Analytical Methods

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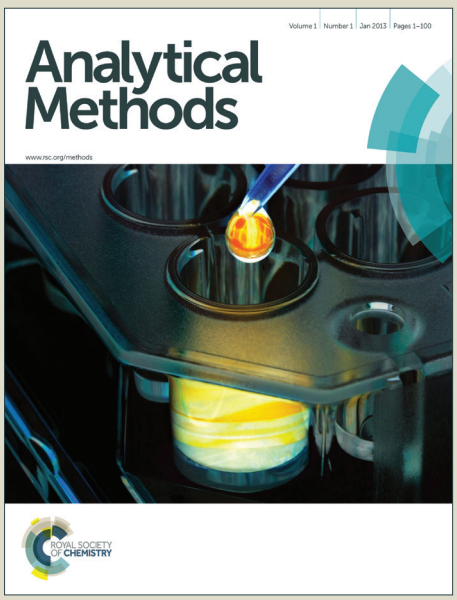

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Analytical Methods

ARTICLE

Combination of poly(3,4-ethylene-dioxythiophene) electrode in presence of sodium dodecyl sulfate with centri-voltammetry

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Poly(3,4-ethylene-dioxythiophene) (PEDOT) electrode was prepared by electroporimerization of 3,4-ethylene-dioxythiophene (EDOT) in the presence of sodium dodecyl sulfate (SDS). The electrode was combined with centri-voltametry for the first time and applied for dopamine (DA) detection. Under the working conditions, SDS brings PEDOT electrode high density of negative charges which attracts positive charged DA. Also by applying centrifugation, effective accumulation of DA onto electrode surface was achieved. Two linear ranges $1x10^{-9}$ M – $1x10^{-5}$ M and $2x10^{-5}$ M – $1x10^{-1}$ M with two LOD values 5.9 nM and 3.1 nM were found for the developed system. Sample application and interference study were also conducted.

Introduction

Electroanalytical methods have been extensively used for the determination of dopamine which is an important neurotransmitter in brain tissue [1-6]. The usage of conducting polymers (CP) for the detection of DA, provides immense development in chemical and biological sensor areas [7-11].

Among these CPs, poly(3,4-ethylenedioxythiophene) (PEDOT) is a class of polythiophenes with very high electrochemical stability in oxidized states and a low band-gap [12,13] due to the presence of the two electron donating oxygen atoms coupled to the thiophene ring [14,15]. With the usage of oxidants like ferric chloride, it can be produced chemically [13,16] or in the presence of appropriate solvents, it can be produced electrochemically [13]. PEDOT has some advantages compared to unsubstituted polythiophene and other polythiophene derivatives. One of them is caused by ethylenedioxy substituent. This substituent lowers the oxidative doping potential of the polymer and stabilizes its conducting form [17]. Recently, PEDOT modified electrodes have been extensively reported and showed excellent electrocatalytic effect on phenolic compounds [18-21].

Sodium dodecyl sulfate (SDS) is a surfactant. Surfactants can be described as a type of amphiphilic molecules with a hydrophilic head on one side and a long hydrophobic tail on the other. These substances have been widely applied in electrochemistry to improve the property of the electrode/solution interface [22,23]. Also it has been demonstrated that surfactants are important in the electroanalysis of biological compounds and drugs [24,25]. Considering SDS, there are many works that cover selective determination of dopamine (DA) in presence of SDS in the literature [26-29].

Centri-voltammetry and Biocentri-voltammetry were developed by our group. These methods include the combination of centrifugal force with direct voltammetric scan afterwards without applying any filtration, decantation or any other separation methods [30-39]. For the application of this method, specially designed centri-voltammetric cell is used where working electrode is at the bottom of the centri-voltammetric cell (Scheme 1.). Recently we manage to apply centri-voltammetry for the detection of DA and very promising results were obtained [39].

