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# Polymer platforms for selective detection of cocaine in street samples adulterated with levamisole

Anca Florea[a], Todd Cowen[b], Sergey Piletsky[b], Karolien De Wael[a*]

[a] *University of Antwerp, Department of Chemistry, Groenenborgerlaan 171, B-2020, Belgium*

[b] *University of Leicester, Department of Chemistry, LE1 7RH, UK*

[*] *Corresponding author, E-mail address: karolien.dewael@uantwerpen.be*

## Abstract

Accurate drug detection is of utmost importance for fighting against drug abuse. With a high number of cutting agents and adulterants being added to cut or mask drugs in street powders the number of false results is increasing. We demonstrate for the first time the usefulness of employing polymers readily synthesized by electrodeposition to selectively detect cocaine in the presence of the commonly used adulterant levamisole. The polymers were selected by computational modelling to exhibit high binding affinity towards cocaine and deposited directly on the surface of graphene-modified electrodes via electropolymerization. The resulting platforms allowed a distinct electrochemical signal for cocaine, which is otherwise suppressed by levamisole. Square wave voltammetry was used to quantify cocaine alone and in the presence of levamisole. The usefulness of the platforms was demonstrated in the screening of real street samples.

Graphical abstract
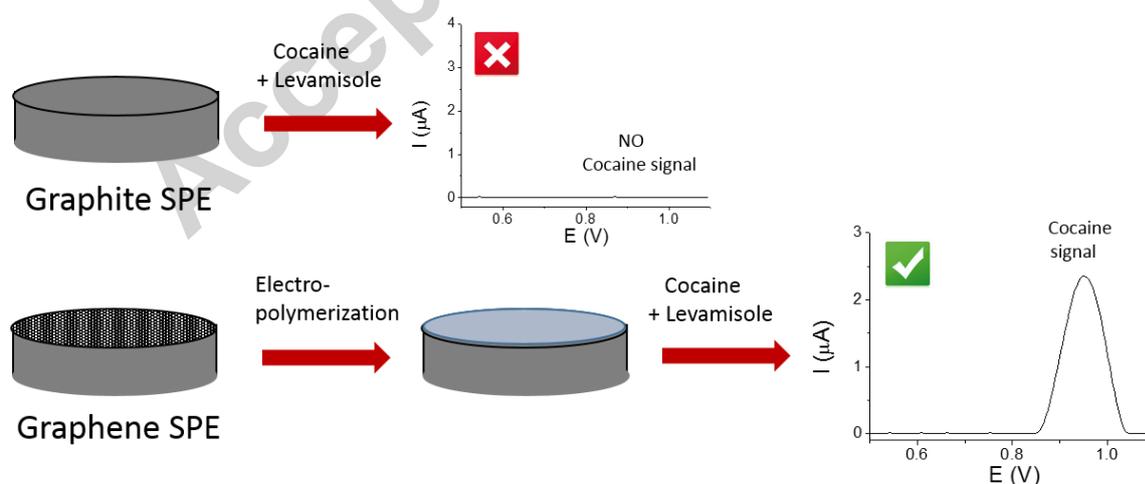
## 1. Introduction

The marked escalation of global production, trafficking and abuse of illicit drugs in the recent decades has negatively impacted human and environmental health, societies and national economies. The latest World Drug Report elaborated by UNODC estimated that a quarter billion people aged 16-54 used drugs at least once in 2015, with 28 million years of "healthy" life lost worldwide due to premature death and drug use disabilities [1], while the National Drug Intelligence center estimated an economical burden of US$ 193 billion in 2007 due to drug related healthcare costs and crimes [2]. In this light, there is a demand for accurate and efficient tools to detect illicit drugs at the borders, roadside, hospitals or workplaces. Currently used screening methods for on-site detection of illicit drugs include immunoassays [3, 4] or complexation reactions (e.g. Scott test for cocaine) [5]. These screening methods usually require confirmation by expensive chromatography-mass spectrometry methods, and sometimes exhibit poor selectivity leading to false negative and false positive results in the presence of cutting- and masking- agents that are commonly added to adulterate street powders [6].

