

Selective Electrochemical Sensing of Dopamine and Ascorbic Acid Using Carbon Paste Electrode Modified with Cobalt Schiff Base Complex and a Surfactant

Naghmeh Hassanzadeh¹, Hamid Reza Zare-Mehrjardi^{1,2,*}

¹ Department of Chemistry, Payame Noor University, PO BOX 19395-3697 Tehran, Iran

² Research Center of Environmental Chemistry, Payame Noor University, Ardakan, Yazd, Iran

*E-mail: hr_zare@pnu.ac.ir, zareanalyst@gmail.com, hr.zaremehr@yahoo.com

Received: 8 October 2016 / Accepted: 26 February 2017 / Published: 12 April 2017

The complex N,N'-bis(3-ethoxysalicylidene)-4,5-dimethyl-1,2-phenylenediamino cobalt (II) chloride (CoL) and 1-octanaminium,N,N,N-trioctyl bromide (as a cationic surfactant) are used for the preparation of the modified carbon paste electrode (CPE). By using the cyclic and differential pulse voltammetric methods (CV and DPV), the electrochemical behavior of dopamine (DA) and ascorbic acid (AA) is studied at the surface of the cobalt Schiff base complex-modified CPE containing different percents of cationic surfactant. The anodic peak potential of AA is decreased, by introducing the cobalt Schiff base complex in the matrix of the modified CPE. On the other hand, in pH 4.0 buffer solutions, in which all studies are carried out, DA exists as the positively charged species whereas AA is mainly as the neutral form. Therefore, there is low electrostatic attraction between the neutral form of AA and cationic surfactant. However by application of cobalt Schiff base complex-modified CPE containing cationic surfactant, the anodic overpotential for DA oxidation is increased. This effect is the result of the electrostatic repulsive interaction between the cationic form of DA and cationic surfactant at the surface of the modified electrode and results in very good resolution between the anodic peaks of DA and AA. The effects of the buffered solution pH and potential sweep rate on the response of the electrode, toward AA and DA, and the peak resolution is thoroughly studied by CV and DPV. Using the modified electrode, the best peak separation for these compounds is obtained in solutions with pH 4.0. These results reveal that the modified CPE has an effective electrocatalytic activity for the electrochemical oxidation of DA and AA and a peak resolution nearly 440 mV is obtained for two compounds. The very easy preparation and surface regeneration of the modified electrode together with the efficient electrocatalytic property and very good peak resolution and reproducibility of the voltammetric responses designate the modified CPE appropriate for simultaneous voltammetric determination of DA and AA.

Keywords: cobalt Schiff base complex, cationic surfactant, modified carbon paste electrode

1. INTRODUCTION

In recent years, the design and manufacture of new electrochemical sensors has been of notable interest [1,2]. Specially, the improvement of voltammetric sensors for the detection of secretion neurotransmitters, such as ascorbic acid (AA) and dopamine (DA) as a vital nutritional factor, received many interests. DA is a significant neurotransmitter in mammalian central nervous system [3]. In the extra-cellular fluid of the central nervous system the primary content of DA is very low [4]. Both of the plant and animal kingdoms contain AA or vitamin C. Among animal organs, anterior pituitary lobe, leukocytes and the liver represent the highest content of AA. Vitamin C is also added in various biological systems and multivitamin preparations, which are often used as supplement for inadequate dietary intake [5]. A serious problem in its detection is the overlapping of the voltammetric responses of AA and coexisting DA and the fact that its concentration is commonly much lower than AA. At common solid electrodes, DA is oxidized at potentials close to that of AA, resulting in overlapped anodic peaks. Several methods have been used to overcome this problem. For example, the electrochemical behavior of DA was investigated at a new carbon paste electrode [6], organic polymers-modified electrodes [7–9] and complexes of metal [10,11] and so on. Recently, application of carbon nanotube as a modifier in preparation of the modified electrodes has performed to detect DA [12–14]. For the detection of these biologically important compounds, the electrochemical sensors based on chemically modified electrodes (CMEs) have widely been applied. Application of functionalized carbon nanotubes [15-17], polymeric nanomaterials [18–20], complexes of transition metal [21–23] and organic electron mediators [24–26] in preparation of CMEs have attracted most consideration in this regard. Using the electron mediators in modification of the electrodes, causes to decrease the overpotential of electrochemical oxidation of the considered analyte and of course improve the sensitivity and selectivity of the response sensor.

Previous works showed that cobalt Schiff base complexes are efficient electron mediators and the oxidation process of different biological compounds, such as AA can be catalyzed using them [23, 27–31]. The major drawback in the using of these compounds as redox mediators in the modification of the electrodes is lack of selectivity for simultaneous determination of different analytes in the mixed samples. On the other hand, due to the electrostatic interactions between charged analytes and the surfactant, application of an electron mediator together with the ionic surfactant in the preparation of modified electrode, can be separate the voltammetric peaks of different compounds and improve the selectivity for their simultaneous detection. Respect to the charge sign of the ionic surfactant and various analytes, the electrostatic interactions can be exclusive or inclusive that is important for the improvement of the voltammetric resolution between the analytes peak. A Nafion/Reduced Graphene Oxide prepared film on a carbon electrode has been used in electrocatalytic oxidation of ascorbic acid [32]. Modification of carbon paste electrode using thionine/nafion ion pair has been reported [18]. This electrode has been successfully used for simultaneous voltammetric determination of AA and DA by a differential pulse voltammetric method. Neutral surfactants (e.g. triton X-100) have been used for modification of the glassy carbon electrode [33]. Results of this work revealed that the hydrophobicity of the surfactant at the surface of the electrode is effective in promoting the electrochemical response and the kinetic of the electron transfer process of the studied heme proteins.

In the present work, the electrochemical behavior of dopamine and ascorbic acid at the surface of the modified carbon paste electrode incorporating the Schiff base complex of cobalt/cationic surfactant is studied. Modification of the carbon paste electrode using the cationic surfactant causes an increase in the anodic overpotential for DA oxidation. In order to obtain a better sensitivity and resolution in the voltammetric response of the modified electrode, the effect of the cationic surfactant percent on the separation of the anodic peaks DA and AA is studied. Noteworthy advantages of the modified CPE in this work such as ease of fabrication and surface regeneration by simple polishing, excellent resolution between voltammetric responses of DA and AA and high stability of the Schiff base complex of cobalt and cationic surfactant in its matrix designate it very useful for the sensitive and selective simultaneous detection of DA and AA.