In this work, PEDOT was electrochemically formed onto Pt electrode of centri-voltammetric cell by means of electropolimerization of 3,4-ethylenedioxythiophene (EDOT). Then SDS was added and centrifugation was applied. By this way, centri-voltammetry was combined for the first time with a conductive polymer where DA was chosen as a model analyte. After the optimization of experiment parameters, analytical characteristics were examined. Then developed system was applied for detection of DA in synthetically prepared plasma sample and the interference effects of ascorbic acid (AA) and uric acid (UA) were also examined.

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Experimental Section

Chemicals and reagents

All of chemicals were of analytical grade. DA , EDOT, UA, urea, Trizma hydrochloride (tris-HCl), SDS, potassium dihydrogen phosphate (KH_2PO_4), sodium phosphate dibasic (NaH_2PO_4), potassium chloride (KCl), calcium choride ($CaCl_2$) and Lithium perchlorate ($LiClO_4$) were purchased from Sigma-Aldrich. Sodium chloride (NaCl), D+ Glucose monohydrate, magnesium chloride ($MgCl_2$), acetonitrile, acetone, PC and hydrochloric acid (HCl) were purchased from Merck. Lastly, AA obtained from Scharlau and isopropyl alcohol purchased from Panreac. Ultrapure water was used in all solutions.

All experiments except electrochemical polymerization of EDOT were performed in PBS at room temperature.

PBS of pH:7 was prepared by mixing 60 mL of a 1/15 mol dm^{-3} solution of $Na_2HPO_4.2H_2O$ with 40 mL of a 1/15 mol dm^{-3} solution KH_2PO_4 and adjusting the pH to 7 by adding either KH_2PO_4 or Na_2HPO_4 [40-41] .

Instrumentation

Voltammetric measurements were carried out with a µ-AUTOLAB Type III electrochemical measurement system from Metrohm B.V. controlled by NOVA 1.10 software. The experiments were conducted in a 5.0 mL centri-voltammetric cell, at room temperature (25 °C), using a three-electrode cell configuration. Pt disk was used as the working electrode and Pt wire was used reference and also counter electrode.

Sigma 3-16 PK was used for centrifugation and pH measurements were made with Thermo Electron Corporation.

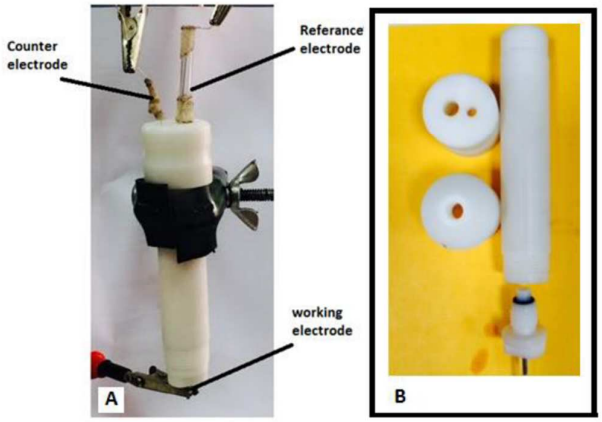
Preparation of PEDOT modified Pt electrode

Pt disk that was used as a working electrode was polished by hand using 0.3 and 0.5 µL alumina slurry on a felt pad. Then the electrode was sonicated in water and acetone for 5 minutes. Before starting each experiment Pt electrode was washed with isopropyl alcohol, and dried by using a blow drier. The potentiodynamic electrodeposition was performed in a solution consisted of 0.1 M $LiClO_4$ in PC solution containing 5 mM EDOT.

The electrodes were polarized in the range of -0.7 - 1.85 V (vs. Ag/AgCl) by applying six cycles at the scan rate of 50 mVs^{-1}. Then the PEDOT films was replaced in monomer free 0.1 M $LiClO_4$ in PC solution and further 4 cycles were applied at 100 mVs^{-1} scan rates in the potentials range of -0.5 V - +1.0 V to obtain stable film. Finally, the PEDOT films obtained on the surface of the working electrode were washed with acetonitrile and dried by using a blow drier before used in buffer solution. For every set of the measurement, the freshly prepared PEDOT film was used.