Through their high sensitivity, rapidity and ease of use electrochemical sensors emerge as a good alternative for on-the-spot applications providing unique fingerprints of the analytes [7]. Several electrochemical strategies have been reported in the literature for the detection of cocaine, which is the second most widely abused drug after cannabis. Modifications of the electrodes are often required to tailor selectivity and reach low detection limits. For example, Abnous et al [8], modified gold electrodes with complementary strands of aptamers to form a conjugate with an aptamer specific for cocaine. Based on the signal of a redox probe good selectivity and low detection limits of 0.228 nM have been achieved. Aptamers have been employed as selective receptors also by Roushani et al [9] in a simple nanoaptasensor for cocaine based on coupling gold nanoparticles modified electrodes with gold nanoparticles functionalized aptamers reaching detection limits as low as 0.5 pM. Although aptamers provide high selectivity, they sometimes suffer from a lack of long-term stability, as well as long analysis time involving many incubation and washing steps. Functionalization with conducting polymers has gained enormous interest lately, through the simplicity of modification and integration with the electrode, low cost and good long-term stability [10-12]. Conductive polymers (CPs) are semiconductors, so to overcome the drawback of low conductivity for electrochemistry applications, composites materials of CPs have been intensively investigated [13]. Carbon-based materials, e.g. graphene, carbon nanotubes, carbon dots and porous carbon, and metal nanoparticles are promising materials to improve the performance of CPs and develop novel sensors [14-17]. Only a few sensing strategies for cocaine based on polymer platforms are reported in the literature and are mostly coupled with optical detection systems [18, 19]. An electrochemical sensor for cocaine based on polymer nanoparticles imprinted with cocaine has been reported by Piletsky's group [20]. The imprinted polymer nanoparticles were produced by solid-phase synthesis and incorporated into an ion-selective membrane integrated with a potentiometric transducer. The sensor was able to detect concentrations of cocaine in the range of 1nM to 1mM. Another electrochemical

sensor was developed by Hashemi et al [21], in which a polymer composite material, namely polyaniline/graphene oxide/gold nanoparticles, was used to anchor aptamers specific for cocaine.

Here, we present the assessment of polymer platforms for selective enrichment of cocaine samples and direct electrochemical detection of cocaine. Levamisole, a common adulterant present in street samples was found to suppress the oxidation signal of cocaine on unmodified electrodes in direct electrochemical detection, leading to false negative results. We improved the selectivity towards cocaine detection in the presence of levamisole by modifications of the electrodes with affinity polymers. Monomers with high binding affinity for cocaine were selected by molecular modelling. Based on the binding scores, polymers made of *o*-phenylenediamine (OPD) and *p*-aminobenzoic acid (PABA) were investigated as selective binders in electrochemical sensing of cocaine. Both OPD and PABA were successfully integrated in electrochemical sensors where they demonstrated good performances [22-25]. Graphene-modified screen printed electrodes were functionalized by electrodeposition of poly(OPD) and poly(PABA) via cyclic voltammetry. Graphene improves the conductivity of the polymer layers and thus the sensitivity of detection, offering at the same time a higher surface area with more binding sites for the analyte [26]. We demonstrate the ability of a graphene electrode modification with polymers to improve the selectivity of cocaine detection in seized street samples adulterated with levamisole, and thus significantly reduce false negative results.

## 2. Materials and methods

### 2.1. Reagents and samples

Cocaine hydrochloride was purchased from Lipomed (Arlesheim, Switzerland). Levamisole hydrochloride was purchased from Acros Organics (Geel, Belgium). *p*-Aminobenzoic acid (PABA), *o*-phenylenediamine (OPD), acetic acid, sodium acetate, potassium monophosphate, potassium chloride, potassium hydroxide were purchased from Sigma-Aldrich (Overijse, Belgium). Three cocaine street samples were provided by NICC, Belgium, with the following composition determined by gas chromatography coupled with mass spectrometry: sample 1, 70% cocaine and 23% levamisole; sample 2, 55% cocaine and 42% levamisole; sample 3, 57% cocaine and 41% levamisole. The following buffers were used: a solution of 20 mM phosphate buffer containing 100 mM KCl (PBS) of pH 7 and a solution of 100 mM acetate buffer containing 100 mM KCl of pH 5.2. Stock solutions of levamisole and cocaine of 10 mM in PBS were prepared and stored in fridge. PABA and OPD solutions were prepared freshly every day, in PBS pH 7 and acetate buffer pH 5.3, respectively. 1 mg street sample powder was dissolved in 1mL PBS pH 7. The solution was then diluted 1:10 with PBS buffer and used for electrochemical measurements. All reagents were of analytical grade. All aqueous solutions were prepared using MilliQ water (R > 18 MΩcm).

### 2.2. Instrumentation

The computational modelling was conducted as described previously by Piletsky's group [20]. A virtual library of electropolymerizable monomers was screened for their interaction with the template using LEAPFROG™ algorithm (SYBYL® 7.3 software package, Tripos International, USA). Energy minimization was conducted to a minimum of 0.001 kcal mol$^{-1}$. The parameters of molecular mechanics were: method - Powell, force field - Tripos and

charges - Gasteiger-Huckel. The monomers were ranked by a relative binding energy and the most stable arrangement of each monomer-target complex was obtained.

