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## Determination of Se(IV) as a 5-nitropiazselenol complex by adsorptive stripping voltammetry at an *in situ* plated bismuth film electrode

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In this paper a simple, selective, sensitive and reproducible stripping method based on adsorption of Se(IV) in the form of a 5-nitropiazselenol complex at the surface of an *in situ* plated bismuth film electrode was introduced. All affecting parameters on adsorption, stripping and complex formation steps were evaluated and studied. Under optimum conditions the established calibration curve obeyed the linear regression equation in the range of 2 to 50  $\mu\text{g L}^{-1}$  of Se(IV) concentrations. The estimated detection and quantification limits were 0.05 and 0.15  $\mu\text{g L}^{-1}$  of Se(IV), respectively. In addition, the mean and RSD for determination of 5  $\mu\text{g L}^{-1}$  of Se(IV) were calculated to be 4.91 and 2.8% ( $n = 5$ ). The accuracy of the method was certified by comparison of the results obtained from the proposed method and those obtained from ICP-OES as the reference method.

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### Introduction

Selenium as an essential trace element has a special role in human's diet. In the human body, many vital processes are affected by selenium compounds. Selenium is present in 25 identified selenoproteins<sup>1,2</sup> such as glutathione peroxidase (GPx) which has the ability to reduce inorganic ( $\text{H}_2\text{O}_2$ ) and organic peroxides (ROOH), and iodothyronine deiodinase which catalyzes thyroxine deiodation to triiodothyronine.<sup>1</sup> Selenium prevents heart diseases, has anti-inflammatory properties, stimulates the immune system, and acts antagonistically to some heavy metals.<sup>1,3</sup> On the other hand excessive selenium intake can cause serious health problems, including selenosis, severe neuronal lesions, gastrointestinal and respiratory symptoms, kidney failure and cardiac disorders.<sup>2</sup> The World Health Organization recommends a daily selenium dose of 30 to 40  $\mu\text{g}$  for adults.<sup>1</sup> The biomonitoring equivalents associated with assuring adequate selenium intake are 100, 80 and 10  $\mu\text{g L}^{-1}$  in whole blood, plasma and urine, respectively.<sup>4</sup>

Essentiality or toxicity of selenium was influenced by its concentration and chemical form,<sup>5</sup> therefore speciation and determination of selenium at trace levels and in different matrices is important. In recent years a variety of sensitive instrumental methods like HPLC-ICP-MS,<sup>6,7</sup> HPLC-MS/MS,<sup>8</sup> GC-ICP-MS,<sup>9</sup> GC-MS,<sup>10</sup> HG-ICP-OES,<sup>11</sup> AAS<sup>12,13</sup> and UV-Vis spectrophotometric methods<sup>14</sup> were successfully used for separation, identification and determination of selenium compounds in

different samples. Most of these techniques are time consuming and expensive.

Among analytical methods, electrochemical techniques, because of their sensitivity, simplicity, easy operation and speed, are more popular. During the last decade of 1990s, a number of polarographic<sup>15–17</sup> and voltammetric<sup>18–24</sup> methods were proposed for determination of Se(IV) at the mercury based electrode surface. The toxicity of mercury limits the applicability of these methods; therefore several alternative electrode materials including gold and platinum,<sup>25</sup> copper amalgam,<sup>26</sup> bismuth<sup>27,28</sup> and silver<sup>29</sup> have been suggested.

Bismuth electrodes have been introduced as a suitable replacement for mercury due to their low toxicity and similar electrochemical behavior.<sup>30</sup> In recent years various kinds of bismuth modified electrodes have been widely used for electroanalysis of heavy metals,<sup>31–36</sup> drugs,<sup>37–39</sup> pesticides,<sup>40–42</sup> azo, nitro aromatic and other organic compounds.<sup>43–48</sup>

Voltammetric behavior of Se(IV) at the bismuth electrode surface has been investigated by some authors and proposed analytical procedures have been used for selenium analysis in different samples.<sup>27,28</sup> In this paper a new method for selenium determination based on *in situ* bismuth film formation and simultaneous adsorption of Se(IV) as a 5-nitropiazselenol complex on the electrode surface has been introduced. All effective parameters were studied and optimal conditions were evaluated. The efficiency of the procedure was examined by determining the selenium contents of whole blood and urine samples and comparing the obtained results with the ICP-OES results as the standard method.