Electrochemical Measurements

After the formation of PEDOT, DA detection was performed by monitoring CV and square wave voltammetry (SWV) signals of DA oxidation in presence of SDS. For this purpose, PEDOT coated working electrode was mounted at the end of centri-voltammetric cell. DA solution which contains $6.7x10^{-5}$ M 150 µL SDS was stirred for 5 minutes and then was transferred into centri-voltammetric cell (Scheme 1). After that, centrifugation was applied for particular amount of time and at proper speed. Finally, the cell was carefully placed on the voltammetric stand and reference and counter electrodes were immersed into working solution. CV was performed with 100 mVs^{-1} scan rate and from potential -0.5 V to + 0.7 V. The parameters for SWV experiments were as follows: potential was scanned from -0.5 V to +0.7 V with 0.02 V amplitude and 0.005 V step potential. On the other hand, for electrochemical impedance spectroscopy (EIS), 250 mV applied potential, 5 mV amplitude, 0.1- 100.000 Hz frequency range were applied. All experiments of DA detection were performed in pH:7 $6.7x10^{-2}$ M PBS containing DA in presence of $6.7x10^{-5}$ M 150 µL SDS unless it is mentioned differently.



Scheme 1. Illustration of centri-voltammetric cell, A) on the stand , B) the parts of centri-voltammetric cell.

Preparation of sample solution

Developed system was applied for DA detection in synthetically prepared plasma sample. For this purpose, synthetic plasma sample was prepared by incorporating the reagents into the 10 mM Tris-HCl including 140 mM NaCl, 4.7 mM D+ Glucose monohydrate, 0.8 mM $MgCl_2$, 4.5 mM KCl, 2.5 mM $CaCl_2$ and 2.5 mM urea [39]. Also, the developed system was applied for Dopamine detection in real samples. For this purpose, Dopamine ampoule which is a type of medicine was used. For this procedure, necessary Dopamine amount was taken directly from the ampoule and spiked into the centri-voltammetric cell as to be 5 x 10^{-5} M. The measurements were repeated for three times.

Results and discussion

By introducing SDS onto PEDOT electrode results with a high density of negative charges covered on electrode surface. For this reason, it is expected to get sensitive and selective

positively charged (at pH 7) DA detection with this electrode [29,43]. On the other hand, centri-voltammetry provides centrifugal force meaning more effective accumulation of analyte onto the electrode surface [39].

Electrochemical polymerization and characterization of Pt/PEDOT electrode

Electrochemical polymerization was conducted via CV. Cyclic voltammograms that were obtained during the polymer growth at 6 cycles were given in Fig. 1.A As the polymer grow on bare Pt disc electrode, by applying successive CVs, the background current increases demonstrating that the electrode is covered with PEDOT. In order to strengthen the formation process, an EIS diagram is also provided (Figure 1 B).