2. EXPERIMENTAL

2.1. Materials

For the synthesis of the complex N,N'-bis(3-ethoxysalicylidene)-4,5-dimethyl-1,2-phenylenediamino cobalt (II) chloride, 2 mmol $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was added to the ethanolic solution of 6,6'-diethoxy-2,2'-[2,3-dimethyl-propylenebis(nitrilomethylidyne)]-diphenol (2 mmol/30 ml) [34]. The mixture was stirred for 30 min with reflux then resultant was filtered and through slow evaporation of the solvents at room temperature over several days, the complex crystals were obtained [34]. Spectroscopic mineral oil (Nujol), Graphite powder (20 μm), 1-octanaminium,N,N,N-trioctyl bromide as a cationic surfactant, acetic acid, phosphoric acid, potassium acetate, potassium dihydrogen phosphate and potassium hydroxide were purchased from Merck. Ascorbic acid and dopamine were obtained from Aldrich and used as received. All the other chemicals were analytical reagent grade, purchased from Merck. Using doubly distilled deionized water, all aqueous solutions were made up.

Stock solutions of DA and AA were freshly made up in 0.10M acetate and phosphate buffer at the desired pH (3.0–7.0) and before voltammetric experiments, purged with pure nitrogen gas (99.999%) for 120 s. The buffered solutions of DA and AA was deoxygenated by purging the pure nitrogen (99.999% from Roham Gas Company), and then was used for voltammetric studies. Nitrogen gas was passed over the surface of the test solutions during the measurements, in order to avoid the influx of oxygen into the solution.

For the detection of the recovery in spiking of dopamine, the sample of fresh human serum prepared from Razi Institute of Vaccine and Serum Co. (Tehran, Iran), was filtered and diluted using a 0.1 M acetate buffer solution of pH 4.0. Each tablet was grounded with a mortar and pestle to detect AA in commercial vitamin preparations then 100 mg of the powdered sample was dissolved in 100 ml of the buffered solution.

2.2. Apparatus

Voltammetric measurements were performed using a computerized potentiostat/galvanostat Autolab model 302 (Eco Chemie Utrecht) controlled with General Purpose Electrochemical System

(GPES) software. A common three-electrode system was applied with a saturated Calomel reference electrode, a platinum wire as a counter electrode and unmodified or modified carbon paste working electrode. For making up the buffered solutions, a digital pH/mV/ion meter (CyberScan model 2500) was used.

2.3. Preparation of modified electrode

To prepare the unmodified CPE, a suitable amount of mineral oil with powder of graphite (~25:75, w/w) was mixed by hand mixing in a mortar and pestle, then a portion of the resulted mixture was packed into the end of a polyamide tube (ca. 2.5 mm i.d.). A copper pin makes the electrical contact into the back of the composite, in the polyamide tube. The cobalt Schiff base complex-modified carbon paste electrode was fabricated by mixing the Schiff base complex of cobalt (3%, w/w) with powder of graphite and a suitable amount of mineral oil, and then the resulted composite was dissolved in dichloromethane in order to better homogeneity and reproducibility by polishing the electrode surface. For fabrication of the cobalt Schiff base complex-modified carbon paste electrode containing surfactant, various percents of cationic surfactant together with 3 wt.% of Schiff base complex of cobalt, powder of graphite and a suitable amount of mineral oil were mixed in an appropriate amount of dichloromethane. The mixture was stirred by a magnetic stirrer till the solvent evaporated completely. The prepared modified composite was then air dried for 24 h and used in the same way as the case of the unmodified electrode.

3. RESULTS AND DISCUSSION

3.1. Voltammetric studies of AA at the prepared electrodes

Our previous work revealed that anodic overpotential for ascorbic acid oxidation is reduced and its oxidation process is catalyzed by cobalt Schiff base complexes [17]. The electrochemical behavior of 1 mM AA in a buffered solution of pH 4.0 at the surface of the unmodified CPE and the cobalt Schiff base complex-modified CPE containing various wt.% of cationic surfactant is investigated by cyclic voltammetry. Results of this study are shown in Fig. 1A. As can be observed at the surface of the unmodified carbon paste electrode, a relatively broad wave in 375 mV is appeared for the anodic oxidation of AA. However, by introducing the cobalt Schiff base complex in the matrix of the carbon paste electrode (CoL/CPE), the overpotential of AA oxidation is decreased to about 280 mV. At the surface of modified electrodes including cobalt Schiff base complex and different wt.% of cationic surfactant, the this overpotential is virtually constant and also, is the same as that for the modified electrode without any surfactant. A comprehensive explanation of the electrocatalytic oxidation of AA using the CoL/CPE is presented in the following. AA, with a pK_a of 4.17, mainly exists as a neutral form under the experimental condition (buffered solution with pH 4.0). Therefore, there is weak electrostatic interaction between the neutral form of AA and the cationic surfactant on the surface of the modified carbon paste electrode (CoL/CS/CPE). The differential pulse voltammograms (DPVs) for

the electrodes in this solution is shown in Fig. 1B. As can be seen, introducing the cobalt Schiff base complex in the matrix of the electrode causes to a decrease in the anodic peak potential of AA. For modified electrodes containing cobalt Schiff base complex and various wt.% of cationic surfactant, this potential is almost constant and also, is the same as that for the electrode without any surfactant.