Cyclic voltammetry (CV), square wave voltammetry (SWV) and linear sweep voltammetry (LSV), were carried out using an Autolab potentiostat/galvanostat (PGSTAT 302N, ECOCHEMIE, The Netherlands) controlled by NOVA software. Graphite screen-printed electrodes modified with graphene (GPH-SPE) consisting of a working electrode (3 mm diameter), a carbon counter electrode and a (pseudo)silver reference electrode were purchased from DropSens (Spain). The following parameters were used for voltammetry measurements: CV for electropolymerization of PABA, potential -0.5 to 1.0V, scan rate 50 mV/s, 10 cycles, in PBS pH 7; CV for electropolymerization of OPD, potential -0.3 to 0.8V, scan rate 50 mV/s, 5 cycles, in acetate buffer pH 5.2; LSV, potential range 0-1.2V, step potential 2 mV, scan rate 5-200 mV/s; SWV, step potential 5 mV, amplitude 25 mV, frequency 10 Hz, in PBS pH 7. For the electropolymerization a drop of 100 μL monomer solution was placed on the electrodes and the CV measurements were run. For the detection a drop of 100 μL analyte solution was placed on the electrodes and left for preconcentration for various timeframes (minutes). Afterwards, the drop was removed and 100 μL double distilled water was placed onto the electrode and left for 10 seconds to wash weakly adsorbed analytes. Then, 100 μL PBS pH 7 was placed onto the electrode and SWV was run. All results obtained by SWV were presented after baseline correction using the mathematical algorithm "moving average" (peak width = 1) contained within NOVA software, to improve the visualization and identification of the peaks over the baseline. All electrochemical experiments were performed at room temperature.

The samples were examined with a Field Emission Gun – Environmental Scanning Electron Microscope (FEG-ESEM) equipped with an Energy Dispersive X-Ray (EDX) detector (FEI Quanta 250, USA; University of Antwerp), using an accelerating voltage of 20kV, a take-off angle of 30°, a working distance of 10 mm and a sample chamber pressure of 10-4 Pa. Imaging was performed based upon secondary electrons, back-scattered electrons.

## 3. Results

### 3.1. Modelling

The library of electroactive monomers bearing amine, carboxyl and hydroxyl functional groups that would yield interaction points with the functional groups on cocaine was ranked depending on the binding energies and the monomers which gave the lowest binding energies with the template were selected, namely *o*-phenylenediamine and *p*-aminobenzoic acid, with binding energies of -190.04 kJ mol$^{-1}$ and -102.38 kJ mol$^{-1}$, respectively.

### 3.2. Electrodeposition of polymers

Polymers were electrodeposited on GPH-SPE under potentiodynamic conditions. Graphene was used to increase the conductivity of the polymer layers (Figure S1 in Supplementary material). Besides high conductivity, which aids both the electropolymerization and the detection process, graphene offers a high surface area leading to more binding sites for the analyte. For the electrodeposition of PABA the potential was swept between -0.5 and 1.0V, for 10 cycles, with a scan rate of 50 mV/s, in a solution of PBS pH 7 containing 2.5 mM PABA. The electrochemical polymerization of OPD was performed in a solution of acetate

buffer pH 5.2 containing 1 mM OPD. The potential range was set between -0.3V and 0.8V at a scan rate of 50 mV/s and the scanning was carried out for five cycles. After the polymerization, the electrodes were rinsed thoroughly with water to remove any unreacted monomer and dried. A blank in PBS pH 7 was recorded each time before employing the modified electrodes for cocaine detection.

Figure 1 shows the cyclic voltammograms for the electropolymerization of PABA and OPD on GPH-SPE. In the first cycle of electropolymerization distinct and irreversible peaks appear in both cases, related to the oxidation of the monomer. Starting with the second electropolymerization cycle a pair of anodic and cathodic peaks arise at more cathodic potentials that increase gradually after each polymerization cycle showing the growth of the polymeric film. The results are in accordance with other literature reports [27-30].

OPD shows a first current peak at 0.26V preceded by a shoulder at 0.18V and a second oxidation peak at 0.45V. The first oxidation peak is ascribed to the oxidation of OPD monomer to its dimer state, while the second one is due to dimer oxidation to a semi-oxidized state followed by total-oxidized state [31]. Camurri et al [27] attributes the presence of a shoulder preceding the first oxidation peak (in neutral KCl solution) to the adsorption of OPD on the electrode before undergoing electrochemical oxidation, due to the fact that the peak disappeared after the first cycle. However, herein the shoulder is present in the following cycles as well and exhibits a stable low signal after the second cycle. The two oxidation peaks of the monomer decreased with each polymerization cycle and slightly shifted to more positive potentials, the growth rate being higher in the first 2 cycles and then slowing down. This shows the formation of a polymer with relatively poor conductivity, as it was also previously reported by other authors [31-33].