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## Experimental

### Chemical reagents

All chemicals were of analytical grade and were used without any purification. HCl,  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , 4-nitro-1,2-phenylenediamine (4-NoPD) (>97%),  $\text{CH}_3\text{COOH}$ , NaOH,  $\text{HNO}_3$ ,  $\text{H}_2\text{O}_2$  and cation salts were purchased from Merck (Darmstadt, Germany). Selenium standard solutions were prepared by dilution of a  $1000 \text{ mg L}^{-1}$  AAS standard (Bernd Kraft GmbH, Duisburg, Germany). All solutions were prepared with double distilled water with a specific conductance of  $2 \mu\text{S cm}^{-1}$ .

### Apparatus

A potentiostat 757 Computrace (Metrohm, Herisau, Switzerland), equipped with glassy carbon, platinum wire and saturated calomel electrodes as working, auxiliary and reference electrodes, respectively, was used for adsorptive stripping analysis. All potentials were measured vs. SCE. An ICP-OES (Varian Vista-PRO, Springvale, Australia) was used to assess the obtained results by the proposed method. The operating conditions were: frequency of RF generator: 40 MHz, RF generator power: 1.2 kW, plasma gas flow rate:  $15 \text{ L min}^{-1}$ , auxiliary gas flow rate:  $1.5 \text{ L min}^{-1}$ , nebulizer pressure: 240 kPa, viewing height: 12 mm, and wavelength used: 196.09 nm. All microwave digestions were run on a Milestone MLS-1200 MEGA (FKV, Bergamo, I).

### Analytical procedure

For synthesis of a 5-nitropiazselenol complex, 10 mL solution containing  $5 \times 10^{-4} \text{ M}$  of 4-nitro-1,2-phenylenediamine as the ligand, 0.01 M HCl (pH = 2) and different amounts of  $\text{Se}(\text{IV})$  were heated in a water bath at  $80^\circ\text{C}$  for 10 minutes. The solution was then cooled to room temperature. After addition of  $\text{Bi}(\text{III})$  and adjusting pH to 4 (the final solution containing  $50 \text{ mg L}^{-1} \text{ Bi}(\text{III})$  and 0.4 M acetate buffer), the solution was transferred into a voltammetric cell. The deposition step was carried out by applying a potential of  $-0.4 \text{ V}$  for 90 s. In the next step, the electrode was rinsed with water and the solution was replaced with 10 mL HCl 0.4 M and the voltammogram was recorded by sweeping the potential from  $-0.4$  to  $-0.75 \text{ V}$  in differential pulse mode. The DP parameters included pulse amplitude: 50 mV, pulse time: 0.04 s, voltage step: 5 mV, voltage step time: 0.4 s and sweep rate:  $15 \text{ mV s}^{-1}$ . According to the suggested mechanism for the electrode reaction, the formation of  $\text{Bi}_2\text{Se}_3$  causes the change of electrode surface composition. Therefore the renewing of the electrode surface is necessary for each measurement, so after each analysis the surface of the electrode was cleaned with 0.3–0.05  $\mu\text{m}$  alumina slurry and rinsed with double distilled water.

## Results and discussion

### Electrochemical behavior of 5-nitropiazselenol at the bismuth film electrode

Fig. 1 shows the electrochemical behaviors of  $\text{Se}(\text{IV})$  ( $50 \mu\text{g L}^{-1}$ ), 4-NoPD ( $5 \times 10^{-4} \text{ M}$ ) and the 5-nitropiazselenol complex

