



# Determination of selenium in natural waters by adsorptive differential pulse cathodic stripping voltammetry

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## ABSTRACT

In this work bovine albumin was used innovatively as a medium for adsorptive accumulation of Se–I<sub>2</sub> on thin mercury film electrode. Se–I<sub>2</sub> was formed by reaction between Se(IV) and iodide in HCl media. The adsorbed Se–I<sub>2</sub> was stripped in 0.05 M HCl by differential pulse cathodic potential scan. The proposed method was successfully applied to analysis of Se(IV) and Se(VI) in natural waters sampled from some lagoons south of Caspian Sea. The optimum reaction conditions and other analytical parameters and influence of cations and anions were studied. The detection limit was 0.37 ng mL<sup>-1</sup>. The obtained results were compared with the results of DPCSV after electrochemical preconcentration, HG-AAS and ICP-AES.

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## 1. Introduction

Physiological significance and distribution of selenium in natural waters has been extensively documented [1–5]. The narrow concentration range at which selenium is on the one hand an essential nutrient and on the other hand a toxic substance in animals and humans has become a point of scientific discussion in medicine [6–8], biochemistry [9], food industries [10], and environmental science [11,12]. The low concentration of selenium in natural waters demands high sensitivity, selectivity and reliability of an applied analytical method for its determination. Today, many methods provide the necessary reproducibility and sensitivity required for this purpose [13–15].

Cathodic stripping voltammetry with hanging mercury drop electrode as working electrode is frequently used for determination of trace amounts of selenium [16–21]. Anodic Stripping voltammetry with other types of working electrodes like glassy carbon and gold and adsorptive stripping voltammetry with applying potential are also used for determination of Se(IV) [22–25]. The reaction between Se(IV) and I<sup>-</sup> to form Se–I<sub>2</sub> was postulated as early as 1950 [26]. The selenious acid–iodide reaction is acid catalyzed and to attain completeness of reaction rapidly, 0.5–1 molar hydrochloric acid can be used. Decreasing the hydrogen concentration decreases the reaction rate but it also increases the stability of Se–I<sub>2</sub> complex [27].

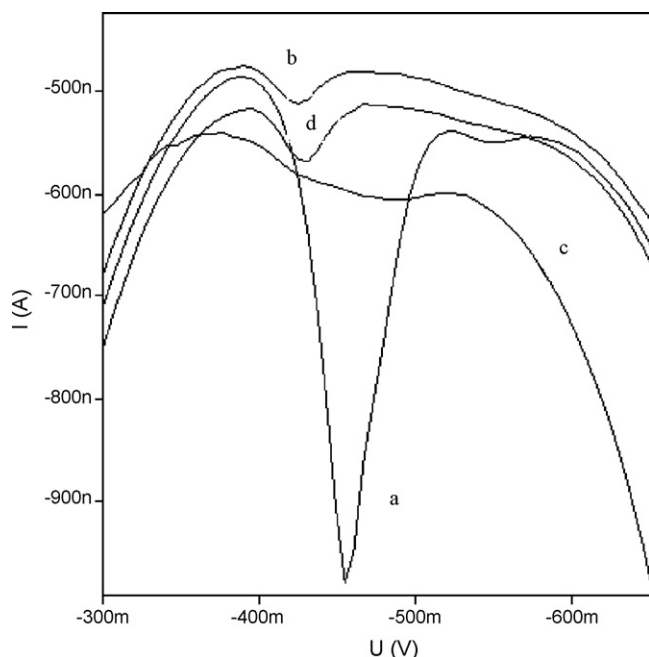
This paper describes a simple method based on self accumulation of Se–I<sub>2</sub> on thin mercury film electrode (TMFE) following by DP cathodic stripping through which adsorbed Se(0) is reduced to Se(–II). Sensitivity of this method is increased in presence of bovine albumin during adsorption process. All parameters which affect the formation of Se–I<sub>2</sub> and its adsorption on TMFE were studied and evaluated. Acid concentration during adsorption and stripping process, iodide and protein concentration, film thickness, time of adsorption, rotating rate of electrode, presence of various cations and anions and oxygen effect are the parameters which were considered. Natural waters were sampled from Anzali lagoon, Kiashahr lagoon, various depths of the south bank of Caspian Sea, Urmia Lake (North West of Iran) and Bandar Abbas shore (Persian Gulf) which are routes used by various birds during immigration from North to South. The samples were collected from 10th to 20th of May, 2008. The results obtained were compared with those obtained by DPCSV after electrochemical preconcentration of Se(IV) on TMFE, HG-AAS and ICP-AES.