PABA presents a peak at 0.73V preceded by a shoulder at 0.63V, ascribed to the oxidation of the monomer. Exhibiting a rather low conductivity, most probable the formed films contain more oligomers rather than long-chain polymeric material, as the conductivity decreases with the decrease in the polymer chain length [34].

The pair of peaks related to the oxidation of the monomer appear in the second electropolymerization cycle at 0.105V and 0.07V in the case of poly(PABA) and 0.02V and -0.02V for poly(OPD), and slightly shift positively (oxidation peaks) and negatively (reduction peaks) due to the formation of layers with low conductivity.

SEM images were taken to obtain information of the surface morphology of the polymer modified electrode show the presence of several aggregates distributed on the GPH-SPE surface, that are attributed to the formation of polymers with a roughened surface (Figure 2).

### 3.3. Optimization of experimental conditions

Since the oxidation signal of cocaine on unmodified graphite electrodes is suppressed in the presence of levamisole (Figure S2 in Supplementary material), the response of the polymer modified electrodes towards cocaine detection has been evaluated and optimized in solutions containing cocaine alone and also in binary cocaine-levamisole mixtures containing 50% levamisole. The conditions in which the signal of cocaine in the binary mixture was higher were selected as optimal. According to data from NICC, Belgium and the Belgian National Report on Drugs levamisole is the most common adulterant in cocaine powders. Levamisole

is present in 48% of samples, in average concentrations of ~ 10% [35]. However seized street samples provided to us by NICC, Belgium contained concentrations of levamisole of 23% up to 42%. Therefore, to ensure a good accuracy of the method the upper limit of 50% levamisole has been set and tested.

### 3.3.1. Monomer concentration

The concentration of the monomer used during electropolymerization has an influence on the growth rate and thickness of the resulting polymer and thus on the analytical response of the electrode. To study the influence of the monomer concentration on the response towards cocaine detection, seven CV scans were performed in PBS pH 7 solutions containing PABA concentrations varying from 1 mM to 7.5 mM. In the case of OPD, five cycles were performed using acetate buffer pH 5.2 as supporting electrolyte and the concentration was not increased further than 5 mM, since the oxidation signals of cocaine obtained at this concentration were already extremely low. SWV were then recorded on the polymer modified electrodes in PBS pH 7 after the accumulation of 0.5 mM cocaine solution in PBS pH 7 for 5 min. The results are presented in Figure 3. The current intensities correspond to cocaine that remains physically adsorbed on the surface of the polymers after a washing step. Washing step was introduced subsequent to cocaine accumulation in order to remove weakly adsorbed levamisole and thus improve the selectivity of the sensor towards cocaine (Figure S3 in supplementary shows the response for levamisole with and without a washing step). Due to the high affinity of the polymer layer for cocaine, cocaine is more strongly adsorbed and retained onto the polymer. The washing step consisted of 10 seconds wash with 100 μL double distilled water placed onto the electrode.

The current response for the oxidation of cocaine on poly(PABA) layers was found to increase (both in pure solution and in binary mixtures) with the increase of PABA concentration from 1 to 2.5 mM. This may be due to the formation of multiple polymer layers which increases concentration of binding sites available for the adsorption of cocaine. When the PABA concentration is increased further than 5mM, the cocaine signals start to decrease due to the formation of thicker films with lower conductivity and poorer diffusion ability.

Poly(OPD) layers give lower current peaks for cocaine, since a less conductive layer is formed at the electrode surface. A high signal for pure cocaine is observed at lower concentrations of monomer (1mM). Further increasing the concentration lead to significantly lower cocaine signals due to the formation of thicker films with lower conductivity and poorer diffusion ability.

Although the modification of the electrode with polymers offers improved selectivity towards the cocaine in presence of levamisole, some suppression effect is still observed for both investigated polymers. Since the mechanism of suppression is not yet completely understood, one can assume that some amount of levamisole is also partly adsorbed on the electrode, but to a lesser extent than cocaine, thus still affecting the signal of cocaine, as seen in Figure 3, grey bar compared to blue bar.

The concentrations of 2.5 mM PABA and 1mM OPD were considered suitable to form effective polymer cocaine-sensing layers on the electrodes and were used in the following experiments.