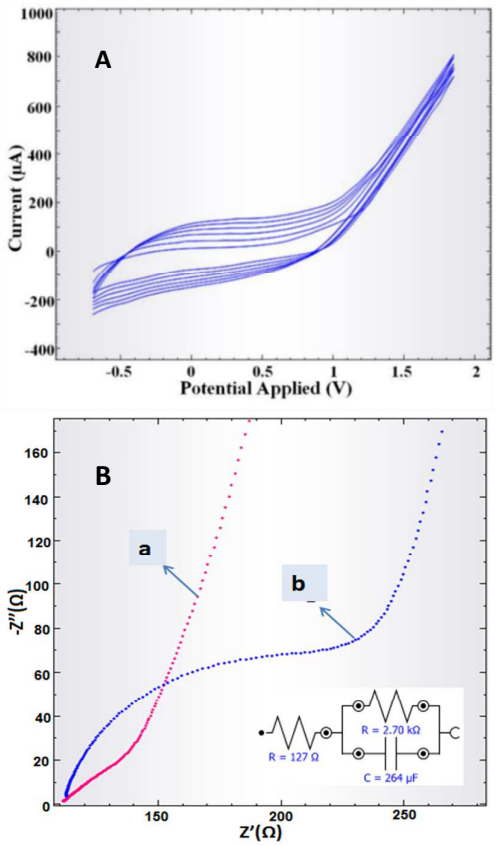


Fig.1 A) CV voltammograms of electrochemical polymerization of EDOT. Conditions: 5 mM EDOT in propylene carbonate (PC) solution containing 0.1 M $LiClO_4$, working potential: -0.7 V to +1.85 V and scan rate 50 mVs^{-1}. **B)** Nyquist diagrams for the EIS measurements at **a.** Pt/PEDOT electrode **b.** Pt electrode and equivalent circuit of Pt/PEDOT electrode. Working conditions: In $6.7x10^{-2}$ M pH 7.0 PBS including $5.0x10^{-5}$ M DA and 150 µL SDS at potential 250 mV, amplitude: 5 mV, frequency range: 0.1- 100.000 Hz.

The formation of PEDOT onto Pt electrode is clearly seen from the Figure just by comparing the diameters of semicircles. As can be seen from the Figure, formation of PEDOT onto Pt electrode decreases the diameter of semicircle together with electron transfer resistance.

Optimization of experiment conditions

Optimizations of experiment parameters are important in order to achieve high sensitivity and better reproducibility; thus the amount of SDS, centrifuge speed and centrifuge time were optimized.

Optimization of SDS amount: SDS forms a monolayer on PEDOT surface and the electrochemical response of DA is improved in presence of SDS due to the enhanced accumulation of protonated DA via electrostatic interactions. For this reason, SDS amount was optimized. The response signals of DA ($5.0 x10^{-5}$ M) oxidation in presence of 0 µL, 25 µL,50 µL,75 µL,100 µL,150 µL and 200 µL of $6.70x10^{-5}$ M SDS were recorded, respectively (Fig. 2). As can be seen from the Fig. 2, the current value increases up to 150 µL and then a decrease was obtained. Following these findings, 150 µL SDS was selected as the optimum SDS amount and used for further studies.

The current increment in the presence of SDS is explained by the aggregation of this surfactant on the electrode surface in the form of bilayers, cylinders, or surface micelles [25]. The electron transfer process will take place when the electroactive species approaches the vicinity of the electrode surface. There are three suggestions for explaining the charge transfer: the first one is the displacement of the adsorbed surfactant by the analyte, second one is the approach of the analyte to the surface of the electrode within the space of one to two head groups of adsorbed surfactant moieties and the third one includes the formation of ion-pair that anchor onto the surface of the electrode that should posses some hydrophobic character [42,43]. As mentioned before due to electrostatic attraction and by following the second suggested mechanism we believe that current increases up to some point of increased SDS concentration. Then since increment of SDS amount may block the electrode surface, after some SDS concentration, DA cannot reach the electrode surface and as a result a decrease in the current value is observed. At this point it is not possible to suggest the exact mechanism, but above explanation could be an alternative to that behaviour.

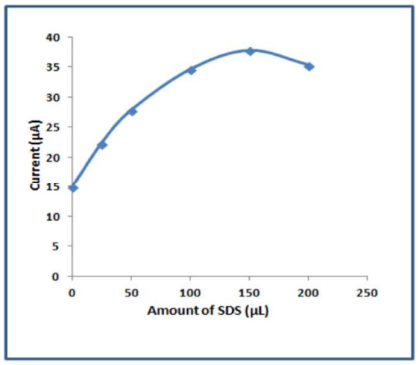


Fig.2 The effects of different amount of SDS on the sensor response for $5.0x10^{-5}$ M DA. Conditions: in $6.7x10^{-2}$ M phosphate buffer solution (PBS) (pH 7.0), working potential: -0.5 V - +0.7 V and scan rate 100 mVs^{-1}.

