Determination of Cocaine by Square Wave Voltammetry with Carbon Paste Electrodes

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Abstract. We compare the electrochemical behavior of cocaine hydrochloride (in acidic medium) and its free base form (in acetonitrile) by a simple, cheap, and fast square wave voltammetry method for cocaine analysis based on carbon paste electrodes without chemical modification. The electrodes performed better than the electrodes obtained for analysis on commercial screen-printed electrodes, which we also tested here. We conducted the analyses in aqueous solution containing 0.1 mol·L^{-1} NH$_4$ClO$_4$ as supporting electrolyte. For cocaine in acidic medium, the linear correlation coefficient, the LOD, and the LOQ were 0.996, 4.66×10^{-6} mol·L^{-1}, and 1.55×10^{-5} mol·L^{-1}, respectively. For cocaine in acetonitrile medium, the linear correlation coefficient, the LOD, and the LOQ were 0.994, 9.77×10^{-6} mol·L^{-1}, and 3.26×10^{-5} mol·L^{-1}, respectively. The specificity of the methodology is advantageous when the response of different interfering substances analyzed in this work (lidocaine, procaine, caffeine and phenacetine) is concerned.

Keywords: Forensic chemistry; Cocaine; Voltammetry; Carbon paste electrode.

1. Introduction

Among the several currently available psychotropic substances, cocaine is one of the most often used drugs both in Brazil and worldwide. In Brazil, cocaine users

correspond to 2.9% of the country's population (2005)[1]. In global terms, cocaine users make up 0.4% of the total world population (2015)[2].

The main issues attached to drugs go beyond health: trafficking troubles and organized crime are abundant and family members engage in conflicts, not to mention problems related to addiction livelihood, violence, etc.[3]. To protect the population and to ensure safety, drug control policies exist. In Brazil, the National Anti-Drug Policy (PNAD), decreed in 2002, establishes objectives and guidelines to develop strategies for prevention, treatment, recovery and social reinsertion, health and social damage reduction, trafficking repression and studies, as well as research and evaluation due to improper drug use[4].

Cocaine is a central nervous system stimulant that can be extracted from *Erythroxylum coca* leaves[5], mostly found in South America. This drug is commonly found in two main forms (Figure 1): as a salt (a crystalline powder that is generally inhaled or dissolved and injected) and as an alkaloid (which is volatile at low temperatures and is usually smoked; e.g., crack cocaine)[6]. Despite constant decline in *Erythroxylum coca* cultivation, this illicit drug is still present in the society and causes serious damage[7].
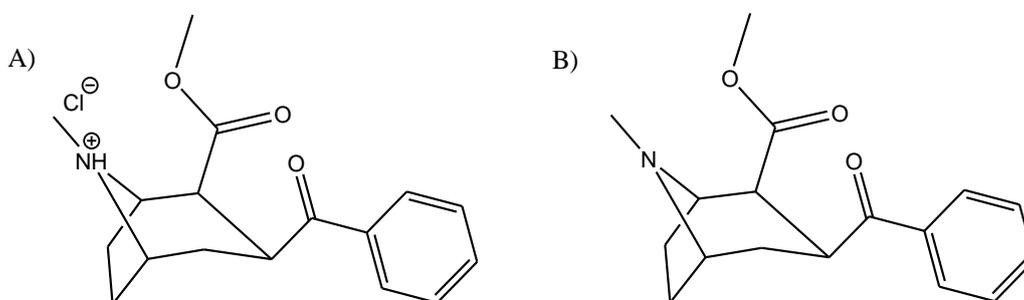
Figure 1. Cocaine (A) salt form and (B) base form.

Given the negative consequences of cocaine (and other drugs), drug control has an essential role in preserving social order. Therefore, Civil and Federal Polices need drug determination methods that are not only reliable (once the analysis result will mean someone's sentence), but also practical, fast, and cheap, allowing a larger number of analyses and meeting the high police demand.