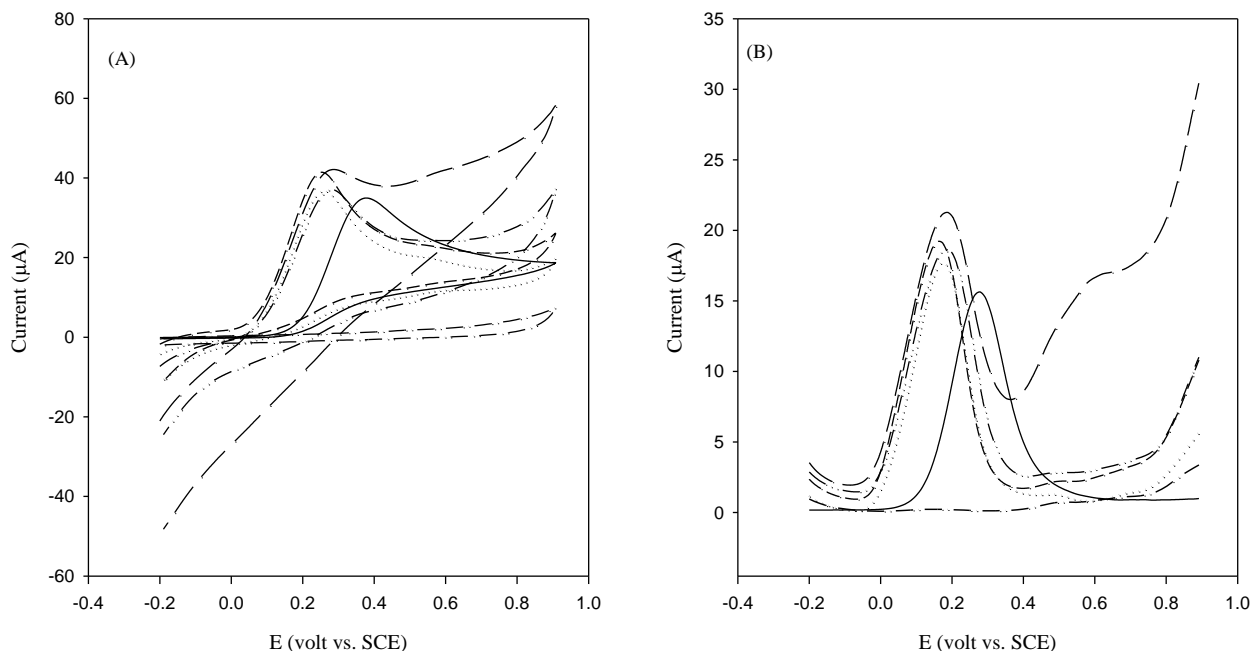


Figure 1. (A) CV and (B) DPV responses of blank buffered solution of pH 4.0 using CoL/modified CPE containing 2%CS (-.-) and of 1 mM AA in the same buffer at the surface of unmodified CPE (—), CoL/modified CPE containing 0%(.....), 1%(---), 2% (-.-) and 3%CS (- - -). Sweep rate: 100 mVs^{-1} ; pulse amplitude: 50 mV.

Results of this investigation reveal that the higher percents of cationic surfactant, because of decreasing the electrical conductivity of the electrode and unsuitable mechanical properties, cause worsening the voltammetric behavior of the modified electrode, e.g. enlargement of the capacitive background current, broadening the wave shape and lowering the anodic peak. Hence, the percent of cationic surfactant in the matrix of the modified carbon paste electrode is optimized to obtain the best resolution between the anodic peaks of DA and AA and also, better sensitivity in voltammetric responses (lower background current and greater anodic peak current).

3.2. Voltammetric studies of DA at the prepared electrodes

The electrochemical behavior of 1 mM DA in a buffered solution of pH 4.0 at the surface of the unmodified CPE and the cobalt Schiff base complex-modified CPE containing various wt.% of cationic surfactant is investigated by cyclic voltammetry. The results of this study are shown in Fig.

2A. A pair of redox peaks with anodic and cathodic peak potentials respectively, 552 and 68mV ($\Delta E_p = 484\text{mV}$) were observed for DA at CoL/CPE. In these experiments, the ratio of cathodic to anodic peak current ($I_{p,c}/I_{p,a}$) for DA was nearly 0.85. These results corroborate a quasi-reversible electrochemical reaction of DA at the surface of the cobalt Schiff base complex-modified CPE and relative stability of the oxidation product of DA under the empirical conditions (pH 4.0).

Results of previous literatures revealed that DA incorporated in an intermolecular 1 + 4 Michael nucleophilic addition in solutions of higher pHs [35] and the product of anodic oxidation of DA suffers a nucleophilic addition of its amine external group leading to leucodopaminochrome. Thus buffered solution of pH 4.0 was selected for all experiments of DA in order to obtain a simple electron transfer and prevent the following reactions in the mechanism of DA. On the other hand in solutions with $\text{pH} \leq 5$, DA contains protonated amine group and mostly exists in cationic form. Therefore, in acidic solutions the product of anodic oxidation of DA will be nearly stable and can be obtained a ratio of about 1 for $I_{p,c}/I_{p,a}$.

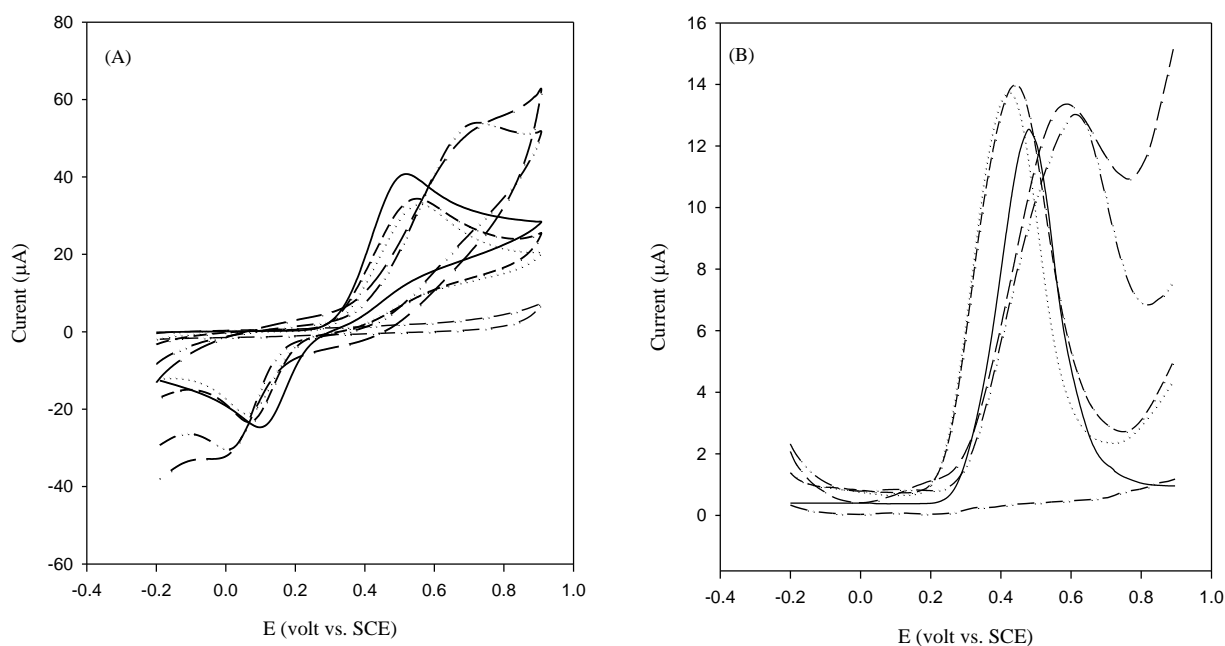


Figure 2. (A) CV and (B) DPV responses of blank buffered solution of pH 4.0 using CoL/modified CPE containing 2%CS (-.-) and of 1 mM DA in the same buffer at the surface of unmodified CPE (—), CoL/modified CPE containing 0% (.....), 1% (---), 2% (-.-) and 3%CS (---). Sweep rate: 100 mVs^{-1} ; pulse amplitude: 50 mV.

