carried out and used to determine the recovery rate, which is close to 98%. A calibration curve of $R^2 = 0.9999$ was obtained (Koffi *et al.*, 2019). All these results show the reliability, reproducibility, sensitivity and selectivity of the method.

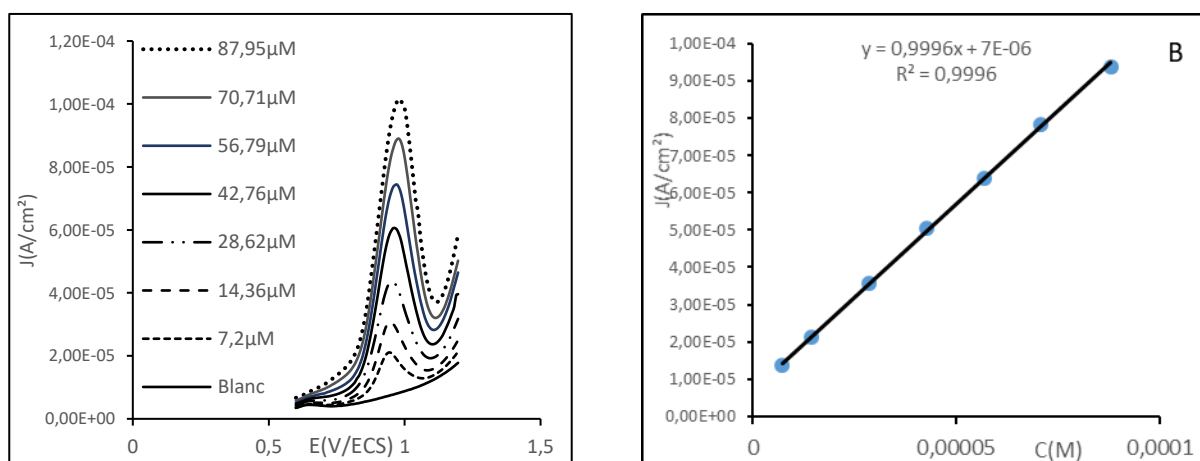


Figure 4 : Differential pulse voltammograms at different concentrations of ceftriaxone in HClO_4 solution on BDD electrode by DPV ; the concentrations varies from 7.2 μM to 87.95 μM (A) and method calibration curve (B).

Voltammograms for CTX determination in 0.1M HClO_4 medium are shown in **Figure 4 A**, using the previously optimized conditions. The peak current increases as the solute concentration in the reaction medium increases. In addition, the oxidation potential of these peaks is around 1V/ECS. The representation of the regression line over the CTX concentration range mentioned above confirms linearity. (**Figure 4 B**).

The regression coefficient of 0.9996 in this linearity range testifies to satisfactory linearity of the method. After removing the blank effect, the limits of detection and quantification obtained by differential pulse voltammetry are 1.4 μM and 4.67 μM respectively. Recovery rates ranged from 91.5 ± 0.1 to 101.4 ± 2.7 .

3.4 Simultaneous determination of OMP, PCM and CTX

Based on previous results, this suggested voltammetric method was employed to detect OMP, PCM and CTX in pharmaceutical formulations at the same time. The DPV graphs obtained demonstrate effective separation of the peak potentials, clearly facilitating simultaneous determination of these compounds. However, to assess the feasibility of the proposed method for simultaneous determination of OMP, PCM and CTX at different concentrations, a DPV series was recorded. This series was carried out by keeping the concentration of two components constant and varying the concentration of the other, as illustrated in the **figure 5** above, as well as by simultaneously varying the concentration of all three compounds (**figure 6**).

In the first situation, a increase in the concentration of one compound was observed in the presence of unchanged concentrations of the other two compounds (**Figure 5**). Voltammograms for different OMP concentrations are shown in **Figure 5A**, with a 12.8 μM concentration of PCM and a 34.9 μM

concentration of CTX (with relatively constant oxidation current peaks). Depending on the concentration **47.24-254.4 μ M**, the oxidation peak current of OMP increases proportionally with its concentration.