## 2. Materials and methods

### 2.1. Instrumentation and reagents

All experiments were carried out by potentiostat 757 VA Computrace (Metrohm, Herisau, Switzerland) with conical vessel and three electrode system consisting of SCE, Pt counter electrode and glassy carbon as working electrode. Mercury film was formed before every measurement. A 10 mL solution containing  $1 \times 10^{-3}$  M Hg(II) and HCl (0.1 M) was electrolyzed at –0.3 V (vs. SCE) for 120 s. After the end of every experiment the surface of glassy carbon

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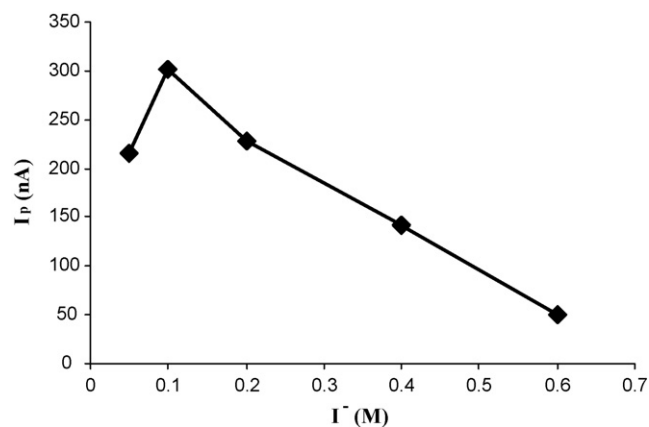
**Fig. 1.** DP adsorptive stripping voltammograms of (a) Se(IV) ( $50 \text{ ng mL}^{-1}$ ) at optimized condition, (b) blank solution without Se(IV), (c) Se(IV) ( $50 \text{ ng mL}^{-1}$ ) is reduced with hydrazine hydrochloride, and (d) blank solution containing  $0.5 \text{ mg L}^{-1} \text{ I}_2$  in  $0.1 \text{ M KI}$ .

electrode was cleaned for 40 s by  $\text{Al}_2\text{O}_3$  powder and rinsed with HCl (1 M) and double distilled water. The DP parameters were: pulse amplitude: 50 mV, pulse time: 0.04 s, voltage step: 5 mV, voltage step time: 0.4 s and sweep rate:  $15 \text{ mV s}^{-1}$ .

A HG-AAS Varian (Malgrave, Victoria, Australia) AA220 with vapor generation accessory VGA-77 and ICP-AES Varian Vista-PRO (Springvale, Australia) were used for comparing the obtained results. For determination of the total selenium concentration, real samples were digested in a homemade UV reactor with a high-pressure krypton lamp (400 W, Osram, Munchen, Germany) as irradiation source. All solutions were prepared daily with double distilled water with specific conductance of  $2 \mu\text{S cm}^{-1}$ . Selenium solutions were prepared by dilution of a  $1000 \text{ mg L}^{-1}$  AA standard (Bernd Kraft GmbH, Duisburg, Germany).  $\text{HgCl}_2$ , KI and HCl (p.a. grade) were purchased from Merck (Darmstadt, Germany) and used without any further purification. Bovine albumin (96%), gelatin and catex (Dowex 50X2-100) were purchased from BDH (Poole, England) and Sigma–Aldrich (St. Louis, MO, USA) respectively. Standard reference material analyzed for method validation was trace elements in water (SRM 1643e) from NIST (National Institute of Standard and Technology, Gaithersburg, USA).

## 2.2. Procedure

A 10 mL solution containing  $2\text{--}50 \text{ ng mL}^{-1}$  Se(IV) and potassium iodide, HCl and albumin under the optimized condition (HCl 0.4 M, KI 0.1 M, albumin  $0.04 \text{ mg mL}^{-1}$ , see Section 3) was transferred into a voltammetric vessel with pre-filmed glassy carbon electrode (TMFE). After 5 min deaeration with high purified  $\text{N}_2$ , the gas stream was passed over the solution and the adsorption process was continued for 5 more minutes. After this, the electrodes were rinsed with double distilled water and the solution was replaced with a 10 mL deaerated HCl solution (0.05 M). By replacing the solution before stripping, only cathodic peak of adsorbed compounds will be recorded. DP cathodic stripping was performed from  $-0.3$  to  $-0.650 \text{ V}$ . Fig. 1 shows the voltammograms. Three blank solutions were prepared. One is background current without Se(IV); the sec-



**Fig. 2.** Dependence of peak current of  $50 \text{ ng mL}^{-1}$  Se(IV) in  $0.4 \text{ M HCl}$  and  $0.04 \text{ mg mL}^{-1}$  albumin and adsorption time of 600 s on iodide concentration.

ond is adsorptive voltammogram of  $\text{I}_2$  ( $0.5 \text{ mg mL}^{-1}$  in  $0.1 \text{ M KI}$ ), and the third is adsorptive voltammogram of Se(IV) ( $50 \text{ ng mL}^{-1}$ ) which is reduced with hydrazine hydrochloride (85%) at pH 7. After reduction of Se(IV) to Se(0), the solution was heated slowly to dryness to remove excess hydrazine hydrochloride [27].