Application of the cationic surfactant in the matrix of the modified carbon paste electrode causes an increase in anodic overpotential of DA oxidation, because of the electrostatic repulsive interaction between the positive charge of cationic surfactant and the cationic form of DA at the surface of the modified electrode. As a result, the reversibility of the electrochemical process at the surface of the electrode is decreased (ΔE_p is increases) and the anodic peak of DA is appeared in more positive potentials. As can be seen in Fig. 2A by increasing the percent of cationic surfactant in the

matrix of the modified CPE, this effect is intensified. Fig. 2B shows the differential pulse voltammetric waves for prepared electrodes in this solution. As can be observed, the anodic overpotential of DA oxidation is increased by adding the cationic surfactant into the matrix of the modified CPE. The result of this effect is excellent resolution between the anodic peaks of AA and DA.

3.3. Voltammetric studies in the mixed solutions of DA and AA

Making an approach for separation of anodic peaks and simultaneous detection of AA and DA is very important in clinical and analytical chemistry. At the traditional solid electrodes, the anodic overpotential for oxidation of AA is the same as that of DA; furthermore, both of AA and DA are present simultaneously in mammalian brain which will cause to overlap the voltammetric responses of these species [36]. Many efforts have been made on the fabrication of the modified electrodes that are capable to separate the voltammetric responses and provide the feasibility of simultaneous determination of these compounds [21-26].

In order to simultaneous voltammetric determination of DA and AA, the cobalt Schiff base complex-modified CPE containing cationic surfactant was used. The electrochemical behavior of 1 mM of both DA and AA in a buffered solution of pH 4.0 at the surface of the unmodified CPE and the cobalt Schiff base complex-modified CPE containing various wt.% of cationic surfactant is investigated by cyclic voltammetry. The results of this study are shown in Fig. 3A. Fig. 3B shows the differential pulse voltammograms (DPVs) for these electrodes in this solution. These figures revealed that at the surface of the unmodified CPE, only a quasi-reversible wave can be observed for DA and a distinguished wave cannot be obtained for AA, therefore this electrode (unmodified-CPE) isn't suitable for the simultaneous detection of DA and AA. By introducing the cobalt Schiff base complex in the matrix of carbon paste electrode (CoL/CPE), a little resolution of anodic peaks of these compounds is obtained but the detection of each species in the presence of the other isn't possible because of the overlapping of their anodic peaks. Application of cobalt Schiff base complex-modified CPE containing cationic surfactant, results in more resolution of anodic peaks for DA and AA, due to positive shift of anodic peak of DA. As can be seen in Fig. 3, in the presence of 2 wt.% of cationic surfactant in the matrix of modified carbon paste electrode, the complete resolution between anodic peaks of DA and AA is obtained. The positive shift in anodic peak potentials of DA under the experimental condition (buffered solution of pH 4.0) is a result of the electrostatic repulsion effects between cationic surfactant and cationic form of dopamine. A better resolution does not obtained by using higher percents of cationic surfactant, whereas the sensitivity for response to DA is decreased because of the made anodic overpotential and kinetic limitation for DA. Moreover, this investigation revealed that the presence of higher percents of cationic surfactant in the matrix of modified CPE caused to increase the capacitive background current and limit the voltammetric detection limit for DA and AA. These efficacies can be obviously seen by comparing of the CVs or DPVs for the different modified CPEs in Fig. 3. As a result, the cobalt Schiff base complex-modified CPE containing 2 wt.% cationic surfactant was selected for simultaneous detection of DA and AA.

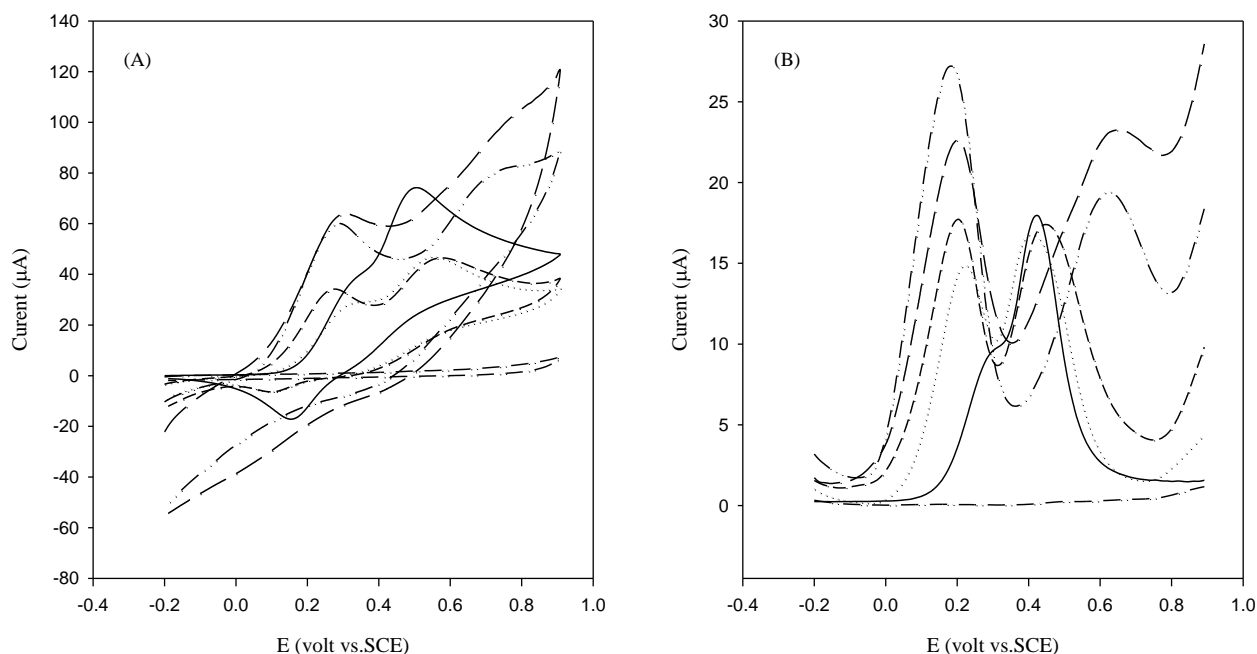


Figure 3. (A) CV and (B) DPV responses of blank buffered solution of pH 4.0 using CoL/modified CPE containing 2%CS (-.-) and of a mixture of 1 mM AA and 1 mM DA in the same buffer at the surface of unmodified CPE (—), CoL/modified CPE containing 0%(.....), 1%(- - -), 2%(-.-) and 3%CS(- - -). Sweep rate: 100 mVs^{-1} ; pulse amplitude: 50 mV.