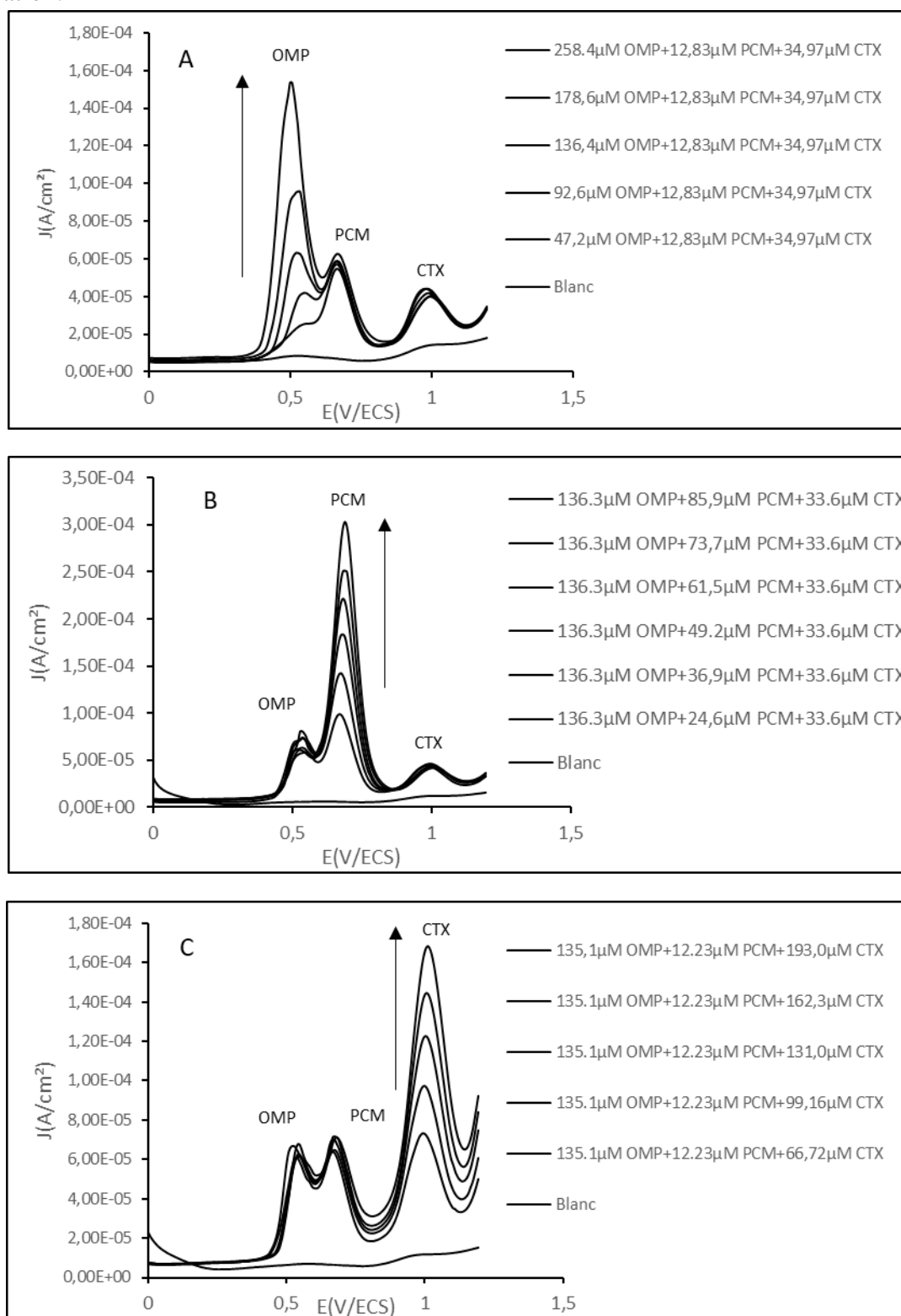


Figure 5: DPV curves with different concentrations of (A) OMP (47.24-254.4 μ M) in the presence of fixed concentrations of 12.8 μ M PCM and 34.9 μ M CTX; (B) PCM (24.68-85.99 μ M) in the presence of fixed concentrations of 136.3 μ M OMP and 33.64 μ M CTX; (C) CTX (66.72-193 μ M) in the presence of fixed concentrations of 135 μ M OMP and 12.2 μ M PCM. Epr=-2V/ECS, tEp=90s, MA=0.1V/ECS, tM=0.05s and Δ Ep=0.007V/ECS

The concentrations of OMP and CTX were subsequently set at **136.3 μ M** and **33.64 μ M** respectively (with relatively constant maximum oxidation currents), while that of PCM was adjusted in the range **24.68 to 85.99 μ M** (**figure 5B**). DP voltammograms of various CTX concentrations (**66.72-193 μ M**) are shown in **Figure 5C**, in a solution containing **135 μ M** OMP and **12.2 μ M** PCM (with relatively constant oxidation current peaks). In the latter cases, an increase in oxidation peak current is also observed as a function of varying analyte concentration. Furthermore, in this study of simultaneous detection of the three compounds, the voltammograms show that the oxidation peak potentials of OMP ($E=0.5V/ECS$), PCM ($E=0.7V/ECS$) and CTX ($E=1V/ECS$) remain identical to the values found in their individual studies. This result demonstrates the selectivity of the method used in this work.

Figure 6 shows differential pulse voltammograms of OMP, PCM and CTX recorded in 0.1M $HClO_4$ medium. These voltammograms were obtained by simultaneously varying the concentration of the three pharmaceutical compounds in the reaction medium. The calibration curves for OMP ($R^2=0.9995$; **Figure 7A**), PCM ($R^2=0.9995$; **Figure 7B**) and CTX ($R^2=0.999$; **Figure 7C**) obtained under the same operating conditions show good linearity. The detection limits calculated for OMP (LOD=8.22 μ M), PCM (LOD=1.40 μ M) and CTX (LOD=5.43 μ M) are of the same order of magnitude as those found when the three molecules were analyzed individually. Simultaneous detection of omnipak, paracetamol and ceftriaxone is therefore just as effective as their individual detection by this method. The proposed method was able to detect all three pharmaceutical compounds simultaneously, with recovery rates ranging from:

90.8 \pm 0.5 to 98.1 \pm 0.2 for OMP, from 97.4 \pm 1.6 to 100.7 \pm 0.3 for PCM and from 98.6 \pm 0.1 to 101.8 \pm 0.5 for CTX (Table 1).

These results show that the simultaneous detection of these three molecules is as effective as their individual detection.