### 3.3.2. *Number of electropolymerization cycles and scan rate*

The thickness of the polymer film has an influence on the electrochemical performance of the electrode in terms of signal intensity and response time. The thickness increases with the increase of the number of cycles and can thus be simply tuned by varying the number of cycles for electropolymerization.

The number of electropolymerization cycles was varied and SWV responses of solutions of 0.5 mM cocaine and 1:1 cocaine:levamisole binary mixtures (0.5 mM:0.5 mM) were recorded on the polymer modified electrode after 5 min accumulation.

In the case of poly(PABA) the number of cycles was varied between 7 and 15 (Figure 4). The signal of cocaine slightly decreased as the number of cycles increased due to the growth of polymer layer. As the resulted polymer is less conductive than the GPH-SPE the electron transfer resistance increases. Cocaine in the binary mixture gave rise to the highest signal when 10 electropolymerization cycles were performed. This can be due to the fact that the polymer covers a higher surface of the electrode thus impeding any electrode process that might be related with the suppression of cocaine peak by levamisole. For 15 cycles both the signal of cocaine and of binary mixtures decreased due to the increase of the polymer thickness and of the electron transfer resistance. Since the highest signal for cocaine in the binary mixture was obtained when 10 scans were applied, and the signal intensity of pure cocaine was not significantly higher for 7 cycles, 10 cycles were considered optimum for further experiments.

Since OPD results in polymer layers with lower conductivity than PABA the number of cycles studied in this case was lower, between 5 and 10, in order to maintain a fairly good conductivity of the surface. It was observed that the signal of cocaine drastically decreased as the number of cycles are increased from 5 to 10, due to the formation of thicker polymer layers with increased resistance to the electron transfer. The signal of cocaine in binary mixture was not significantly higher for 7 electropolymerization cycles. Thus 5 cycles was selected as optimal number of cycles for the polymerization of OPD.

The electrochemical behavior of 1mM cocaine in PBS pH 7 on polymers-modified electrodes was studied by LSV at different scan rates. It was found that the oxidation peak current of cocaine increased linearly with the increase of the scan rate from 5 to 200 mV/s, for both poly(PABA) and poly(OPD), as described by the equations Ip $(\mu A) = 0.798$ $\upsilon(mV\ s^{-1}) + 15.419$; $R^2 = 0.996$ and Ip $(\mu A) = 0.429$ $\upsilon(mV\ s^{-1}) + 16.353$; $R^2 = 0.993$, respectively (Figure S4 in supplementary material). This suggests that the electrode reaction of cocaine is a predominantly adsorption-controlled process for both poly(PABA) and poly(OPD).

### 3.3.3. Accumulation time of cocaine

To assess the effect of the accumulation time on the response of the polymer layers, the polymer modified electrodes were left in contact with solutions of 0.5 mM cocaine and 1:1 cocaine:levamisole mixtures for a time period ranging from 1 to 15 minutes. After washing with double distilled water for 10 seconds SWV was performed to evaluate the amount of analyte adsorbed at the surface of the polymer. The results are presented in table S1 in

supplementary material. The signal of pure cocaine increased significantly with the accumulation time due to a higher amount of analyte adsorbed on the polymer and reached a steady state after 10 min, for both polymers. The cocaine signal in the binary mixture increased with the accumulation time up to 7 min on poly(PABA). Further increasing the time did not result in a significantly higher signal, therefore 7 min accumulation time was used to obtain a maximum enrichment with the analyte. Cocaine signal in the binary mixtures on poly(OPD) increases as the time increases up to 15 min. Cocaine signals are significantly lower on poly(OPD) than on poly(PABA), and do not improve with a longer accumulation time. Thus, although OPD showed higher affinity for cocaine in computational modelling, PABA was considered a better option for the detection of cocaine, leading to higher oxidation signals for cocaine.

### 3.4. Performance of poly(PABA) towards the detection of cocaine

Since poly(PABA) layers allowed to obtain higher signals for cocaine than poly(OPD), PABA was selected as optimal monomer and was further employed to evaluate its SWV response to various concentrations of cocaine. The experiments were performed using the previously optimized conditions. Poly(PABA) was electrodeposited by CV in a solution of PBS pH 7 containing 2.5 mM PABA, by running 10 cycles, in the potential range from -0.5 to 1V, at 50 mV/s. The resulting polymer layer was rinsed with double distilled water, dried with a stream of $N_2$ and left in contact with solutions of cocaine in PBS pH 7 of various concentrations for 7 min. After washing with distilled water for 10 seconds, to remove non-specifically adsorbed levamisole, SWV measurement were recorded in PBS solution pH 7.0. The relation between the peak current and the concentration of cocaine in standard solutions was found to be linear in the range up to 500 μM defined by the equation $y=0.0196x+0.546$, $R^2=0.973$, mean RSD 15.8%, with the lowest concentration detected experimentally of 50 μM. In binary mixtures with 30% levamisole, the sensor exhibited a linear response for cocaine in the range of concentrations up to 500 μM ($y=0.010x+0.230$, $R^2=0.985$, mean RSD 12.09%), with 100 μM being the lowest detectable concentration by SWV (Figure 5). As the aim is to screen street powder samples for the presence of cocaine the achieved detection limits were considered sufficient.