Optimization of centrifugal parameters: The centrifugation parameters are very important in centri-voltammetry [30-39]. In this study, SDS molecules should be deposited onto electrode surface in order to obtain electrostatic interaction with DA. For this purpose, centrifuge speed and centrifuge time were optimized. Firstly, centrifuge speeds of 0 rpm, 1000 rpm, 2000

rpm, 3000 rpm, 4000 rpm, 5000 rpm and 6000 rpm were applied on centri-voltammetric cell for 5 minutes. Best current value was obtained at 5000 rpm (Fig. 3A). For optimization of centrifuge times, 0 min., 1 min., 3 min., 5 min. and 7 min. were applied on centri-voltammetric cell at 5000 rpm. As a result, best result current value was obtained at 5 minutes (Fig. 3B).

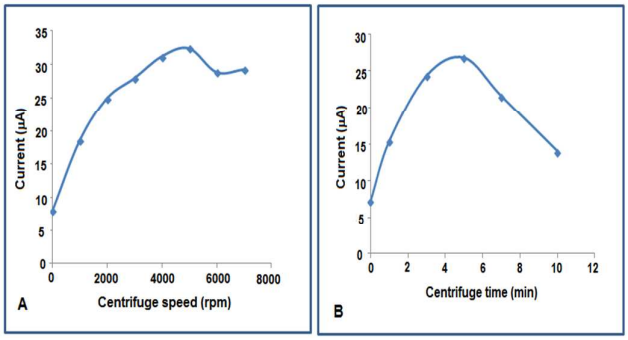


Fig.3 The effects of centrifugation parameters on the sensor response, **A)** centrifuge speed, **B)** centrifuge time for 5.0x10-5M DA. Conditions: in 6.70x10^{-2} M PBS (pH 7.0) in presence of 6.70x10^{-5} M 150 µL SDS, working potential: -0.5 V - +0.7 V and scan rate 100 mVs^{-1}.

The increase in current values that were obtained due to increased centrifugation time and speed can be attributed to the accumulation of analyte layer onto the electrode surface [30-39] . On the other hand the decrease that was obtained when centrifugation time was increased can be due to desorption of the analyte from the electrode surface due to long centrifugation period[30-32,36,38,39]. The other possible explanation for this phenomenon could be the accumulation of supporting electrolyte ions onto the electrode surface instead of DA. At this point, it is not possible to state the exact reason but these two explanations seem reasonable to us. On the other hand, current decrease at the higher speeds might be due to destruction of analyte layer that was on the electrode surface[30-32,36,38,39] . All optimization of centrifugal parameters experiments were performed in presence of 5.0x10^{-5} M DA in 6.7x10^{-2} M pH:7 PBS.

Effect of scan rate on the voltammetric response of DA

Fig. 4A shows the CV of 5.0x10^{-5} M DA in 6.7x10^{-2} M pH:7 PBS containing 150 µL SDS at Pt/PEDOT electrode at different scan rates (from 10 mVs^{-1} to 250 mVs^{-1}). Fig. 4B also shows a comparison of linear relationship for DA at Pt/PEDOT in 6.7x10^{-2} M, pH:7 PBS containing 150 µL SDS and 6.7x10^{-2} M, pH:7 PBS without SDS versus square root of scan rate.

As it is expected with SDS higher current values were obtained compared with plain PEDOT electrode. Examination of data in terms of effect of scan rate, reveals that the linearity of the relationship is observed up to a square root of scan rate of 100 mVs^{-1}in the presence and absence of SDS. A deviation from the linearity is obtained for at higher scan rates. This demonstrates a partial diffusion control process for charge transfer process for both situations. However, as can be seen from the Figure, more deviations are observed for scan rates higher than 100 mV/s in the presence of SDS. This could be accepted as a confirmation of aggleregation of SDS at the vicinity of electrode hence the higher flux of DA via SDS through the electrode surface.