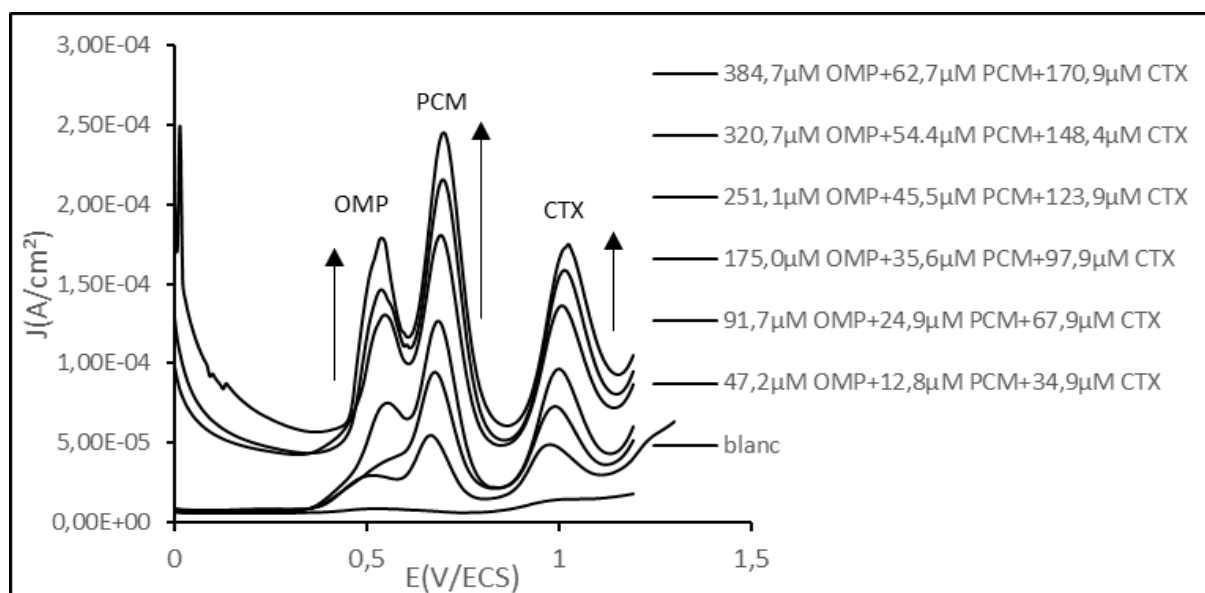


Figure 6: VID for a mixture in 0.1M $HClO_4$ medium of varying concentrations of OMP (47.24-384 μ M), PCM (12.83-62.7 μ M) and CTX (34.97-170.9 μ M). $E_{pr}=-2V/ECS$, $t_{Ep}=90s$, $MA=0.1V/ECS$, $t_M=0.05s$ and $\Delta E_p=0.007V/ECS$

These high recovery rates obtained in this study are comparable and of the same order as those found by [Kalambate et al. 2016](#), in the simultaneous determination of paracetamol, cetirizine and phenylephrine using a modified carbon paste electrode as well as those found by [Taei and Ramazani](#).

2014 obtained for the simultaneous determination of acetaminophen, norepinephrine and tyrosine using a glassy carbon electrode.

It is important to point out that there is no document mentioning a voltammetric procedure for the simultaneous determination of OMP, PCM and CTX in pharmaceutical formulations or in vegetable juices and wastewater. These results therefore testify to the effectiveness of the method presented here for the simultaneous determination of these compounds in pharmaceutical formulations and in vegetable juices and wastewater. Successive measurements ($n=6$) of OMP, PCM and CTX were made to assess intra-day repeatability of peak current magnitude at different concentrations. Inter-day repeatability of peak current magnitude was assessed by measuring peak current for similar fresh solutions over 3 days.