The literature contains descriptions of many methods for analysis of cocaine[8-20] and its metabolites[10,12,14,18,19,21]. The reported methods have advantages and disadvantages. Voltammetry is worth highlighting: it is practical and relatively

reliable; it is not a definitive test like some spectroscopic and spectrometric methods, but it is more reliable than regularly employed colorimetric tests[8]. Besides being cheaper (potentiostats cost less and demand cheaper solvents) and faster than definitive tests, voltammetry is simple, sensitive, specific, and easy to operate, and it can be adopted for qualitative and quantitative purposes, as well as for elucidation of the action mechanisms of drugs[22,23].

Voltammetry is an electroanalytical method during which a potential variation is applied to the system; an electric current is detected as response. In this method, a three-electrode system is required: the working electrode (where the main redox reaction occurs), a reference electrode, and the auxiliary electrode (the current generated by redox reaction flows between the auxiliary electrode and the working electrode)[24]. Finally, a supporting electrolyte, which is a non-reactive salt dissolved in the medium, is necessary because it accounts for the current flow and hence decreases the solution resistance.

In the forensic area, voltammetry is widely used to analyze seized drugs, biological matrixes, contaminated water, explosives, gunshot residues (GSR), and toxins[25–30]. Chemically modified electrodes are often employed, as well. Chemical modification is achieved by depositing a modifier on the working electrode surface. The modifier interacts with the target analyte, to increase the current and thus improve sensitivity. Schiff bases are examples of electrode modifiers[17,31,32].

Cheaper solvents and reagents, faster methods, and portable systems (for *in loco* analyses) are some of the advantages of voltammetric methods. The need for modifiers, extreme pH, and toxic reagents and solvents may constitute disadvantages of these methods. All the advantages and disadvantages should be considered when choosing the best method for a certain analysis.

We propose a simple and cheap methodology to quantify cocaine in acidic solution and in organic solution by using carbon paste electrode.

2. Experimental

2.1. Apparatus and chemicals

All chemical reagents were of analytical grade, and all aqueous solutions were prepared with deionized water. Aqueous 0.1 mol·L⁻¹ KCl (Cinética Reagentes & Soluções), KNO_3 (ECIBRA), $KClO_4$ (Vetec), $NaClO_4$ (Riedel-de Haen), $LiClO_4$ (Dinâmica), or NH_4ClO_4 (MATHERSON, COLEMAN & BELL) was used as supporting

electrolyte in 0.05 mol·L^{-1} K_2HPO_4 (J. T. Baker) buffer solution. Acetonitrile (J. T. Baker) and HCl (F. Maia) were employed as solvents of cocaine solutions.

An AutolabIII potensiostat (Metrohm) controlled by a microcomputer was used for square wave voltammetry measurements in a 5.0-mL conventional electrochemical cell comprising a Ag/AgCl (saturated aqueous KCl) reference electrode and carbon paste working and auxiliary electrodes.

To manufacture the carbon paste electrodes (Figure 2), graphite powder (Synth) and commercial paraffin were employed. The working electrode and the counter electrode had different proportions of the components graphite and paraffin (50:50 and 60:40, respectively).

Figure 2. Carbon paste electrode after done.

After each voltammetric analysis, the working and the auxiliary electrodes were polished with paper. To perform the analyses, a potential range from 0 to 1.5 V was applied; the amplitude and the frequency were 0.025 V and 25 Hz (no pre-concentration), respectively, for cocaine in acetonitrile. For cocaine in acidic medium, a potential range from 0 to 1.5 V was applied; the amplitude and the frequency were 0.6 V and 30 Hz, respectively. Pre-concentration was accomplished at 0.8 V for 10 s.

The cocaine standard and the cocaine samples were obtained from a scientific partnership between this research group and the laboratory of toxicological analysis – Institute of Criminalistics – city of Ribeirão Preto – state of São Paulo, Brazil.

Analysis of interfering substances involved addition of standard caffeine, lidocaine, procaine and phenacetine solutions – all the standards, in the powder form, were purchased from Sigma–Aldrich. These interferents were dissolved in the same solvents as cocaine.

2.2. Samples and solutions

A 2.5 10^{-3} mol·L^{-1} cocaine hydrochloride solution in acidic medium was prepared by addition of HCl, until pH 3. A 2.5 10^{-3} mol·L^{-1} cocaine free base solution in acetonitrile was also prepared. Cocaine standard, 96% purity, was employed in both cases. The linear dependence of cocaine detection was carried out in concentrations from 9.96 10^{-6} mol·L^{-1} to 7.43 10^{-5} mol·L^{-1}.