In order to observe more clear effect of addition of SDS, dependence of the anodic peak current density on the scan rate has been used to calculate the "apparent" diffusion coefficient (D_{app}). D_{app} calculated from Randles Sevcik equation such as the below.

$$I_{p} = 0.4463\ (F^3 / RT)^{1/2}\ n^{3/2}\ v^{1/2}\ D_0^{1/2}\ A\ C_0$$

In these equations: I_p is the peak current density (A cm^{-2}), n is the number of electrons appearing in half-reaction for the redox couple, v is the rate at which the potential is swept (V s^{-1}), F is Faraday's constant (96.485 Cmol^{-1}), C_O is the analyte concentration (5×10^{-5} mol cm^{-3}), A is the electrode area (0.126 cm^2), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K=298), and D is the electroactive species diffusion coefficient (cm^2 s^{-1}).

D_{app} value was calculated as 1.05x10^{-8} cm^{2}s^{-1} in absence of SDS and 1.62x10^{-8} cm^{2}s^{-1} in the presence of SDS. The anionic surfactant SDS affects positively the diffusion component of the charge transfer at the electrode surface as indicated by the Dapp values.

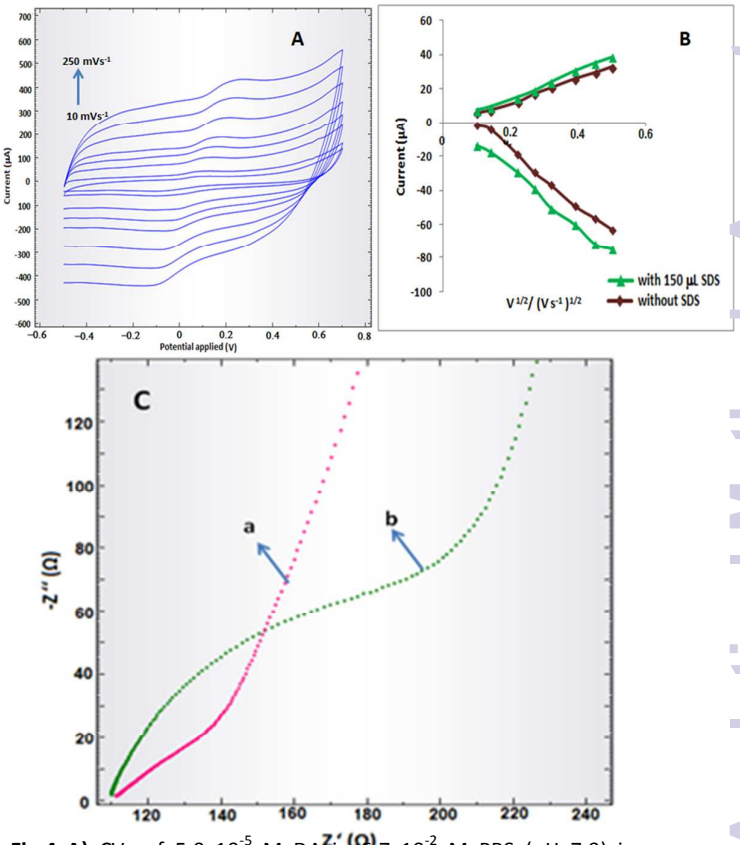


Fig.4 A) CVs of 5.0x10^{-5} M DA in 6.7x10^{-2} M PBS (pH 7.0) in presence of 6.7x10^{-5} M 150 µL SDS at different scan rates (10 mVs^{-1}– 250 mVs^{-1}). **B)** Linear relationship of anodic and cathodic current vs. scan rate, in the presence of SDS and in the absence of SDS. **C)** Nyquist diagrams for the EIS measurements at Pt/PEDOT electrode in 6.7x10^{-2} M pH 7.0 PBS including 5.0x10^{-5} M DA **a.** In the presence of SDS **b.** In the absence of SDS. For the EIS measurements working conditions: at potential 250

mV, amplitude: 5 mV, frequency range: 0.1- 100.000 Hz.