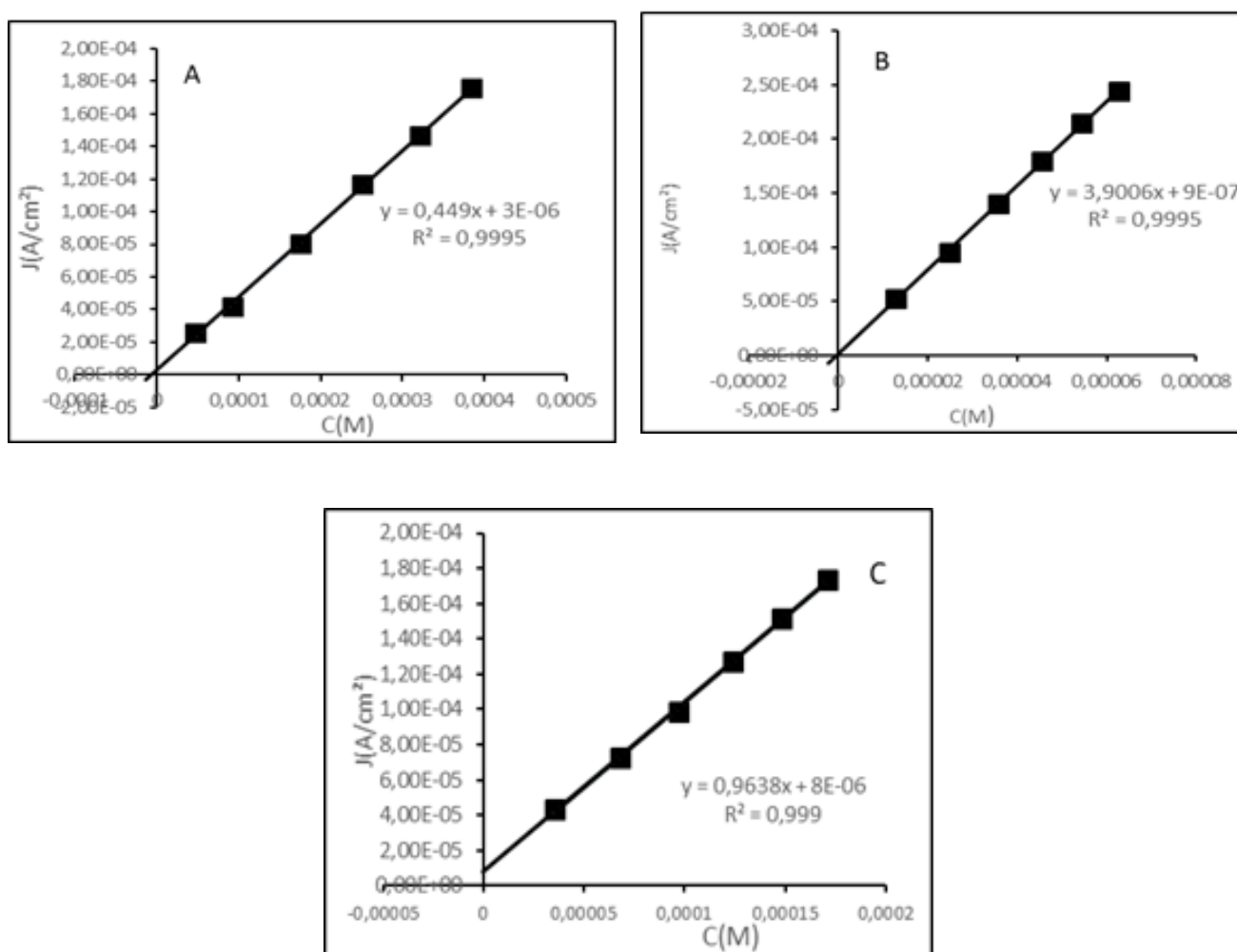


Figure 7: Calibration curves for OMP (A), PCM (B) and CTX (C)

3.5 Interference studies

Potential interferents, such as starch, povidone, and magnesium stearate, which are typically found in the pharmaceutical formulations under analysis, were added to a standard solution containing OMP, PCM, and CTX with concentration ratios (standard solution : interfering compound such as K^+ , Cl^- , SO_4^{2-} , NO_3^- , HPO_4^{2-} , and some organic compounds) of 1:1, 1:10, and 10:1 (w/w) in order to evaluate the selectivity of the suggested method. A comparison was made between the matching oxidation current peaks and those that were produced without each interferent. These chemicals do not

significantly (<5%) interfere with the determination of OMP, PCM, and CTX under the working circumstances used, according to the results of the study of the replies received.

3.6 Application to the simultaneous detection of OMP, PCM and CTX in carrot, cucumber juice and wastewater

To assess the applicability of the proposed method, PCM, CTX and OMP were detected in complex media such as wastewater, tomato, cucumber, carrot and orange juices. These complex media were used as electrolyte carriers. The method developed was used to analyze these pharmaceutical products, as described in the experimental section. Well-defined quantities of these pharmaceutical substances were simultaneously introduced into these media. OMP, PCM and CTX were detected by simultaneously increasing their concentrations in a solution of carrot juice, cucumber juice and wastewater.

Table 1: Recovery rates for simultaneous detection of OMP, PCM and CTX

Drugs	Number of the sample	Added mL	Added μM	Found μM	Recover Rate \pm SD
OMP	1	2	47.2	46.3	98.1 \pm 0.2
	2	4	91.7	83.2	90.8 \pm 0.5
	3	8	175.1	161.5	92.2 \pm 0.1
	4	12	251.1	234.8	93.5 \pm 0.1
	5	16	320.7	295.4	92.1 \pm 0.1
	6	20	384.7	354.2	92.0 \pm 0.1
PCM	1	0.1	12.8	12.7	99.2 \pm 0.6
	2	0.2	24.9	24.2	97.4 \pm 0.1
	3	0.3	35.6	35.7	100.3 \pm 0.2
	4	0.4	45.4	45.7	100.5 \pm 0.2
	5	0.5	54.4	54.8	100.7 \pm 0.3
	6	0.6	62.7	62.3	99.5 \pm 0.3
CTX	1	1	34.9	34.4	98.6 \pm 0.1
	2	2	67.9	68.9	101.4 \pm 0.1
	3	3	97.2	96.4	99.2 \pm 0.1
	4	4	123.9	126.2	101.8 \pm 0.5
	5	5	148.4	149.1	100.4 \pm 0.3
	6	6	170.9	170.5	99.7 \pm 0.1

Figures 8 show the differential pulse voltammograms obtained for the carrot juice, cucumber juice and wastewater solution respectively, each containing well-defined quantities of OMP, PCM and CTX per measurement. The voltammograms obtained per medium show good selectivity for the oxidation peaks of OMP, PCM and CTX, with potentials around 0.5V, 0.7V and 1V/ECS respectively. These values are identical to those observed when the detection of the three pharmaceutical products was studied individually in 0.1M HClO₄. The current densities observed on these different voltammograms and the calibration curves plotted during the simultaneous study of these three pharmaceutical substances in 0.1M HClO₄ medium gave rise to recovery rates recorded in **Tables 2**. These rates range from 75.8 \pm 1.4 to 102.3 \pm 0.5 and are comparable to those found by [Kalambate et al., 2016](#) in their study of the

simultaneous detection of paracetamol, cetirizine and phenylephrine in some pharmaceutical, urine and blood serum samples on a modified carbon electrode.