Cocaine solutions of confiscated samples were prepared by pre-treating small aliquots of the water-soluble cocaine chlorhydrate samples with aqueous sodium bicarbonate solution to remove HCl from its chlorhydrate form. Then, chlorhydrate-free cocaine – which is insoluble in water – was removed by filtration, rinsed with deionized water, dried, and dissolved in acetonitrile.

For both samples of cocaine (in acid medium and in acetonitrile), a 0.1 mol·L^{-1} NH_4ClO_4 aqueous solution was utilized as supporting electrolyte with a 0.05 mol·L^{-1} K_2HPO_4 buffer solution to carry out the analysis. The difference between the analysis of cocaine in acid medium and in acetonitrile was the pH of 11 and 6, respectively.

2.3. Manufacture of carbon paste electrodes

The carbon paste electrode was constructed with a disposable syringe containing a copper piston (as electrical contact). The syringe tip was cut and sanded, to provide a smooth and circular surface. Then, the carbon paste was inserted into the syringe and compacted by pressing the piston against a planar surface.

To prepare the carbon paste, the desired graphite and paraffin ratio was weighed and mixed in a porcelain mortar with a pestle. The mortar was heated at 50 ºC for 20 min on a hot plate, under agitation, until the mixture melted and became homogeneous.

2.4. Calculation of analytical parameters

The analytical curve provided the analytical parameters that allowed us to evaluate method sensitivity and limits. We obtained the LOD (limit of detection) and LOQ (limit of quantification) values by using 3*SD/m and 10*SD/m, respectively, where SD is the standard deviation, and m is the curve amperometric sensitivity[33].

From the analytical curve equation, we have the sensibility as the angular coefficient and the standard deviation (SD) as the linear coefficient.

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3. Results and discussion

According to the literature, cocaine is an electroactive substance with oxidation peak around 1.0 V (depending on the electrode). This peak is associated with oxidation of the tertiary amine present in its structure[34,35].

3.1. Cocaine in acidic medium

We recorded the response of the cocaine solution in acidic medium during square wave voltammetry in different electrolytes, at pH 11. We tested perchlorate salts such as lithium, potassium, and ammonium perchlorates as well as potassium chlorate and potassium nitrate as supporting electrolytes. Ammonium perchlorate afforded the most intense peak, followed by potassium and sodium perchlorates, which gave similar results, and then lithium perchlorate, potassium chlorate, and potassium nitrate. We therefore selected ammonium perchlorate as supporting electrolyte for the subsequent analyses.

3.1.1. Kinetic study

The cyclic voltammogram revealed an anodic peak at 1.15 V (Figure 3). The relationship between the scan rate and the current values provides information about the kinetics of the underlying electrochemical reaction. The linear relation between the current peak and the square root of the scan rate indicated that diffusion controlled the oxidative processes in this work.
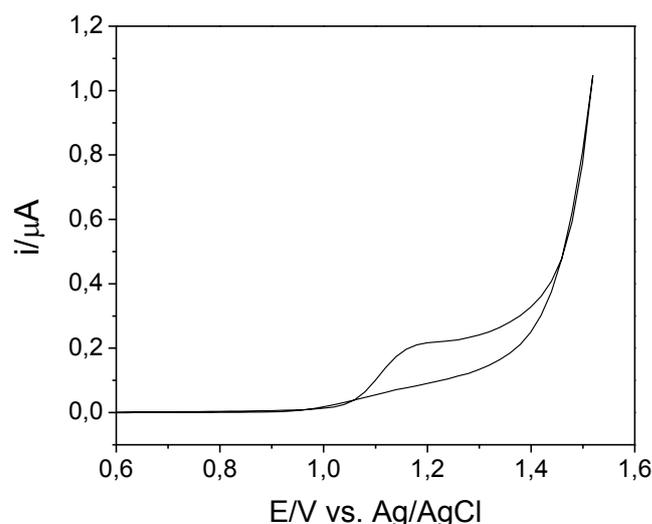

Figure 3. Cyclic voltammogram for 29.6 µmol·L^{-1} cocaine (acidic medium) in the electrochemical cell (v = 50 mV s^{-1}).