The resulting resolution between the anodic peaks of DA and AA in this work (440 mV) is significantly more desirable than other reported voltammetric sensors. Glassy carbon electrode modified with nanocomposite of graphene and carbon dots/ferrocene derivative functional Au NPs obtained a peak resolution of ca. 180 mV for AA and DA using differential pulse voltammetry [37]. Application of a nanocomposite containing polypyrrole/ Cu_xO -ZnO in modification of glassy carbon electrode for voltammetric determination of AA and DA resulted in a peak separation of 150 mV [38]. The electrode modified with nanoparticles of $\gamma\text{-WO}_3$ is applied using differential pulse voltammetry for simultaneous detection of DA and AA and a peak separation of 133 mV is obtained [39]. In comparison to the reported works, the decay of current between anodic peaks of DA and AA is taken place close to the capacitive background by using the cobalt Schiff base complex-modified CPE containing cationic surfactant. The resulted decay of current significantly decreases the overlapping of the anodic waves of DA and AA, and simultaneous detection of these compounds in mixture samples possesses a more desirable accuracy. Moreover the reproducibility of the detections is improved, due to more stability of DA and AA in slightly acidic condition (pH 4.0).

3.4. The effect of pH and sweep rate

Voltammetric studies of the buffered solutions with different pHs containing AA and DA were carried out to find out the optimized pH for acquiring the maximum sensitivity and an excellent

resolution between their anodic peaks. In these experiments, 0.1 M acetate was applied in preparation of buffered solutions of pH 4.0 and 5.0, and 0.1 M phosphate for pHs 3.0, 6.0 and 7.0. Table 1 shows the peak currents and peak potentials of cyclic voltamograms obtained at the surface modified CPE in the mixture solutions of DA and AA with different pHs. These results reveal that the best peak separation is resulted in pH 4.0. Therefore in all voltammetric studies, the buffered solution with pH 4.0 was applied as supporting electrolyte.

In order to study of the effect of the potential scan rate, cyclic voltammetric experiments were carried out in the buffered solution with pH 4.0. The results revealed that the peak currents ($I_{p,a}$) of DA and AA vary linearly with the square root of the scan rate ($v^{1/2}$) in the range of 25–200 mVs^{-1} . These results corroborate the diffusion-controlled anodic oxidations of DA and AA at the surface of the modified CPE. The current function ($I_p/v^{1/2}$) for AA decreased with $v^{1/2}$, which corroborates a catalytic manner for AA at the surface of the modified CPE, whereas for DA can't be seen this effect.

Table 1. Variation of peak current and peak potential for mixture solutions of DA and AA with pH using CoL/modified CPE containing 2 wt.% of cationic surfactant

pH	AA		DA		ΔE_p
	$I_{p,a}$ (μA)	$E_{p,a}$ (mV)	$I_{p,a}$ (μA)	$E_{p,a}$ (mV)	
3	18.6	361	21.2	779	418
4	28.3	280	20.2	719	439
5	19.4	260	15.2	558	298
6	14.9	265	11.5	500	231
7	3.4	264	10.2	409	140

3.5. Analytical characterization

The differential pulse voltammetric method using the cobalt Schiff base complex-modified CPE containing 2 wt.% of cationic surfactant was applied as a sensitive electrochemical method with low detection limits for detections of AA and DA in a wide concentration range. Supporting electrolyte for these experiments was buffered solutions of pH 4.0. Fig. 4 shows some obtained DPV waves in these experiments. By drawing the anodic current signal versus the concentration (the calibration curves), a linear range is obtained that is 2.0×10^{-6} – 1.0×10^{-3} M for AA and 8.0×10^{-6} – 1.0×10^{-3} M DA (Fig. 5). A slope of 23344 $\mu\text{A/M}$ with $R^2 = 0.9975$ is resulted for AA, and a slope of 8348 $\mu\text{A/M}$ with $R^2 = 0.9935$ for DA. The relative standard deviations (R.S.D.) for these slopes on the basis of five replicates were 3.4 and 3.1% for DA and AA, respectively and were less than 3.5% for both DA and AA, based on six measurements in a period of one month. So the prepared modified CPE in this work revealed to be very stable.