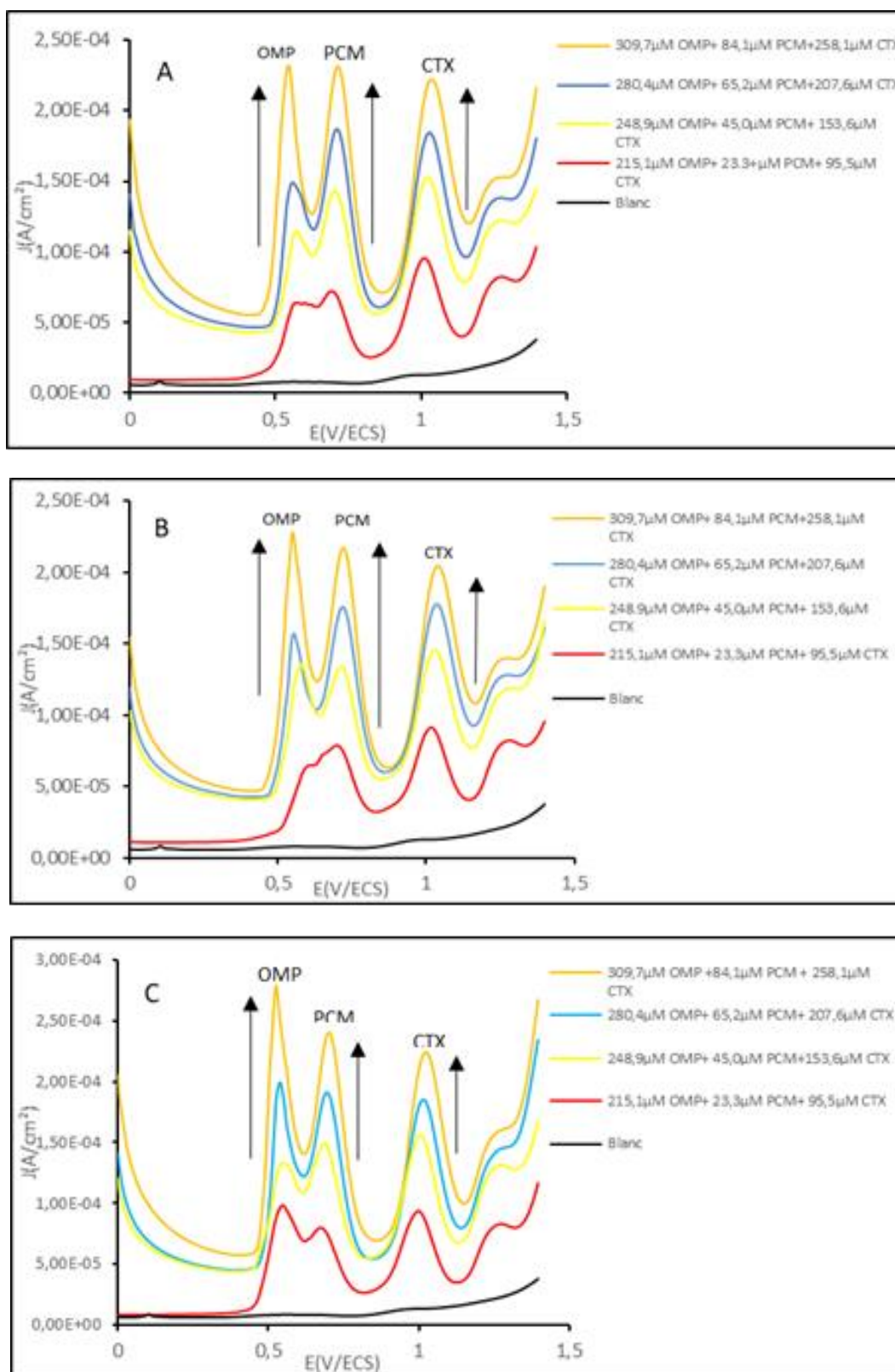


Figure 8: DPV for a mixture of varying concentrations of OMP (0-309.7 μM), PCM (0-84.1 μM) and CTX (0-258.1 μM) in (A) carrot juice, (B) cucumber juice or (C) wastewater $E_{pr}=-2V/ECS$, $t_{Ep}=90s$, $MA=0.1V/ECS$, $tM=0.05s$ and $\Delta E_p=0.007V/ECS$ medium.

Table 2 : Recovery rates for OMP, PCM and CTX in perchloric acid, carrot juice, cucumber juice and wastewater