To investigate the feasibility of real samples analysis, poly(PABA)/GPH-SPE were used for the screening of seized street samples containing cocaine and levamisole. Three street samples seized by NICC, Belgium (see composition in Section 2. Materials and methods) were screened for the presence of cocaine, as public authorities are interested in point-of-use screening methods that would allow to check whether confiscated powders contain the drug or not. As seen in Figure 6 the signal of cocaine on bare graphite electrodes is suppressed for all three analyzed samples leading to false negative results (inset), while on poly(PABA)/GPH-SPE the signal of cocaine is clearly evident. This points to the potential application of polymer-modified electrodes in real street samples for more accurate analysis, avoiding false negative results.

### 4.    Conclusion

We have investigated a straightforward method to avoid false negative results in the screening of drug samples containing cocaine adulterated with levamisole. By readily covering the surface of electrodes with polymer layers the suppression of the electrochemical signal of cocaine that occurs on unmodified graphite electrodes is avoided. To ensure high selectivity monomers with high affinity for cocaine have been selected by computational modelling. Although OPD showed higher binding score for cocaine, PABA proved to be more appropriate for the electrochemical detection of cocaine, due to the higher conductivity. Graphene was introduced to improve the conductivity of polymers and give a higher surface area for analyte binding. The composite platforms were characterized by SEM and electrochemical methods. They exhibit good analytical performance, detecting cocaine in the concentration range 50-500 μM and respectively in the range of 100-500 μM, when present together with 30% levamisole, respectively. The usefulness of the platform for screening of real seized samples for the presence of cocaine has also been proved.

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**Figure Captions**

Fig. 1. Cyclic voltammograms for electrochemical polymerization of 2.5 mM PABA in PBS pH 7 (A) and 1mM OPD in acetate buffer pH 5.4 (B) at GPH-SPE. Scan rate 50 mV/s.

Fig. 2. SEM images of bare GPH-SPE (A) and GPH-SPE modified with poly(PABA) (B) and poly(OPD) (C)

Fig. 3. Optimization of the concentration of PABA (A) and OPD (B) solutions in PBS pH 7 and acetate buffer pH 5.2, respectively, based on SWV responses of 0.5mM cocaine (•) and its 1:1 binary mixture with levamisole (•) in PBS pH 7.

Fig. 4. Optimization of number of cycles for the electropolymerization of PABA (A) and OPD (B) based on SWV responses of 0.5mM cocaine (•) and its 1:1 binary mixture with levamisole (•) in PBS pH 7.

Fig. 5. Calibration graph obtained by SWV on poly(PABA) for the oxidation of (a) 50, (b) 100, (c) 200, (d) 250, (e) 300, (f) 400, (g) 500 μM cocaine (A) and cocaine mixture with 30% levamisole (B) in PBS pH 7.