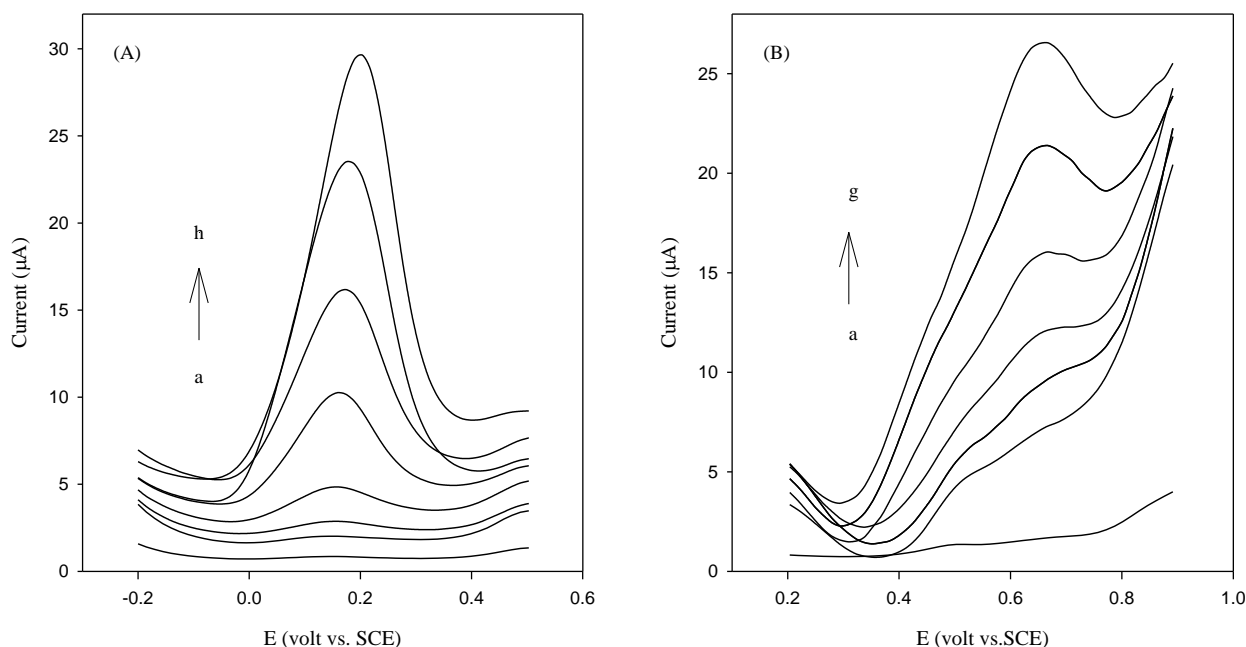


Figure 4. Differential pulse voltammograms of buffered solution of pH 4.0 containing (A): (a) 0.0, (b) 0.008, (c) 0.02, (d) 0.06, (e) 0.2, (f) 0.4, (g) 0.8 and (h) 1.0 mM AA and (B): (a) 0.0, (b) 0.02, (c) 0.08, (d) 0.2, (e) 0.4, (f) 0.8 and (g) 1.0 mM DA (down to up). Pulse amplitude: 50 mV.

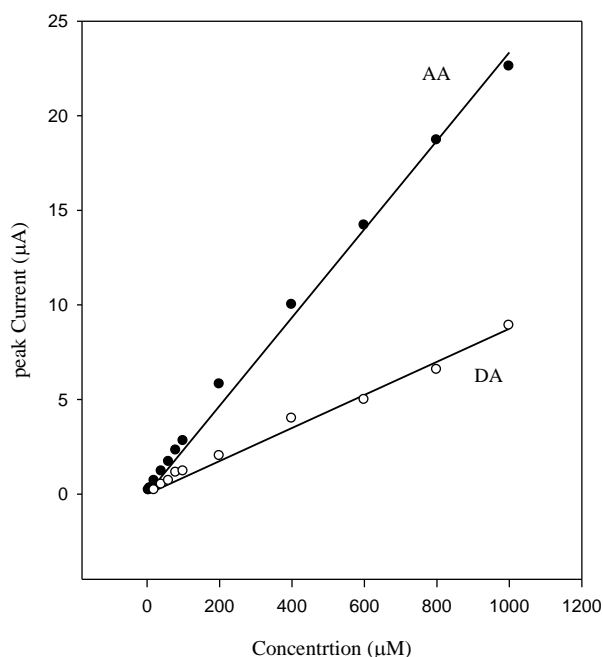


Figure 5. Linear calibration curves of anodic peak currents versus AA and DA concentration in the range 4.0 to 1000.0 µM.

The differential pulse voltammograms obtained in solutions containing 2×10^{-4} M AA and five various concentrations of DA from 8×10^{-5} to 8×10^{-4} M are shown in Fig. 6A. The waves obtained in

solutions containing 2×10^{-4} M DA and various concentrations of AA in the range of 8×10^{-5} to 1×10^{-3} M is represented in Fig. 6B. Using the modified CPE in this work, a linear range for AA in buffered solutions of pH 4.0 is acquired in the range from 4×10^{-6} to 1×10^{-3} M and for DA from 1×10^{-5} to 1×10^{-3} M. The respective detection limits ($S/N = 3$) were 2×10^{-6} M and 4×10^{-7} M for DA and AA, respectively. These linear ranges and detection limits were nearly similar to the detections in solutions containing only one of AA or DA. In the presence of 2×10^{-4} M AA, the slope of calibration curve For DA was $8121 \mu\text{A/M}$ with $R^2 = 0.9937$, which was about 97% of the slope value of the curve resulted from the separate solutions of DA. This slope for AA, in the presence of 2×10^{-4} M DA was $22878 \mu\text{A/M}$ with $R^2 = 0.9958$. Table 2 shows a comparison of analytical properties for the detection of DA and AA at the prepared electrode in this work and various electrodes.