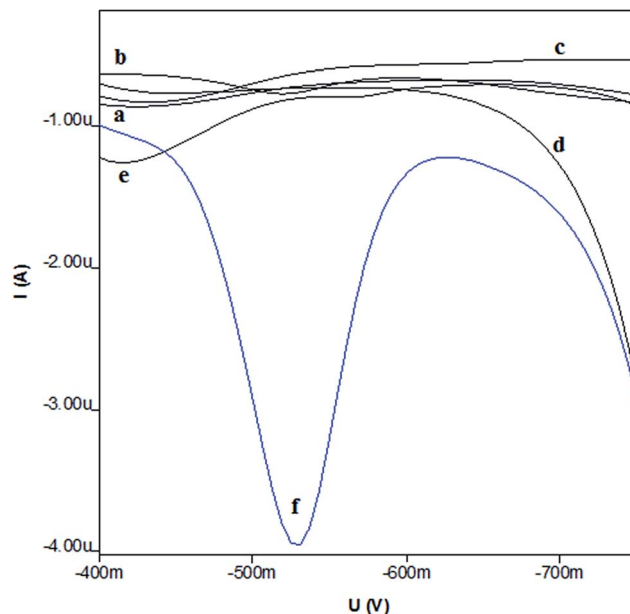


Fig. 1 The voltammograms of  $50 \mu\text{g L}^{-1}$  of  $\text{Se}(\text{IV})$  (without (a) and after addition of  $\text{Bi}(\text{III})$  (b)),  $5 \times 10^{-4} \text{ M}$  4-nitro-1,2-phenylenediamine (without (c) and after addition of  $\text{Bi}(\text{III})$  (d)) and 4-nitropiazselenol complex (without (e) and after addition of  $\text{Bi}(\text{III})$  (f)).

(formed by  $50 \mu\text{g L}^{-1}$  of  $\text{Se}(\text{IV})$ ) on glassy carbon and *in situ* plated bismuth film electrodes. Comparison of the obtained results revealed that the necessary conditions for the cathodic peak to appear are formation of the piazselenol complex and the presence of the bismuth film at the electrode surface. In other cases adsorption of electro-active species at the electrode surface is negligible and the related peak cannot be observed in those situations.

### Optimization of experimental conditions

All important parameters which could affect the experimental results were determined and the dependence of related cathodic signals on these parameters was evaluated. For deposition of the bismuth film and simultaneous adsorption of the piazselenol complex, time and applied potential, buffer pH and its concentration, bismuth concentration and the concentration of HCl during stripping were assumed as main factors. In addition, for piazselenol formation, time, temperature, pH and ligand concentration were considered as effective factors.

### Effect of buffer's pH and its concentration

The pH of supporting electrolytes is considered as an important factor in many electrochemical systems. Sometimes the reaction mechanism is very sensitive to the pH value and with small changes in pH, the reaction changes. Therefore the buffer's pH can play an important role in bismuth film formation and piazselenol adsorption processes. The influence of pH on cathodic peak current was examined in the range of the pH = 0 to 6 by using different HCl and acetate buffer solutions (the pHs of 0, 1 and 2 were achieved by using HCl solutions and pHs of 3

to 6 were achieved by using acetate buffer solutions with a total concentration of 0.4 M). The obtained results are shown in Fig. 2. With pH increasing from 0 to 4 a rising trend in peak current can be observed. At a pH value of 4 to 5 the maximum current was recorded but at pH = 6, due to low solubility of bismuth and 4-NoPD, the peak current decreased.

The concentration of buffer is another factor which can control the ionic strength and buffer capacity. To study the effect of buffer concentration, the deposition of the bismuth film and simultaneous adsorption of the piazselenol complex were carried out in the presence of different concentrations of acetate buffer solution in the range of 0.1 to 0.9 M. The relationship between the buffer concentration and peak current was also investigated. According to the obtained results the highest peak current corresponded to the buffer solution with a concentration of 0.4 M. Therefore the concentration of 0.4 M and pH = 4 were chosen as optimum values.

### Effect of bismuth concentration

Certainly, the properties of the deposited bismuth film are affected by the concentration of Bi(III) in electrolysis solution. To investigate how this factor can influence cathodic peak current, a set of experiments with various concentrations of Bi(III) (5–80 mg L<sup>-1</sup>) were performed. Comparison of the obtained results shows that the highest peak current could be achieved at a concentration of Bi(III) equal to 50 mg L<sup>-1</sup> (Fig. 3). Probably, in other concentrations the resulting film thickness is not suitable and does not show appropriate performance.