Also an EIS diagram is provided to enlighten the charge transfer process in the presence of SDS (Fig. 4C) The difference in Nyquistic diagrams in the presence and absence of SDS is pretty obvious. The addition of SDS definitely decreases the semicircle diameter hence increase the charge transfer rate

Comparison of obtained voltammograms under different conditions

The effects of SDS together with centrifuge for electrochemical detection of $5.0x10^{-5}$ M DA were investigated. For this purpose, the experiments were performed in presence of SDS, in the absence of SDS, with centri-voltammetry and without centri-voltammetry. When the experiment were performed in presence of SDS, with centri-voltammetry and without centri-voltammetry, the current values were obtained as 28.2 µA (with SDS and centri-voltammetry) and 15.3 µA (with SDS and without centri-voltammetry), respectively. When the experiments were performed in the absence of SDS, for with centri-voltammetry and without centri-voltammetry, the current values were obtained as 16.6 µA (without SDS, with centri-voltammetry) and 4.3 µA (without SDS and centri-voltammetry) respectively.

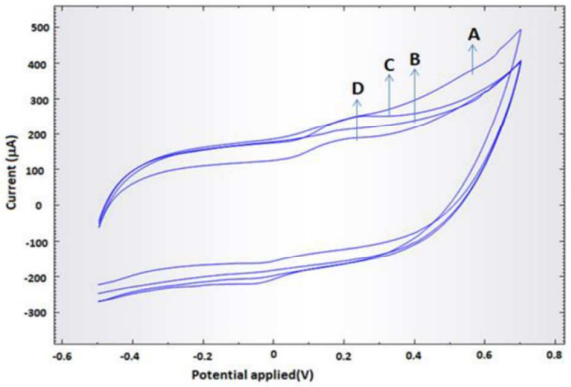


Fig.5 CV voltammograms show the effects of SDS and centri-voltammetry for electrochemical detection of $5.0x10^{-5}$ M DA. **A)** without SDS and centrifuge, **B)** with SDS and without centrifuge, **C)** with SDS and centrifuge and **D)** without SDS and with centrifuge.

As can clearly be seen from the Fig. 5, best current value was obtained under the working conditions when SDS was added and when centri-voltammetry was applied to the system (Fig. 5C).

Analytical characteristics

After the optimization of experimental conditions, analytical characteristics were investigated. As can be seen from Fig. 6, two linear ranges of $1.0x10^{-9}$ M – $1.0x10^{-5}$ M and $2.0x10^{-5}$ M – $1.0x10^{-1}$ M DA with the correlation coefficients of 0.995 and 0.993 were obtained. Following these data, the detection limits were calculated as 5.9 nM and 3.1 nM, respectively. For two linear range, LOQ values were also calculated and found as $1.9x10^{-8}$ M and $1.0x10^{-8}$ M. Finally, RSD values were calculated for $5.0x10^{-5}$ M DA (n=3) and found as 1.6 %. The comparison of developed system was made with similar systems and presented at Table 1. From the Table it is clear that developed system has one of the largest linear ranges with higher sensitivity. The introduction of PEDOT and SDS to centri-voltammetry definitely improves linear range and sensitivity in terms of DA detection.

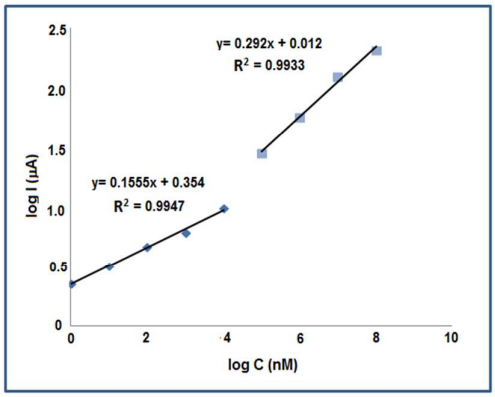


Fig.6 Calibration graph for DA concentrations between $1.0x10^{-9}$ M – $1.0x10^{-5}$ M and $2.0x10^{-5}$ M – $1.0x10^{-1}$ M. Centrifugation speed 5000 rpm, centrifugation time 5 min.