Fig. 6. Square wave voltammograms obtained for three real cocaine street samples on poly(PABA) modified electrodes. Numbers 1-3 correspond to samples 1-3 described in section 2. Inset: Square wave voltammograms obtained for real cocaine street samples on graphite SPE showing suppression of cocaine peak at 0.91±0.05V
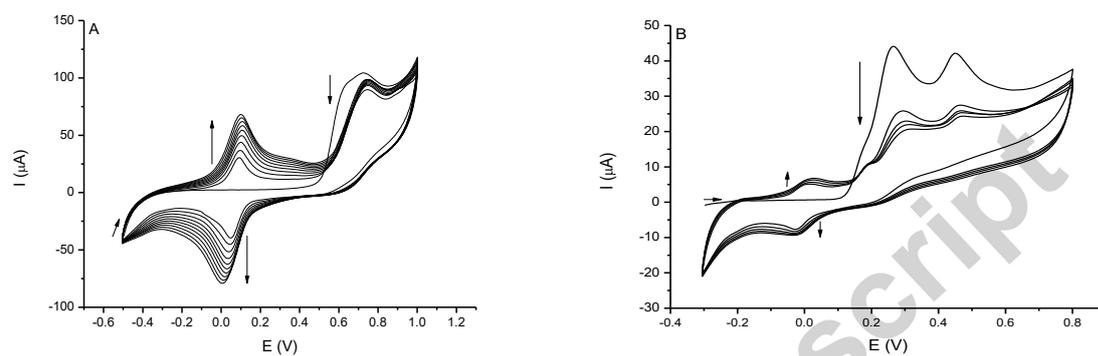
Fig. 1
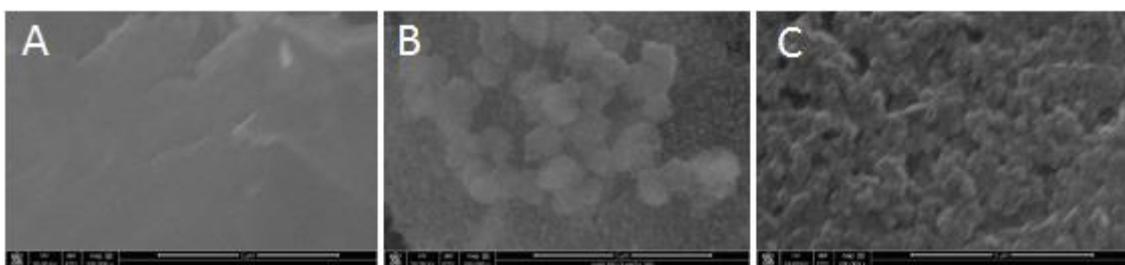
Fig. 2
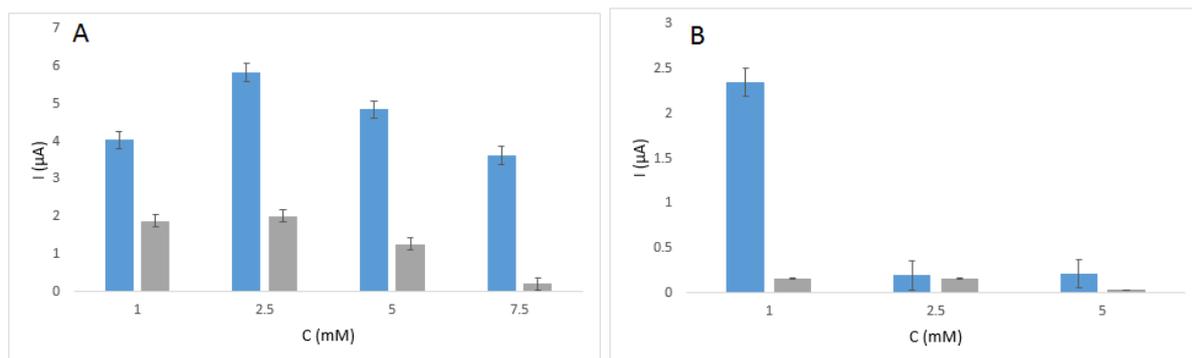
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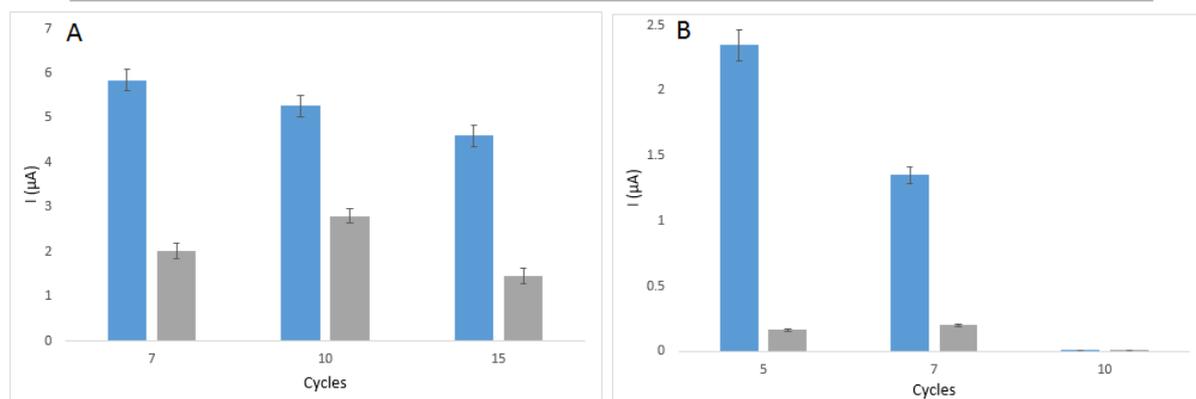