### Effect of applied potential and deposition time

During the deposition step, the bismuth film was formed at the electrode surface and simultaneous adsorption of the piazselenol complex on the surface of the *in situ* plated film occurred. Therefore selection of a suitable potential and time for the deposition step is very important. In order to evaluate the influence of applied potential on peak current, this factor was changed between -0.2 and -0.6 V (the pH of electrolysis

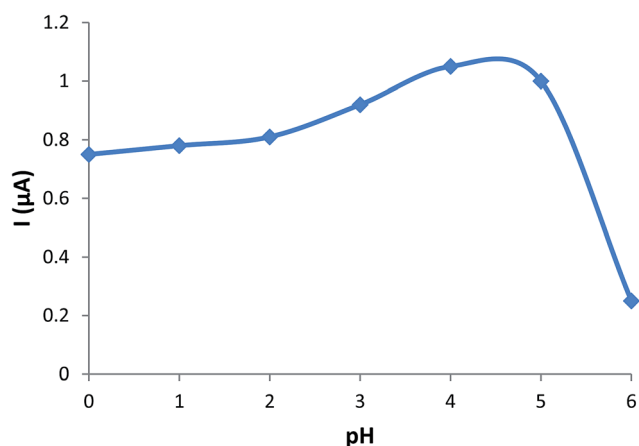


Fig. 2 The effect of buffer's pH on peak current, [Se(IV)] = 20 μg L<sup>-1</sup>, [4-NoPD] = 5 × 10<sup>-4</sup> M, [Bi(III)] = 50 mg L<sup>-1</sup>, [buffer] = 0.4 M, *t*<sub>dep</sub> = 100 s, *E*<sub>dep</sub> = -0.4 V, *t*<sub>reaction</sub> = 10 min, pH<sub>reaction</sub> = 2, *T*<sub>reaction</sub> = 60 °C.

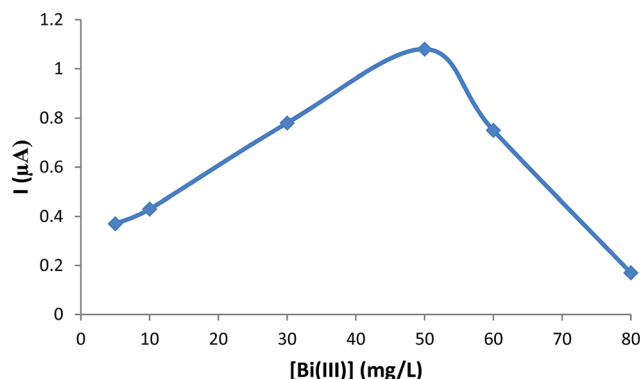


Fig. 3 The effect of Bi(III) concentration on peak current, [Se(IV)] = 20 μg L<sup>-1</sup>, [4-NoPD] = 5 × 10<sup>-4</sup> M, [buffer] = 0.4 M, pH<sub>buffer</sub> = 4, *t*<sub>dep</sub> = 100 s, *E*<sub>dep</sub> = -0.4 V, *t*<sub>reaction</sub> = 10 min, pH<sub>reaction</sub> = 2, *T*<sub>reaction</sub> = 60 °C.

solutions was adjusted to 4). The obtained results are illustrated in Fig. 4. As it is evident, the peak current remained constant by applying a potential in the range of -0.4 to -0.6 V. However, to avoid the interference effect of coexisting ions, a potential of -0.4 V was selected as the optimum value. To confirm that the chosen potential is suitable and interference effects of coexisting ions are avoided, some experiments in the absence of Se(IV) were carried out and no considerable peak was observed.

In the next step to estimate a suitable time for deposition of the bismuth film and also accumulation of the Se(IV) complex, the potential of -0.4 V was applied to the electrode for different time intervals and the resulting peak currents were recorded. The results showed that the highest peak current was obtained at a time of 90 s.