3.1.2. Analytical curve construction

Square Wave Voltammetry is a more sensitive technique than Cyclic Voltammetry. We observed the same oxidation peak around 1.08 V as a direct response for the presence of cocaine. Thus, we chose the Square Wave Voltammetry technique to quantify the analyte.

We constructed the analytical curve (Figure 4A) by successively adding cocaine in acidic medium to the electrochemical cell. The anodic peak emerged at approximately 1.08 V. Figure 2 illustrates the voltammetric response for successive additions of the drug to the electrochemical cell. The linear fit of the calibration curve gave Equation 1, with R = 0.996 and standard deviation (SD) of $1.33 \cdot 10^{-8}$ A.

$$Ia = 8.68 \cdot 10^{-2} \text{ A L mol}^{-1} \text{ [Cocaine]} + 1.33 \cdot 10^{-8} \tag{1}$$
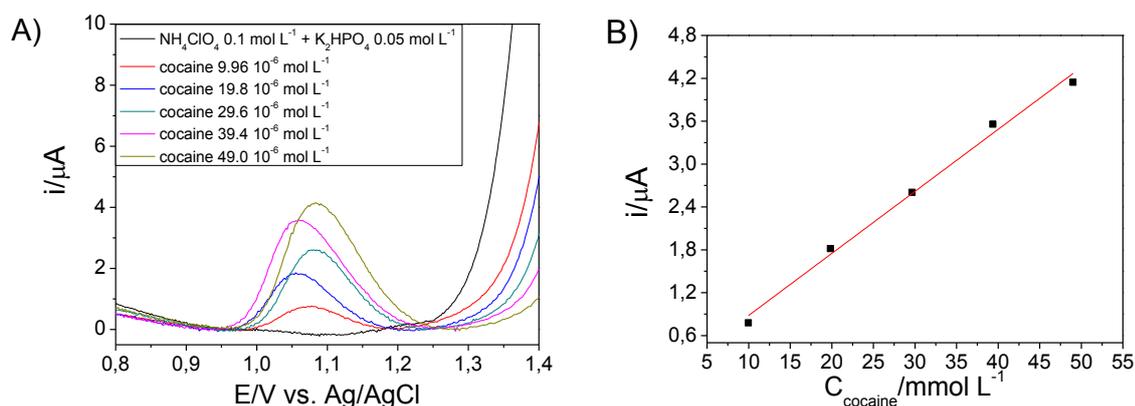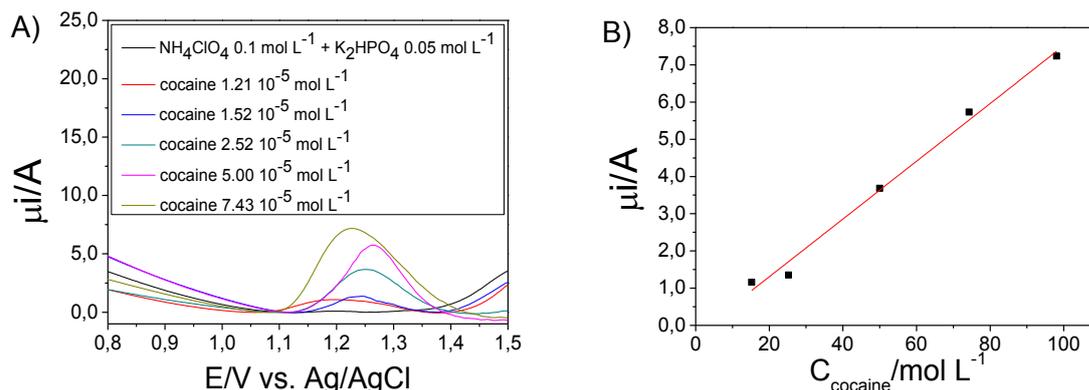

Figure 4. (A) Square wave voltammograms for successive additions of cocaine (acid medium) to the electrochemical cell (frequency = 30 Hz, amplitude = 0.06 V); (B) Analytical curve that establishes the linear relation between the current and the cocaine concentration (in acidic medium).