Electrolyte support	OMP				PCM				CTX			
	Added mL	Added μ M	Found μ M	Recover rate \pm SD	Added mL	Added μ M	Found μ M	Recover rate \pm SD	Added mL	Added μ M	Found μ M	Recover rate \pm SD
Perchloric acid	4	91.7	83.2	90.8 \pm 0.5	0.2	24.9	24.3	97.4 \pm 0.1	2	67.91	68.9	101.4 \pm 0.1
	8	175.0	161.4	92.2 \pm 0.1	0.3	35.7	35.7	100.3 \pm 0.2	3	97.2	96.5	99.2 \pm 0.1
	12	251.1	234.8	93.5 \pm 0.1	0.4	45.4	45.7	100.5 \pm 0.2	4	123.93	126.2	101.8 \pm 0.1
	16	320.7	295.4	92.1 \pm 0.1	0.5	54.4	54.8	100.7 \pm 0.3	5	148.41	152.7	102.9 \pm 0.3
Tomato juice	10	215.1	163.2	75.8 \pm 0.2	0.2	23.3	20.9	89.5 \pm 0.2	3	95.57	93.8	98.2 \pm 0.1
	12	248.9	253.7	101.9 \pm 0.1	0.4	45.0	38.5	85.5 \pm 0.2	5	153.59	153.8	100.2 \pm 0.1
	14	280.4	275.3	98.2 \pm 0.2	0.6	65.2	52.4	80.3 \pm 0.4	7	207.6	194.8	94.3 \pm 0.1
	16	309.7	–	–	0.8	84.1	–	–	9	258.0	–	–
Cucumber juice	10	215.1	177.1	82.3 \pm 0.4	0.2	23.3	20.7	88.9 \pm 0.1	3	95.57	92.0	96.3 \pm 0.2
	12	248.9	248.3	99.9 \pm 0.4	0.4	45.0	40.5	89.9 \pm 0.3	5	153.59	152.0	99.1 \pm 0.1
	14	280.4	287.0	100.3 \pm 0.6	0.6	65.2	52.5	80.5 \pm 0.3	7	207.6	200.2	96.9 \pm 0.2
	16	309.7	–	–	0.8	84.1	–	–	9	258.0	–	–
Wastewater	10	215.1	218.6	101.4 \pm 0.1	0.2	23.3	21.7	92.3 \pm 0.1	3	95.57	94.2	98.7 \pm 0.7
	12	248.9	248.6	99.8 \pm 0.3	0.4	45.0	39.5	87.5 \pm 0.1	5	153.59	154.7	100.7 \pm 0.2
	14	280.4	273.1	97.4 \pm 0.1	0.6	65.2	57.8	88.8 \pm 0.9	7	207.6	202.0	97.6 \pm 0.1
	16	309.7	–	–	0.8	84.1	–	–	9	258.0	–	–

The findings of Nabatian et al. are in good agreements when determining simultaneous quantitative determination of resorcinol and hydroquinone (Nabatian *et al.*, 2022). These results indicate that the method developed in this work is applicable to the simultaneous detection of several pharmaceuticals in both synthetic HClO₄ 0.1M and complex matrix media such as cucumber juice, carrot juice and wastewater.

Conclusion

In this study, results show that BDDE can be used to simultaneously determine OMP, PCM and CTX in pharmaceutical formulations, with very low detection limits and high recovery rates obtained in 0.1 M HClO₄ medium. The method was also used to simultaneously determine the same pharmaceutical substances, this time, in vegetable juice and wastewater media, with recovery rates as high as before. Thus, the combination of DPV and a cathodically pre-treated BDDE constitutes a reliable and beneficial option for simultaneously assessing OMP, PCM and CTX in complex matrices such as fruit and vegetable juices, as well as wastewater, as it is very easy, inexpensive and fast.

References

- Akerman-Sanchez, G., Rojas-Jimenez, K. (2021). Fungi for the bioremediation of pharmaceutical-derived pollutants: A bioengineering approach to water treatment, *Environmental Advances*, 4, 100071. <https://doi.org/10.1016/j.envadv.2021.100071>