### Effect of HCl concentration in the stripping step

Undoubtedly, the supporting electrolyte and its concentration play an important role in electrochemical reactions. In some cases two main factors including peak current and its potential could be easily changed by using another electrolyte or changing its concentration or pH. Therefore finding a suitable electrolyte is a substantial issue. According to some primary studies, HCl, H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> were used as the electrolyte

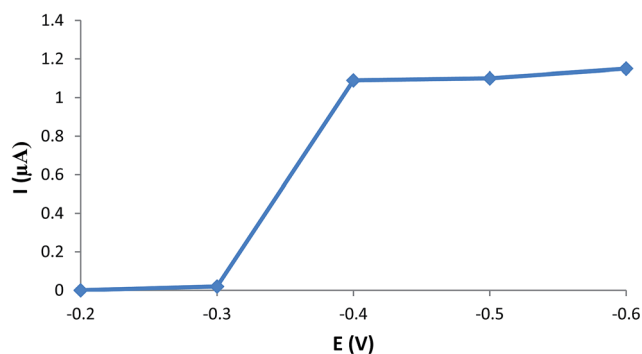


Fig. 4 The effect of applied potential on peak current, [Se(IV)] = 20 μg L<sup>-1</sup>, [4-NoPD] = 5 × 10<sup>-4</sup> M, [buffer] = 0.4 M, pH<sub>buffer</sub> = 4, *t*<sub>dep</sub> = 100 s, *t*<sub>reaction</sub> = 10 min, pH<sub>reaction</sub> = 2, *T*<sub>reaction</sub> = 60 °C.

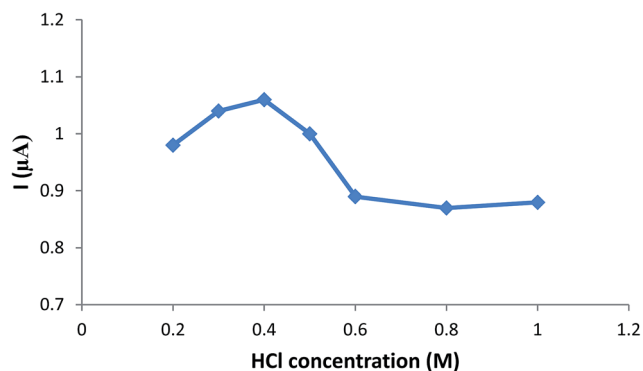
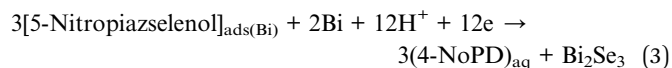
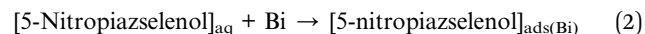
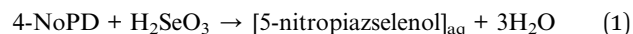


Fig. 5 The effect of HCl concentration on peak current in the stripping step,  $[\text{Se(IV)}] = 20 \mu\text{g L}^{-1}$ ,  $[\text{4-NoPD}] = 5 \times 10^{-4} \text{ M}$ ,  $[\text{buffer}] = 0.4 \text{ M}$ ,  $\text{pH}_{\text{buffer}} = 4$ ,  $E_{\text{dep}} = -0.4 \text{ V}$ ,  $t_{\text{dep}} = 90 \text{ s}$ ,  $t_{\text{reaction}} = 10 \text{ min}$ ,  $\text{pH}_{\text{reaction}} = 2$ ,  $T_{\text{reaction}} = 60^\circ\text{C}$ .

during the stripping step. In  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$  media, the obtained voltammograms were undefined with high background current, but a defined peak with low background current was obtained in HCl medium. Therefore HCl was selected as the best electrolyte for the stripping step. In the next step, in order to determine the optimum supporting electrolyte concentration, the proposed analytical procedure was repeated in the presence of HCl solutions with a concentration of 0.2 to 1 M. The cathodic peak disappears in diluted HCl solutions ( $<0.2 \text{ M}$ ). The highest current could be obtained in the presence of 0.4 M HCl and at higher concentrations, the peak current remains nearly constant (Fig. 5). In addition, by changing the HCl concentration from 0.2 to 1 M, the peak potential shifted from  $-0.537$  to  $-0.513 \text{ V}$ .