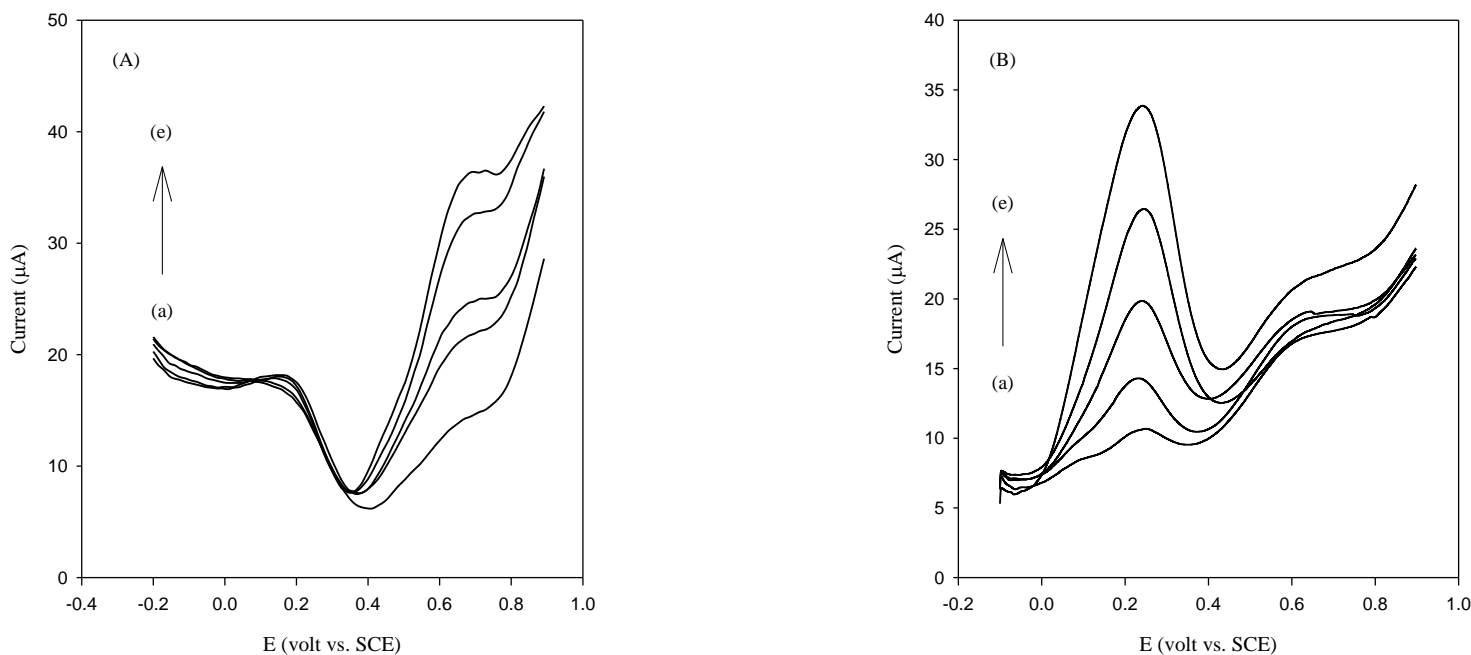


Figure 6. Differential pulse voltammograms for buffered solution of pH 4.0 containing (A) 0.2 mM AA (constant) and various concentrations of DA: (a) 0.08, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8 mM. (B) 0.2 mM DA (constant) and various concentrations of AA: (a) 0.08, (b) 0.2, (c) 0.4, (d) 0.8 and (e) 1.0 mM. Pulse amplitude: 50 mV.

The cobalt Schiff base complex-modified CPE containing 2 wt.% of cationic surfactant was successfully used in determination of AA in pharmaceutical preparations (single and multi-vitamins) using the standard addition method. The analyzed vitamin preparations were effervescent tablets (Osvah Co.), multivitamin drops (Shahre Daro Co.) and vitamin C tablets (Osvah Co.). The multivitamin drops in addition to vitamin C, contained vitamins A, D, E, B₁, B₂, B₃, B₆, and B₁₂ and sodium saccharin. As a reference method, the method of U.S. Association of Official Analytical Chemists (AOAC) [41] based on using 2,6-dichloro-phenolindophenol was used.

Table 2. Various modified electrodes: DA and AA analytical properties

Electrode	Experimental condition	Method	ΔE_p (mV)	Linear range (μA)		DL (μA)		Ref.
				DA	AA	DA	AA	
Carbon Paste-modified GCE	pH 7.0 PBS	DPV	187	3.84 - 27.0	19.2 - 135	1.5	8.3	[6]
CPE modified with [Cu(bp)(H ₂ O) ₂] _n	pH 5.0 PBS	DPV	200	0.05 - 30.0	0.05 - 30.0	0.04	0.02	[18]
GCE modified with CuNP/p-TA _{ox}	pH 4.0 PBS	DPV	205	0.6 - 21.6	240 - 750	0.03	5.0	[20]
Polyethylene oxide-modified GCE	pH 5.0 PBS	DPV	216	5.0 - 40	300 - 1700	0.25	50	[25]
CCE modified MWCNTs-MIP	pH 4.5 PBS	DPV	300	1.72-11.58	16.83-226	0.21	2.24	[26]
GCE modified with ZnO-Cu _x O-PPy	pH 4.0 BR solution	DPV	150	0.1-130	0.2-1.0	0.04	25.0	[38]
GCE modified with γ -WO ₃	pH 7.0 PBS	DPV	133	0.1-600	–	0.024	–	[39]
CoL/modified CPE containing 2 wt.% of cationic surfactant	pH 4.0 0.1M acetate buffer	DPV	440	8.0-1000	2.0-1000	2.0	0.4	This work

Note: CP, carbon paste; GCE, glassy carbon electrode; [Cu(bp)(H₂O)₂]_n, polymer of 4,4'-dicyanamidobiphenyl Cu(II) complex; CuNP, Copper nanoparticles; p-TA_{ox}, overoxidized poly(3-amino-5-mercapto-1,2,4-triazole); MWCNTs, multiwalled carbon nanotubes; MIP, molecularly imprinted polymer; PPy, polypyrrole; γ -WO₃, monoclinic structure of Tungsten trioxide nanoparticles.

The results of experiments in different vitamin samples together with the results of the spiked samples with AA standard solutions are shown in Table 3. These results reveal that the modified electrode in this work could be efficiently used for the detection of AA in pharmaceutical samples because of the good enough precision and recovery. This modified electrode was also used for the recovery measurement in dopamine hydrochloride spiking to human serum samples. The results of these experiments are shown in Table 4.

Table 3. Results of analysis of AA in vitamin preparations using CoL/modified CPE containing 2 wt.% of cationic surfactant

Sample	Sample preparation	AA found (mg/100 mg powdered sample) ^a		
		Present method	Reference method	Recovery (%)
1	Vitamin C tablet	64.6 (± 1.9)	65.2	-
2	Sample 1 + 10.0 mg AA	72.5 (± 2.1)	-	97.1
3	Sample 1 + 20.0 mg AA	86.8 (± 2.4)	-	102.6
4	Sample 1 + 30.0 mg AA	93.2 (± 2.2)	-	98.5
5	Effervescent tablet	30.2 (± 1.2)	31.4	-
6	Sample 5 + 10.0 mg AA	38.8 (± 1.1)	-	96.5
7	Sample 5 + 20.0 mg AA	49.5 (± 1.5)	-	98.6
8	Sample 5 + 30.0 mg AA	61.5 (± 0.14)	-	102.2
9	Multivitamin drop ^b	32.0 (± 1.5)	33.1	-
10	Sample 9 + 10.0 mg AA	41.2 (± 2.0)	-	98.1
11	Sample 9 + 20.0 mg AA	49.7 (± 2.0)	-	95.6
12	Sample 9 + 30.0 mg AA	60.4 (± 2.0)	-	97.4

^a Number of replicates was 5.

^b Labeled value for AA was 35 mg/ml. Determined values are also in mg/ml.

Table 4. Results of recovery of the spiked DA to 10.0 ml of the diluted (10-fold) human serum sample

No.	Amounts of added DA (μM)	Amounts of found ^a DA (μM)	Recovery (%)
1	10.0	10.4	104.0
2	25.0	24.7	98.8
3	50.0	50.2	100.4
4	75.0	74.4	99.2
5	100	96.2	96.2

^a R.S.D. for five replicates in the spiked range of DA concentration was less than 4.0%.