- Alaqarbeh M., Al-hadidi L., Hammouti B., Bouachrine M. (2022), Water pollutions: sources and human health impact. A mini-review, *Mor. J. Chem.* 10 N°4, 891-900, <https://doi.org/10.48317/IMIST.PRSM/morjchem-v10i4.34497>
- Bannwarth, B., (2006). Acetaminophen or NSAIDs for the treatment of osteoarthritis. *Best Practice & Research Clinical Rheumatology*, 20, 117-129. DOI: [10.1016/j.berh.2005.09.004](https://doi.org/10.1016/j.berh.2005.09.004)
- Batista, E.F., Sartori, E.R., Medeiros, R.A., RochaFilho, R.C. and Fatibello-Filho, O. (2010). Differential Pulse Voltammetric Determination of Sildenafil Citrate (Viagra®) in Pharmaceutical Formulations Using a Boron-Doped Diamond Electrode. *Analytical Letters*, 43, 1046-1054. DOI:[10.1080/00032710903491153](https://doi.org/10.1080/00032710903491153)
- Benito-Pena, E., Partal-Rodera, A. I., Leon-Gonzalez, M. E., Moreno-Bondi. M. C. (2006). Evaluation of mixed mode solid phase extraction cartridges for the preconcentration of beta-lactam antibiotics in wastewater using liquid chromatography with UV-DAD detection. *Analytica Chimica Acta* 556, 415–422. <https://doi.org/10.1016/j.aca.2005.09.054>
- Bosch, M.E., Sanchez, A.J.R., Rojas, F.S., Ojeda, C.B. (2006). Determination of Paracetamol: Historical Evolution. *Journal of Pharmaceutical and Biomedical Analysis*, 42, 291-321. <https://doi.org/10.1016/j.jpba.2006.04.007>.
- Carlos, F., Zbynek, H., Rene, K., Thippeswamy, R., Agnieszka, B., Nadimul, H. F. (2015). Pharmaceutical Electrochemistry: the Electrochemical Oxidation of Paracetamol and Its Voltammetric Sensing in Biological Samples Based on Screen Printed Graphene Electrodes. *International Journal of Electrochemical Science*, 10, 9, 6872-7892. [https://doi.org/10.1016/S1452-3981\(23\)17361-5](https://doi.org/10.1016/S1452-3981(23)17361-5)
- Chen, X., Zhu, J., Xi, Q., Yang, W. (2012). A high-performance electrochemical sensor for acetaminophen based on single-walled carbon nanotube-graphene nanosheet hybrid films. *Sensors & Actuators B*, vol. 161, pp. 648-654. <https://doi.org/10.1016/j.snb.2011.10.085>
- Einaga Y. (2018) Development of electrochemical applications of boron-doped diamond electrodes, *Bull. Chem. Soc. Jpn*, 91, 1752-1762, <http://dx.doi.org/10.1246/bcsj.20180268>
- El Abdouni A., Bouhout S., Merimi I., et al. (2021), Physicochemical characterization of wastewater from the Al-Hoceima slaughterhouse in Morocco, *Caspian J. Environ. Sci.* 19(3), 423-429
- Errami M., Salghi E., Abidi N., Bazzi L., et al. (2011), Electrooxidation of Bupirimate: A Comparative Study of SnO₂ and Boron Doped Diamond Anodes, *Int. J. Electrochem. Sci.*, 6 N°10, 4927-4938. [https://doi.org/10.1016/S1452-3981\(23\)18378-7](https://doi.org/10.1016/S1452-3981(23)18378-7)
- Errami, M., Salghi, R., Zougagh, M. et al. (2013). Electrochemical degradation of buprofezin insecticide in aqueous solutions by anodic oxidation at boron-doped diamond electrode. *Res Chem Intermed* 39, 505–516, <https://doi.org/10.1007/s11164-012-0574-1>
- Ferre-Aracil, J., Valcárcel, Y., Negreira, N., López A. M., Barceló, D., Cardona, S.C., Navarro-Laboulais, J. (2016) *Science of the Total Environment*, 556, 70–79.
- Joshi R. K., Weber J. E., Hu Q., Johnson B., Zimmer J.W., Kumar A. (2010), Carbon monoxide sensing at room temperature via electron donation in boron doped diamond films, *Sens Actuators, B*, 145 527-532, <https://doi.org/10.1016/j.snb.2009.12.070>
- Koffi, K.M., Ouattara L. (2019) Electroanalytical investigation on paracetamol on boron-doped diamond electrode by Voltammetry. *Am. J. Anal. Chem.*, 10, 562-578. <https://doi.org/10.4236/ajac.2019.1011039>
- Koffi, K. S., Foffié, T. A. A., Kouadio, K. E., Kimou, K. J., Kone, S., Ouattara L. (2021). Cyclic and differential pulse voltammetry investigations of an iodine contrast product using microelectrode of BDD, *Mediterranean Journal of Chemistry*, 11(3), 244-254. <http://dx.doi.org/10.13171/mjc02109301594lassiné>
- Majdi, S., Jabbari, A., Heli, H., Yadegari, H., Moosavi-Movahedi, A. A., Haghgoo, S. (2009). Electrochemical oxidation and determination of ceftriaxone on a glassy carbon and carbon-nanotube-modified glassy carbon electrodes, *J Solid State Electrochem*, 13, 407–416. DOI:[10.1007/s10008-008-0567-6](https://doi.org/10.1007/s10008-008-0567-6)
- Martin, K.K., Placide, S.S., Albert, K.B., Quand-Même, G.C., Appia, F.T.A., Sylvestre, K.K. and Ouattara, L. (2023). Differential Pulse Voltammetric Simultaneous Determination of Paracetamol and