### 5-Nitropiazselenol formation and electrode reaction

In this study, the electrode reaction can be explained as follows:



As can be inferred from the above equations and referring to Fig. 1, 5-nitropiazselenol is the only electro-active species which can be adsorbed at the electrode surface. Therefore the kinetics of the first reaction can affect the sensitivity of the proposed method. For this reason, the factors which could affect the rate of the first reaction like time, temperature, pH and 4-NoPD concentration were studied. The obtained results are demonstrated in Fig. 6. Based on the collected data, the optimum conditions for synthesis of piazselenol are as follows: a temperature of  $80^\circ\text{C}$ , a reaction time of 10 min,  $5 \times 10^{-4} \text{ M}$  of 4-NoPD and  $0.01 \text{ M}$  HCl.

### The effect of foreign ions

Accepting an error of 5% in peak currents of  $20 \mu\text{g L}^{-1}$  of selenium, 2-fold concentration of  $\text{Pb(II)}$ , 10-fold concentrations of cations such as  $\text{Cd(II)}$ ,  $\text{Zn(II)}$ ,  $\text{Co(II)}$ ,  $\text{Mn(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Fe(III)}$ ,  $\text{Cr(III)}$  and 1000-fold concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  did not interfere in selenium determination. In addition to that, 1000-fold concentrations of anions including  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  did not show any interfering effect.

On the other hand, in the presence of 10-fold concentrations of  $\text{Cu(II)}$  and  $\text{Hg(II)}$ , an increase in peak current could be observed. According to the work of some authors<sup>49,50</sup> the  $\text{Cu(II)}$  can also form complex with *o*-phenylenediamine compounds and the stability constant of these complexes are about  $10^6$ , but the conditional stability constant of  $\text{EDTA-Cu(II)}$  (at  $\text{pH} = 4$ ) was greater than this. Therefore by addition of EDTA at  $\text{pH} = 4$ , the

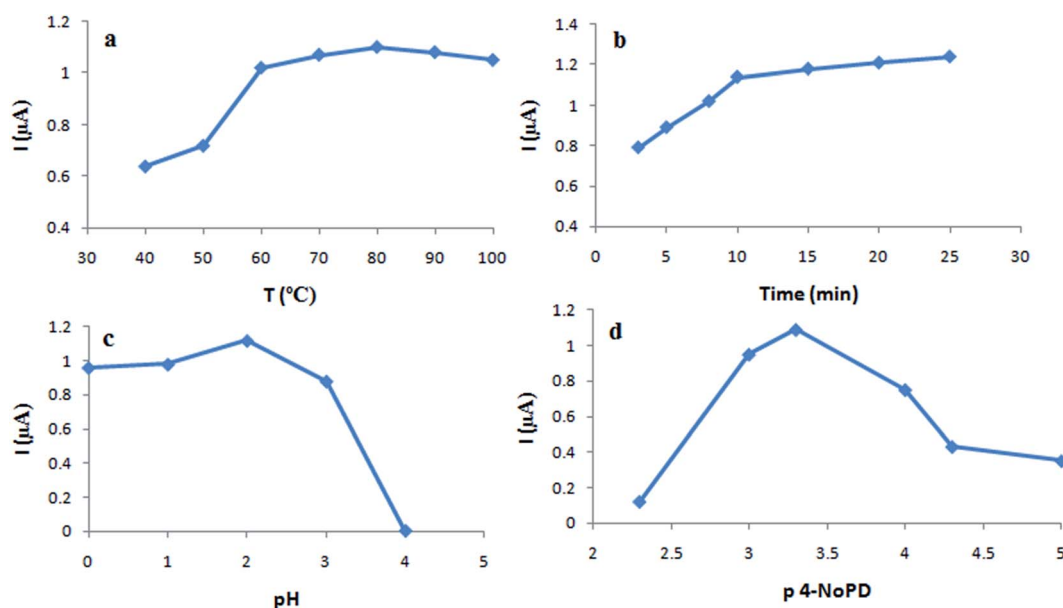


Fig. 6 The effect of temperature (a), time (b), pH (c) and the concentration of 4-NoPD (d) on 5-nitropiazselenol formation reaction,  $[\text{Se(IV)}] = 20 \mu\text{g L}^{-1}$ ,  $[\text{buffer}] = 0.4 \text{ M}$ ,  $\text{pH}_{\text{buffer}} = 4$ ,  $E_{\text{dep}} = -0.4 \text{ V}$ ,  $t_{\text{dep}} = 90 \text{ s}$ .