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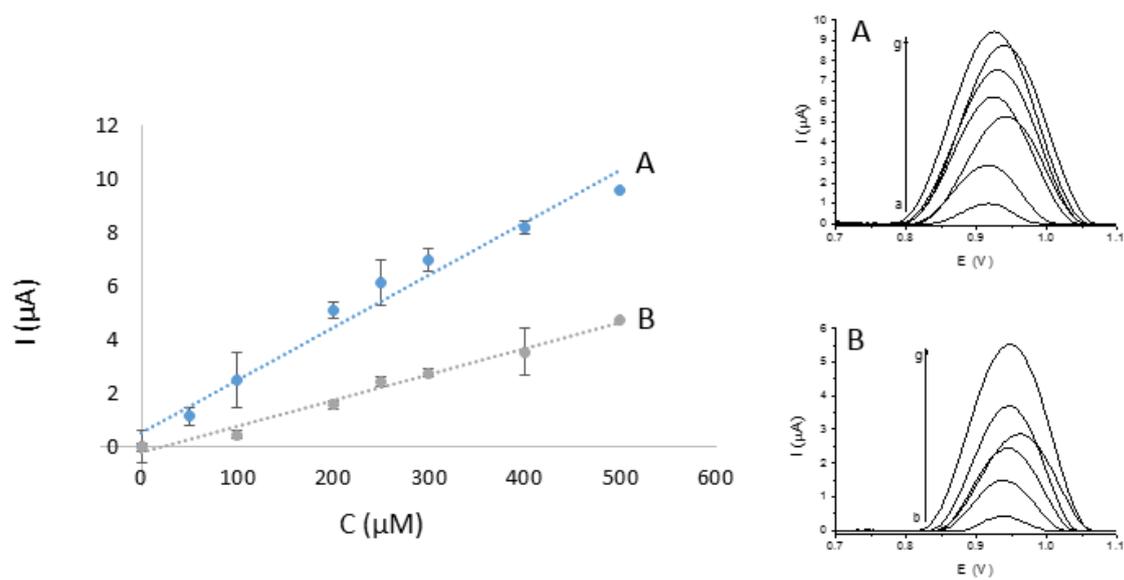
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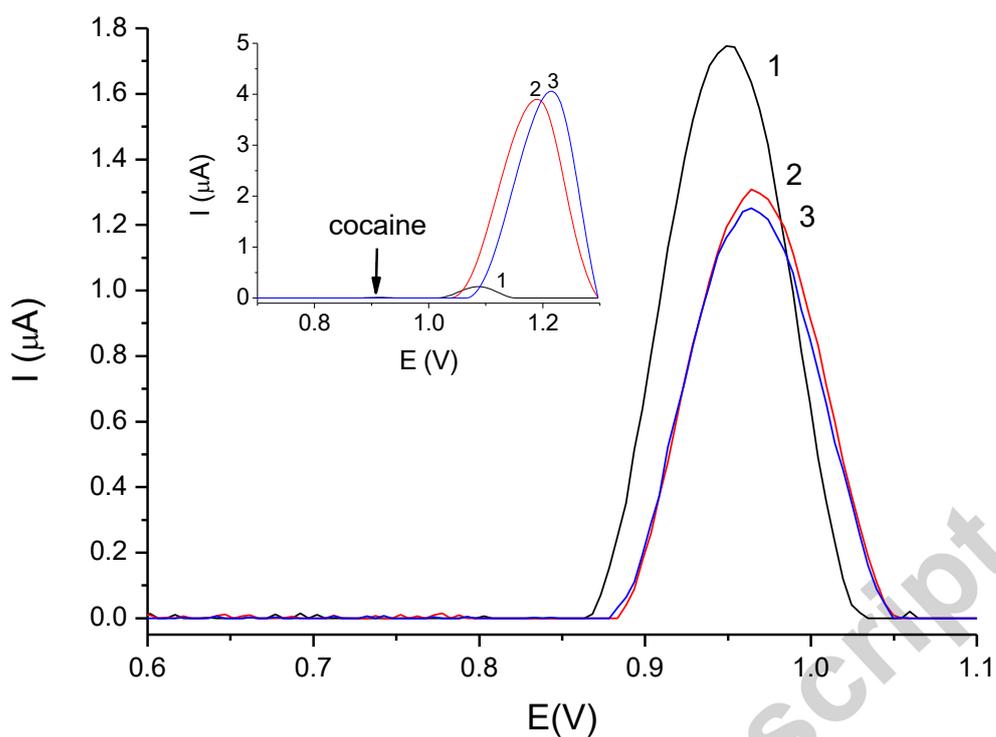
Fig. 6

Highlights

- Polymers were electrodeposited for cocaine detection in adulterated powders
- Polymers with affinity for cocaine were selected by computational modelling
- Cocaine signal suppression by levamisole was overcome
- Selective detection of cocaine in presence of levamisole was achieved