4. CONCLUSION

The cobalt Schiff base complex-modified CPE containing cationic surfactant prepared in the present work can enhance the resolution and selectivity of voltammetric responses of DA and AA. This modified CPE has been revealed to be capable to separate the voltammetric peaks of DA and AA. Resulted resolution is much better than the previous reported works. Application of the modified CPE in differential pulse voltammetric method in this work, results in a good resolution more than 400mV for anodic peaks of DA and AA making it very appropriate and useful for simultaneous detection of these compounds. Very easy preparation and surface regeneration of the modified electrode together with the acceptable selectivity and sensitivity, low detection limit and good reproducibility make the prepared system very effective in the fabrication of accessible tools for the simultaneous detection of DA and AA in pharmaceutical and clinical preparations.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the Payame Noor University providing research facilities for this work.

References

1. T. Selvaraju and R. Ramaraj, *Electrochem. Commun.*, 5 (2003) 667.
2. G. P. Jin and X. Q. Lin, *Electrochem. Commun.*, 6 (2004) 454.
3. R. M. Wightman, C. Amatorh, R. C. Engstrom, P. D. Hale, E. W. Kristensen, W. G. Kuhr and L. J. May, *Neuroscience*, 25 (1988) 513.
4. A. J. Downard, A. D. Roddick and A. M. Bond, *Anal. Chim. Acta*, 317 (1995) 303.
5. D. W. Martin Jr., P. A. Mayes, V. W. Rodwell (Eds.), *Harper's Review of Biochemistry*, 19th ed., Lange, (1983) Los Altos, CA, p. 112.
6. Y. Li, L. Huang, S. M. Chen, B. S. Lou and X. Liu, *Int. J. Electrochem. Sci.*, 10 (2015) 7671.
7. A. Ciszewski and G. Milczarek, *Anal. Chem.*, 71 (1999) 1055.
8. R. Salgado, R. del Rio, M. A. del Valle and F. Armijo, *J. Electroanal. Chem.*, 704 (2013) 130.
9. J. W. Mo and B. Ogorevc, *Anal. Chem.*, 73 (2001) 1196.
10. H. Razmi, M. Agazadeh and B. Habibi-A, *J. Electroanal. Chem.*, 547 (2003) 25.
11. J. Oni, P. Westbroek and T. Nyokong, *Electroanalysis*, 15 (2003) 847.
12. A. Kutluay and M. Aslanoglu, *Anal. Chim. Acta*, 839 (2014) 59.
13. S. Y. Ly, *Bioelectrochem.*, 68 (2006) 227.
14. B. Yu, H. Yuan, Y. Y. Yang, H. L. Cong, T. Z. Hao, X. D. Xu, X. L. Zhang, Sh. J. Yang and L. X. Zhang, *Chinese Chem. Lett.*, 25 (2014) 523.
15. C. Y. Yang, Y. T. Hung, S. M. Chen, T. H. Tsai, B. S. Lou and X. Liu, *Int. J. Electrochem. Sci.*, 10 (2015) 1128.
16. D. Ragupathy, A. I. Gopalan and K. Lee, *Sens. Act. B*, 143 (2010) 696.
17. S. Shahrokhian and H. R. Zare-Mehrjardi, *Electrochim. Acta*, 52 (2007) 6310.
18. P. Kalimuthu and S. A. John, *Talanta*, 80 (2010) 1686.
19. C. Y. Yang, S. M. Chen and S. Palanisamy, *Int. J. Electrochem. Sci.*, 11 (2016) 2638.
20. B. B. Prasad, D. Jauhari and M. P. Tiwari, *Biosens. Bioelectron.*, 50 (2013) 19.
21. S. B. A. Barros, A. Rahim, A. A. Tanaka, L. T. Arenas, R. Landers and Y. Gushikem, *Electrochim. Acta*, 87 (2013) 140.
22. M. K. Amini, S. Shahrokhian, S. Tangestaninejad and V. Mirkhani, *Anal. Biochem.*, 290 (2001) 277.
23. S. Shahrokhian and M. Karimi, *Electrochim. Acta*, 50 (2004) 77.
24. S. Shahrokhian and M. Ghalkhani, *Electrochim. Acta*, 51 (2006) 2599.
25. H. R. Zare, N. Nasirizadeh and M. M. Ardakani, *J. Electroanal. Chem.*, 577 (2005) 25.
26. S. B. Khoo and F. Chen, *Anal. Chem.*, 74 (2002) 5734.
27. S. Shahrokhian, A. Soury and H. Khajehsharifi, *J. Electroanal. Chem.*, 565 (2004) 95.
28. S. Shahrokhian and M. J. Jannat-Rezvani, *Microchim. Acta*, 151 (2005) 73.
29. S. Shahrokhian, M. Karimi and H. Khajehsharifi, *Sens. Act. B*, 109 (2005) 278.
30. S. Shahrokhian and H. R. Zare-Mehrjardi, *Electroanalysis*, 19 (2007) 2234.
31. S. Shahrokhian and H. R. Zare-Mehrjardi, *Sens. Act. B*, 121 (2007) 530.
32. W. Liao, C. Guo, L. Sun, Z. Li, L. Tian, J. He, J. Li, J. Zheng, Z. Ma, Z. Luo and C. Chen, *Int. J. Electrochem. Sci.*, 10 (2015) 5747.
33. K. Chattopadhyay and S. Mazumdar, *Bioelectrochem.*, 53 (2000) 17.
34. R. Kia, H. Kargar, K. Zare and I. U. Khan, *Acta Cryst.*, E66 (2010) m366.
35. H. Zhao, Y. Zhang and Z. Yuan, *Anal. Chim. Acta*, 441 (2001) 117.
36. E. W. Kristensen, W. G. Kuhr and R. M. Wightman, *Anal. Chem.*, 59 (1987) 1752.

37. L. Yang, N. Huang, Q. Lu, M. Liu, H. Li, Y. Zhang and S. Yao, *Anal. Chim. Acta*, 903 (2016) 69.
38. Kh. Ghanbari and N. Hajheidari, *Anal. Biochem.*, 473 (2015) 53.
39. A. C. Anithaa, N. Lavanya, K. Asokan and C. Sekar, *Electrochim. Acta*, 167 (2015) 294.
40. A. J. Bard, L. L. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, 2nd Ed., Wiley, (2001) New York, USA.
41. P. Gunniff (Ed.), *Official Methods of Analysis of the Association of Official Analytical Chemists (AOAC)*, vol. 2, 16th ed., Association of Official Analytical Chemists, (1995) Arlington, VA.

© 2017 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).