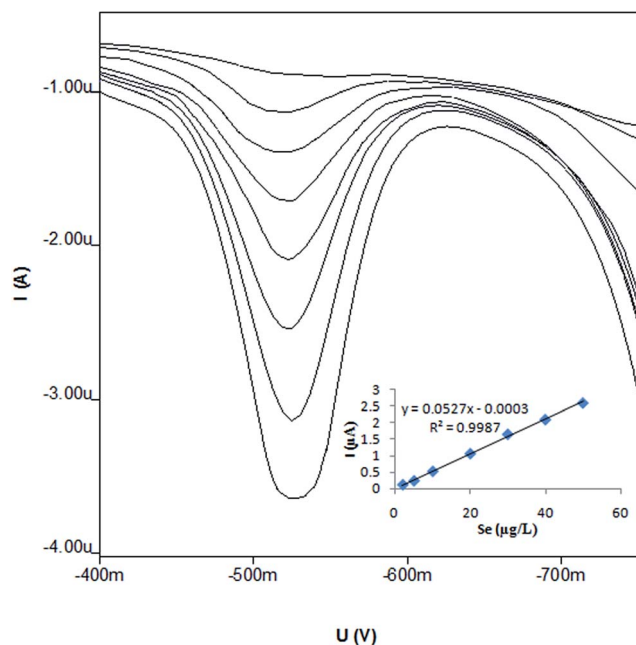


Fig. 7 The differential pulse voltammograms of 0, 2, 5, 10, 20, 30, 40 and 50  $\mu\text{g L}^{-1}$  Se(IV) under optimum conditions. Inset figure shows the dependence of peak current on Se(IV) concentration.

interference of Cu(II) can be eliminated. The concentration of EDTA and maximum tolerable of Cu(II) were  $1 \times 10^{-3}$  M and 10-fold concentration of Se(IV). Mercury interference was not eliminated with EDTA and it can be explained by the formation of the Bi/Hg film at the electrode surface and tendency of this film to adsorb piразselenol.<sup>23</sup>

### Analytical figures of merit

Under optimum conditions, the voltammograms of Se(IV) (as 5-nitropiazselenol) in the concentration range of 2 to 50  $\mu\text{g L}^{-1}$  were recorded. The linear relationship between the cathodic peak current and selenium concentration was shown in the form of calibration curve with the linear regression equation  $I (\mu\text{A}) = 0.0527C (\mu\text{g L}^{-1}) - 0.0003$  ( $R^2 = 0.9987$ ) (Fig. 7). The limits of detection and quantification estimated from 10 times background noise measurement were about 0.05 and 0.15  $\mu\text{g L}^{-1}$ , respectively ( $C = k\delta_B/b$ , in which  $\delta_B$  is the standard

deviation of the population of blank responses,  $b$  is the slope of the regression line and  $k = 3.3$  and 10 for detection and quantification limits).<sup>51</sup> The mean and relative standard deviation for five determinations of 5  $\mu\text{g L}^{-1}$  of Se(IV) were 4.91 and 2.8%. The analytical features of some reported methods for selenium determination are summarized in Table 1. It is evident that the detection limit and linear range of the proposed method are comparable with those of published methods and because of its good performance; it can be easily applied for selenium analysis in various samples.