3.2. Cocaine in acetonitrile

3.2.1. Analytical curve construction

Once the kinetic study provided the same results for cocaine in acidic medium, we constructed the analytical curve (Figure 5B) to quantify cocaine in acetonitrile. The linear fit of the calibration curve gave Equation 2 with R = 0.994 and SD of $2.53 \cdot 10^{-7}$ A (Table 1).

$$Ia = 7.76 \cdot 10^{-2} \text{ A L mol}^{-1} \text{ [Cocaine]} + 2.53 \cdot 10^{-7} \tag{2}$$

Figure 5. (A) Square wave voltammograms for successive additions of cocaine (in acetonitrile) to the electrochemical cell (frequency = 25 Hz and amplitude = 0.025 V) and (B) analytical curve for cocaine establishing the linear relation between the current and the cocaine concentration (in acetonitrile).

Table 1. Linearity parameters for square wave voltammetry analysis in acidic medium and acetonitrile.

Parameter	Acidic Medium	Acetonitrile
LOD (mol·L^{-1})	$4.66 \cdot 10^{-6}$	$9.77 \cdot 10^{-6}$
LOQ (mol·L^{-1})	$1.55 \cdot 10^{-5}$	$3.26 \cdot 10^{-5}$
Linear range (mol·L^{-1})	$9.96 \cdot 10^{-6}$ to $4.90 \cdot 10^{-5}$	$3.26 \cdot 10^{-5}$ to $9.81 \cdot 10^{-5}$
Linearity (R)	0.9955	0.9943
Sensitivity (A·L·mol^{-1})	$8.68 \cdot 10^{-2}$	$7.76 \cdot 10^{-2}$
Reproducibility (Intraday precision)	2.51%	2.33%
Repeatability (Interday precision)	3.82%	4.90%

In organic medium, the signal observed for cocaine shifted approximately 0.1 V toward higher potential as compared to cocaine in acidic medium; the peak current remained unaltered. As previously reported in the literature[33], the mechanism of cocaine oxidation on carbon paste surfaces and in aqueous medium with pH ≥ 6 involves oxidation of the cocaine tertiary amine group. For the cocaine standard in acidic medium, the tertiary amine group is protonated (higher energy barrier required for oxidation)[36], but when the cocaine standard is added to the basic electrolyte medium, the acid form of cocaine is neutralized, facilitating tertiary amine oxidation. Thus, for the cocaine standard in organic medium, the energy barrier required for tertiary amine oxidation increases, and the oxidation potential is displaced toward a higher value, as observed in this work.

3.3. Study of interfering substances

We tested the following possible interferers: lidocaine, procaine, caffeine, theobromine, and phenacetine, both in acetonitrile and in acidic medium. Analysis of the voltammograms (Figure 6) revealed that the peaks due to the interfering did not arise at the potentials of interest, 1.20 V for cocaine in acetonitrile and 1.08 V for cocaine in acidic medium, so these compounds should not affect cocaine detection by the proposed method.
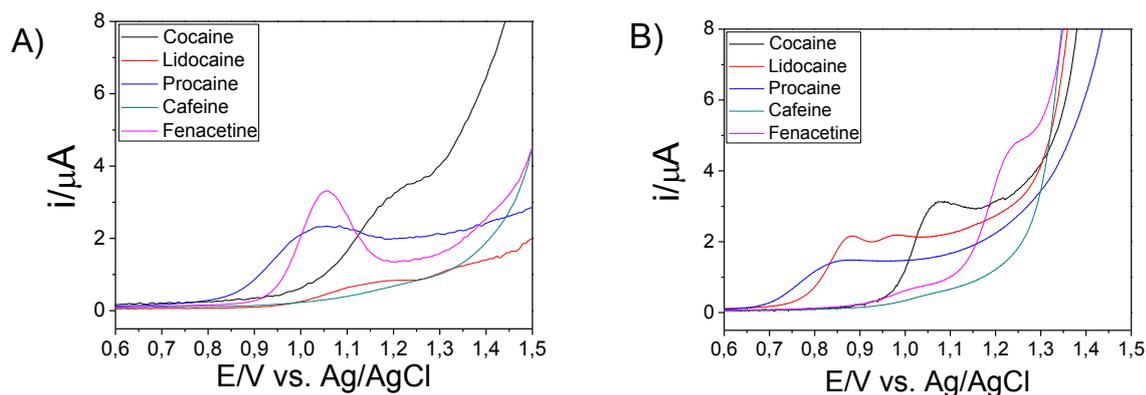
Figure 6. Square wave voltammograms of interfering substances (A) dissolved in acetonitrile ($4.90 \cdot 10^{-5}$ mol$\cdot$L^{-1}) and (B) dissolved in acidic medium ($9.96 \cdot 10^{-6}$ mol$\cdot$L^{-1}), both in the same conditions used for cocaine analysis.