- Omnipaque on Boron Doped Diamond Electrode: Application to Natural Tomato, Carrot, Cucumber Juices and Wastewater. *American Journal of Analytical Chemistry*, 14, 434-450. <https://doi.org/10.4236/ajac.2023.1410025>.
- Minh-Ky N., Chitsan L., Hoang-Lam N., Nguyen T. Q. H., Duong L., Nguyen, X. H., Woong C. S., Chung, W. J., Nguyen, D. D. (2023). Occurrence, fate, and potential risk of pharmaceutical pollutants in agriculture : Challenges and environmentally friendly solutions, *Science of The Total Environment*, Vol 899, P 165323. DOI: [10.1016/j.scitotenv.2023.165323](https://doi.org/10.1016/j.scitotenv.2023.165323)
- Mohiuddin, A. K., Shamsuddin A. M., Seungwon J. (2022) Palladium doped α -MnO₂ nanorods on graphene as an electrochemical sensor for simultaneous determination of dopamine and paracetamol, *Applied Surface Science*, Vol 578. <https://doi.org/10.1016/j.apsusc.2021.152090>
- Nabatian, E., Mousavi, M., Pournamdari, M. et al. Voltammetric approach for pharmaceutical samples analysis; simultaneous quantitative determination of resorcinol and hydroquinone. *BMC Chemistry* 16, 115 (2022). <https://doi.org/10.1186/s13065-022-00905-y>
- Pramod, K., Kalambate, A., Srivastava, K. (2016). Simultaneous voltammetric determination of paracetamol, cetirizine and phenylephrine using a multiwalled carbon nanotube-platinum nanoparticles nanocomposite modified carbon paste electrode, *Sensors and Actuators B*, (2016). <https://doi.org/10.1016/j.snb.2016.04.063>
- Radovan, C. Cofan, C. Cinghita, D. (2008). Simultaneous determination of acetaminophen and ascorbic acid at an unmodified boron-doped diamond electrode by differential pulse voltammetry in buffered media. *Electroanalysis* 20, 1346-1353. DOI: [10.1002/ELAN.200804188](https://doi.org/10.1002/ELAN.200804188)
- Roriz, R., Gevigney, G., Finet, G., Nantois-Collet, C., Borch, K. W., Amiel, M., Beaune, J., Radiol, J. (1999). Comparison of iodixanol (Visipaque) and ioxaglate (Hexabrix) in coronary angiography and ventriculography: a double-blind randomized study. *Journal de Radiologie*, 80, 727-732.
- Salazar-Banda, G.R. andrade, L.S., Nascente, P.A.P., Pizani, P.S., et al. (2006). The Changing Electrochemical Behaviour of Boron-Doped Diamond Surfaces with Time after Cathodic Pre-Treatments, *Electrochimica Acta*, 51, 4612-4619. <https://doi.org/10.1016/j.electacta.2005.12.039>
- Salem B. S., Mezni M., Errami M., Amine K.M., Salghi R., et al. (2015), Degradation of Enrofloxacin Antibiotic under Combined Ionizing Radiation and Biological Removal Technologies, *Int. J. Electrochem. Sci.*, 10(4), 3613-3622, [https://doi.org/10.1016/S1452-3981\(23\)06565-3](https://doi.org/10.1016/S1452-3981(23)06565-3)
- Santos, M., Tarleya, C., Antoniaa, L. D., Sartori. E. (2013). Evaluation of boron-doped diamond electrode for simultaneous voltammetric determination of hydrochlorothiazide and losartan in pharmaceutical formulations, *Sensors and Actuators B*. 188, 263-270. <https://doi.org/10.1016/j.snb.2013.07.025>
- Sartori, E.R., Trench, A.B., Rocha-Filho, R.C., Fatibello-Filho, O. (2013). Determination of Propylthiouracil in Pharmaceuticals by Differential Pulse Voltammetry Using a Cathodically Pretreated Boron-Doped Diamond Electrode, *J. Braz. Chem. Soc.*, 24(9), 1504-1511. <https://doi.org/10.5935/0103-5053.20130190>
- Serge., M. F. (2017). Elaboration de procédés innovants pour l'électroanalyse et la dépollution des eaux contaminées par un résidu médicamenteux (exemple du paracétamol), *Thèse de doctorat*, Université de Dschang, Cameroun.
- Sun, J., Sui, M., Wang, T., Teng, X., Sun, J., Chen, M. (2024). Detection and quantification of various microplastics in human endometrium based on laser direct infrared spectroscopy, *Sci Total Environ*, 906, Article 167760. DOI: [10.1016/j.scitotenv.2023.167760](https://doi.org/10.1016/j.scitotenv.2023.167760)
- Taei, M., Ramazani, G. (2014). Simultaneous determination of norepinephrine, acetaminophen and tyrosine by differential pulse voltammetry using Au-nanoparticles/poly(2-amino-2-hydroxymethyl-propane-1,3-diol) film modified glassy carbon electrode, *colloids and surfaces b-biointerfaces*, 123, 23-32. <https://doi.org/10.1016/j.colsurfb.2014.09.005>
- Triana Y., Ogata G., Einaga Y. (2022), Application of boron doped diamond electrodes to electrochemical gas sensor, *Current Opinion in Electrochemistry*, 36, 101113, ISSN 2451-9103, <https://doi.org/10.1016/j.coelec.2022.101113>

- Waleed, A., Ahmet, C., Irem K. S., Pakorn V., Sibel A. O. (2023). Electrochemical paper-based analytical devices for environmental analysis: Current trends and perspectives, *Trends in Environmental Analytical Chemistry*, **40**, (2023). <https://doi.org/10.1016/j.teac.2023.e00220>
- Whiting, Q.T., O'Connor, K.F., Potter, P.M., Al-Abed, S.R. (2022). A high-throughput, automated technique for microplastics detection, quantification, and characterization in surface waters using laser direct infrared spectroscopy, *Anal Bioanal Chem*, 414(29-30), 8353-8364, <https://doi.org/10.1007/s00216-022-04371-2>
- Vernasqui L.G., A.F. Sardinha, E.J. Corat, N.G. Ferreira, Novel approach to produce 3D boron-doped diamond for pollutant removal from water, *Carbon Trends*, Volume 16, 2024, 100386, ISSN 2667-0569, <https://doi.org/10.1016/j.cartre.2024.100386>
- Xu, Y., Ou, Q., Wang, X., Hou, F., Li, P., Van der Hoek, J.P., Liu, G. (2023). Assessing the Mass Concentration of Microplastics and Nanoplastics in Wastewater Treatment Plants by Pyrolysis Gas Chromatography–Mass Spectrometry, *Environ Sci Technol*, **57** (8), 3114-3123, DOI: [10.1021/acs.est.2c07810](https://doi.org/10.1021/acs.est.2c07810)
- Zhang, J., Fu, D., Feng, H., Li, Y., Zhang, S., Peng, C., Wang, Y., Sun, H., Wang, L. (2024). Mass spectrometry detection of environmental microplastics: advances and challenges, *TrAC Trends Anal Chem*, **170**, (2024), Art 117472, <https://doi.org/10.1016/j.trac.2023.117472>

(2024) ; <http://www.jmaterenvirosci.com>