### Analysis of real samples

In order to evaluate the capability of the proposed method in analysis of real samples, this procedure was applied for determination of selenium contents in blood and urine samples. Blood and urine samples were obtained from healthy university students. The donors were not under medical treatment and did not receive specific dietary instructions. Blood samples of approximately 5 mL were collected in plastic tubes containing heparin as an anticoagulant and digested as received. The urine samples were collected in sterilized polypropylene containers, stored at 4 °C and analyzed within 24 h. Sampling and analysis of blood and urine were in compliance with the relevant laws and under guidelines of research committee of Guilan University. Before analysis for elimination of organic compounds and other interfering agents, the samples were digested according to the method reported elsewhere.<sup>52</sup> Briefly, an aliquot of 0.5 mL blood samples or 2.5 mL urine samples was added to 2.5 mL an oxidizing acid mixture containing nitric acid (65%, w/w), hydrogen peroxide (30%, w/w) in a volume ratio of 5 : 1 and 0.25 g mL<sup>-1</sup> NaCl. Microwave digestion was carried out during three steps as follows: 2 min with an irradiation power of 250 W; 2 min with 0 W and 15 min with 300 W. Then the digested samples were cooled to room temperature and neutralized to pH = 2. After addition of 4-NoPD as the ligand to the solutions, the treated samples were diluted to 10 mL with HCl 0.01 M and used for 5-nitropiazselenol synthesis. All measurements were carried out three times by three standard additions (40, 80, 120 ng of Se(IV) per mL of blood samples and 10, 20, 40 ng of Se(IV) per mL of urine samples). The obtained results are shown in Table 2, in addition, the ICP-OES results were presented as a

Table 1 Analytical characteristic of some stripping voltammetric methods for determination of Se(IV)

Electrode	Method	Electroactive species	Detection limit ( $\mu\text{g L}^{-1}$ )	Analytical range ( $\mu\text{g L}^{-1}$ )	Ref.
TMFE <sup>a</sup>	AdsDPCSV <sup>b</sup>	5-Nitropiazoselenol	0.06	2–20	23
TMFE	AdsDPCSV	Se-I <sub>2</sub>	0.37	2–50	24
BiFE <sup>c</sup>	AdsDPCSV	Se(IV)–ABSA <sup>d</sup>	0.1	2–30	28
BiFE	OSWCSV <sup>e</sup>	H <sub>2</sub> Se <sub>ads(Bi)</sub> <sup>f</sup>	0.025	0.1–1.0	27
				1.0–20.0	
HMDE <sup>g</sup>	DPCSV	Cu <sub>2</sub> Se	0.06	~0.2–16	22
BiFE	AdsDPCSV	5-Nitropiazoselenol	0.05	2–50	Proposed method

<sup>a</sup> Thin mercury film electrode. <sup>b</sup> Adsorptive differential pulse cathodic stripping voltammetry. <sup>c</sup> Bismuth film electrode. <sup>d</sup> *p*-Aminobenzenesulfonic acid. <sup>e</sup> Osteryang square-wave cathodic stripping voltammetry. <sup>f</sup> The H<sub>2</sub>Se<sub>ads(Bi)</sub> induces catalytic hydrogen wave. <sup>g</sup> Hanging mercury drop electrode.



Table 2 Determination of Se(IV) in various samples

Sample	Proposed method Se <sup>a</sup> (μg L <sup>-1</sup> )	ICP-OES Se <sup>a</sup> (μg L <sup>-1</sup> )
Blood (1)	97.4 ± 4.1	99.1 ± 3.0
Blood (2)	81.5 ± 2.8	79.2 ± 3.2
Blood (3)	104.5 ± 5.0	102.4 ± 4.3
Urine (1)	12.5 ± 1.1	11.5 ± 1.2
Urine (2)	8.7 ± 0.9	7.4 ± 0.8
Urine (3)	15.5 ± 1.8	14.4 ± 1.9

<sup>a</sup> All measurements were carried out by three replications.

standard method to assess the accuracy of the proposed method.

## Conclusions

In this study a new adsorptive cathodic stripping voltammetry method was suggested for selenium determination. Investigation of adsorptive behaviour of 5-nitropiazoselenol revealed the high tendency of this complex to adsorb at the bismuth film electrode surface. Therefore it was concluded that a novel voltammetry method can be proposed based on adsorption of this compound at the bismuth electrode. Under optimum conditions this method shows good capability in selenium determination. The accuracy of the proposed method was examined by real samples analysis. Comparison of the obtained results through the proposed method and ICP-OES as a reference method did not show significant difference. This method is very simple, sensitive, selective, low cost and reproducible and it can be easily applied for determination of selenium in various samples.

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