We then conducted a similar study to verify possible interactions between cocaine and these interfering substances when they were all in the same solution. We detected cocaine with unaltered voltammetric profile in all tests, so we discarded interference of these substances. This test proved that the proposed method, between the tested interfering, was specific for cocaine determination in acetonitrile medium or acidic medium.

3.4. Analytical parameters

The LOD values were 1.58 mg$\cdot$L^{-1} in acidic medium and 2.96 mg$\cdot$L^{-1} in acetonitrile. If we consider about 0.1 g of a seized sample in one milliliter of solution, the calculated values were equivalent to detection in the order of 0.003%, which was less than the purity in the samples and enable cocaine detection in them.

The values obtained here pointed to the good sensibility of the technique: they resembled the values obtained by HPLC-DAD (High Performance Liquid Chromatography with Diode Array Detector), which is a very used methods for drug

detection and quantification, with a LOD and LOQ of 3.96 10^{-6} mol·L^{-1} and 1.65 10^{-5} mol·L^{-1}, respectively[10]. By a GC-NPD (Gas Chromatography with Nitrogen Phosphorous Detector) analysis, it was obtained a LOD of 3.30 10^{-7} mol·L^{-1} and a LOQ of 1.65 10^{-6} mol·L^{-1} [36]; this values are better than ours, but not so far. Although our values are not the best, here we have a simpler and cheaper method.

Comparison of the analytical parameters with literature parameters (Table 2) demonstrated that our limits of detection were comparable to literature values in most cases and were in the same order of µmol·L^{-1} [25,26,36]. Although a few reports describe higher limits of detection, the method proposed herein was based on a cheap and easy to prepare working electrode without modification that offered low cost, highly reproducible and sensitive cocaine determination for analysis of seized samples.

Table 2. Comparison of different electrochemical sensing methodologies for cocaine determination. N.R.: Not Reported; BIA: Batch Injection Analysis; BDD: Boron-Doped Diamond; SWV: Square-Wave Voltammetry; SPCEs: Screen-Printed Carbon Electrodes; GCE: Glassy Carbon Electrode; CV: Cyclic Voltammetry; LSV: Linear Sweep Voltammetry; CPE: Carbon Paste Electrode.

Method	Working electrode	Supporting electrolyte	Linear Range (mol·L^{-1})	LOD (mol·L^{-1})	Ref.
LSV	CPE	Britton-Robinson buffers (pH 9)	$1.0\ 10^{-6}$ – $1.0\ 10^{-4}$	N. R.	11
CV	Modified CPE – [UO$_2$(X-MeOSalen)(H$_2$O)]·H$_2$O	KCl	$1.0\ 10^{-7}$ – $1.3\ 10^{-6}$	0. 326 10^{-6}	37
SWV	Modified SPCE – MWCNTs	Phosphate buffer and KCl	$1.0\ 10^{-5}$ – $1.5\ 10^{-4}$	N. R.	38
SWV	SPCE	KCl and KH$_2$PO$_4$ buffer (pH 7).	N. R.	$2.0\ 10^{-6}$	39
LSV	Modified GCE – PANI-β-CD/fMWCNT/	Phosphate buffer (pH 6)	$1.0\ 10^{-5}$ – $8.0\ 10^{-5}$	$1.02\ 10^{-6}$	40
CV	Modified SPCE – [UO$_2$(4-MeOSalen)(-H$_2$O)]·H$_2$O	KCl (water), and LiCl (methanol)	$2.5\ 10^{-4}$ – $3.7\ 10^{-3}$	$1.1\ 10^{-4}$	41
BIA-SWV	BDD	H$_2$SO$_4$	$2.0\ 10^{-5}$ – $9.9\ 10^{-5}$	$0.89\ 10^{-6}$	42