Table 1. Comparison of the same studies about DA detection

Electrode	LOD	Linear range	References
GCE/PEDOT/Pd	500 nM	0.5 µM- 1 µM	44
Pt/PEDOT	61 nM - 86 nM	5 µM – 25 µM and 30 µM – 0.1 mM	29
Pt/PMPy/Pd nano	12 nM	0.1 µM - 10 µM	45
Au/PEDOT/Au_{nano}	0.39 nM and 1.55 nM	0.5-20 µM and 25-140 µM	21
GCPE (centri-voltammetry)	1 nM	$5x10^{-9}$M- $5x10^{-6}$M	39
Pt/PEDOT (centri-voltammetry)	5.9 nM and 3.12 nM	$1x10^{-9}$M – 10^{-5}M and $2x10^{-5}$ M– $1x10^{-1}$ M	This work

GCE: Glassy carbon electrode, GCPE: Glassy carbon paste electrode, Pt: Platinum electrode, Pdnano: Palladium nanoparticles, PMPy: poly(N-methylpyrrole), Au nano: Gold nanoparticles.

Sample application and interference studies

For the sample application, standard addition of DA into synthetic plasma sample solution which its preparation procedure was described in experimental part was conducted. $5.0x10^{-5}$ M DA was added into synthetic plasma solution that contains $6.7x10^{-5}$ M 150 µL SDS. This experiment was repeated for three times. Recovery value was calculated by dividing obtained standard addition current values with DA concentration's current value and multiplying result by 100. As a result, 96% ± 1.2 was calculated as recovery value.

Also centri-voltammetric Dopamine detection was realized in real samples, here in Dopamine ampoules as stated in the experimental part. Three measurements were conducted by spiking 5 x 10^{-5} M Dopamine (from ampoules) into the centri-voltammetric cell. Obtained current values were evaluated and 4.96 x 10^{-5} ± 1.61 M Dopamine was detected.
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It is well known that DA, UA and AA coexist in the extracellular fluid of central nervous system and serum. Therefore, eliminating AA and UA is an important for any DA analytical method. For this purpose, the electrochemical behaviors of DA, UA and AA in a mixture solution were studied by using CV. Two studies were conducted for this purpose. In the first study, $5.0x10^{-5}$ M AA and UA were added into $5.0x10^{-5}$ M DA. In the second study, tenfold more AA and UA were added to the $5.0x10^{-5}$ M DA solution. For the same concentration of AA, UA and DA and in the presence of tenfold more AA and UA, recovery values were calculated as % 105.3 and % 94.2, respectively. These recovery values demonstrate that, developed system can detect DA in the presence of tenfold more AA and UA.

Conclusions

Combination PEDOT in the presence of SDS with centri-voltmmetry yields very sensitive results for DA detection. The negative charge that SDS brings onto the PEDOT electrode and enhanced accumulation of analyte onto this electrode by means of centrifugation are responsible for that. The interference studies stated that DA can be easily detected in the presence of 10 fold more AA and UA. Also the recovery value that was obtained from sample application work demonstrates that developed system is suitable for DA detection in complex matrices like plasma sample. On the other hand, Dopamine detection in real sample was conducted by using medicinal Dopamine ampoules. As can be seen above, very accurate results were obtained demonstrating the usage of developed system for Dopamine detection in real samples Insight of these findings, it can be concluded that, sensitive selective and practical system was developed for DA detection.

Keywords: PEDOT•SDS •Dopamine •Centri-voltammetry

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