The economic advantage over literature methods in terms of the cost of the materials graphite powder and paraffin makes the method easily accessible.

3.5. Analysis of seized samples

The analysis of seized samples (Figure 7) has confirmed the presence of cocaine, what was confirmed with a GC-MS. By the presented method, the potential of cocaine oxidation shifted by 0.1 V, to 1.3 V, probably due to the presence of multiple interfering that were not tested in the interfering study section, but which are very common in such samples.
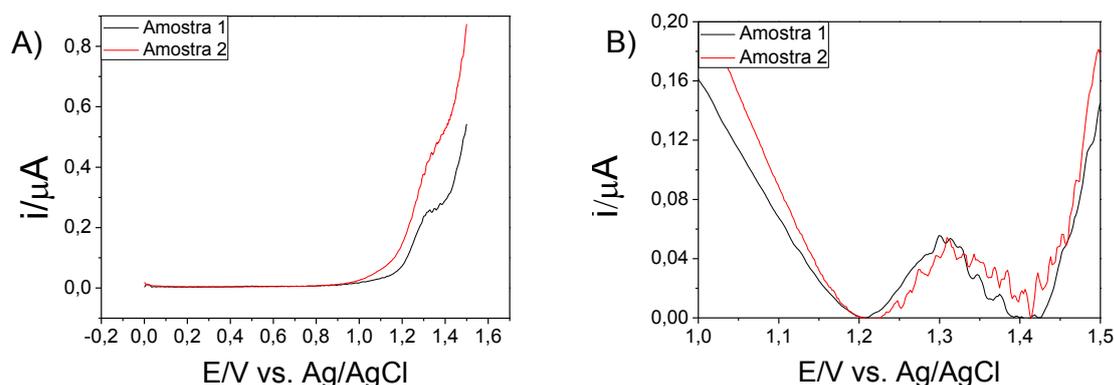
Figure 7. Square wave voltammograms of two seized samples of crack (A) dissolved in acetonitrile and (B) dissolved in acidic medium, in the developed method conditions.

Although the detection has been successful, the quantification was not possible, perhaps due the presence of multiple interfering. The values of quantification, calculated through the analytical curve, were inaccurate, but always lower than the real.

3.6. Analysis with screen-printed electrodes (SPE)

SPE have been widely explored in electrochemical methodologies due to characteristics like portability and simplicity. However, some changes in the electrochemical behavior of the target analyte might be expected as compared to conventional cells. We performed the cocaine analysis with this kind of electrode and obtained an analytical curve with poor linearity when cocaine was dissolved in acetonitrile. SPE just provided a qualitative test for cocaine detection.

For cocaine analysis in acidic medium, we obtained a linear analytical curve with SPE. However, the conventional system based on carbon paste electrode afforded better linearity and limit of detection.

4. Conclusion

The present methodology constitutes a low-cost system to detect and to quantify cocaine as in its two chemical forms: salt and base. In both acetonitrile and acidic medium, sample preparation proved to be a simple process. By using the square wave voltammetry technique, a specific result was available in less than three minutes.

When it comes to real samples, the detection is also possible, even with the presence of multiple interfering, confirming the effectiveness of the method; although the quantification becomes inaccurate. This effectiveness is seen as the peak at the characteristic potential.

Comparing between the solvents employed in this study and given the amperometric intensity of the voltammetric peak, we achieved better results for cocaine in acidic medium. Nevertheless, both methods are important, because the two forms of cocaine are widely seized by the police. Therefore, we can analyze both forms of cocaine by just preparing the sample solutions correctly and changing the voltammetric parameters at the postentiostat.

Acknowledgements

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