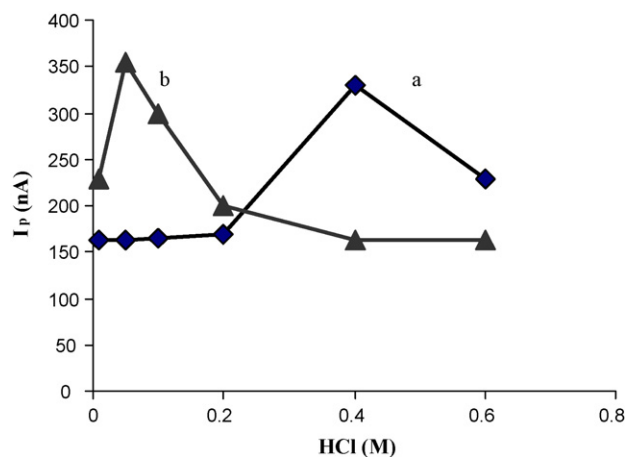
## 2.3. Statistical analysis

Statistical analysis of data was carried out by using SAS v.9.1.2 software including one-way ANOVA to obtain significance test between methods at  $P < 0.05$  and results were expressed as mean  $\pm$  standard deviation (SD) for three replications.

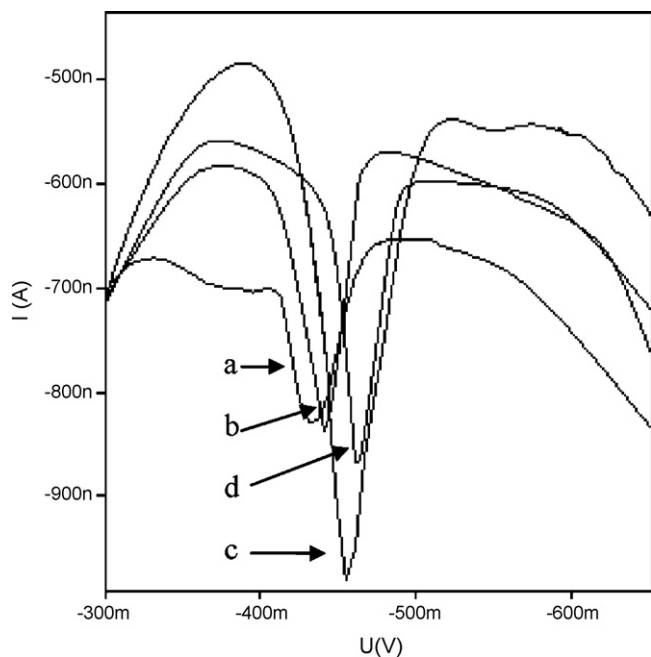
## 3. Results and discussion

### 3.1. Effect of varying the iodide and acid concentration on formation and adsorption of Se–I<sub>2</sub>

The adsorption of Se– $\text{I}_2$  was carried out directly from reaction media. Fig. 2 shows the effect of iodide concentration on the amount of adsorbed Se– $\text{I}_2$ . The best result was obtained in 0.1 M iodide. Higher concentrations of iodide cause the decrease of peak current, which can be due to the production of  $\text{I}_3^-$  and inhibition of the formation of Se– $\text{I}_2$ . The HCl concentration affects the reaction between Se(IV) and  $\text{I}^-$ . Fig. 3a shows that the tendency of adsorption is higher in 0.4 M HCl. With increasing hydrogen ion concentration,



**Fig. 3.** Dependence of peak current of  $50 \text{ ng mL}^{-1}$  Se(IV) in  $0.1 \text{ M KI}$  and  $0.04 \text{ mg mL}^{-1}$  albumin and adsorption time of 600 s on acid concentration; (a) during adsorption, (b) during stripping.



**Fig. 4.** DP adsorptive stripping voltammograms of  $50 \text{ ng mL}^{-1}$  Se(IV) in  $0.4 \text{ M HCl}$  and  $0.1 \text{ M KI}$  and adsorption time of  $600 \text{ s}$  with (a)  $0 \text{ mg mL}^{-1}$ , (b)  $0.02 \text{ mg mL}^{-1}$ , (c)  $0.04 \text{ mg mL}^{-1}$  and (d)  $0.06 \text{ mg mL}^{-1}$  albumin.

the redox reaction is carried out faster, but the stability of  $\text{Se-I}_2$  complex decreases [27] and subsequently the adsorption decreases. No significant current was obtained in  $\text{HNO}_3$ ,  $\text{HClO}_4$  and  $\text{H}_2\text{SO}_4$  media.

### 3.2. Effect of acid concentration on peak current during stripping

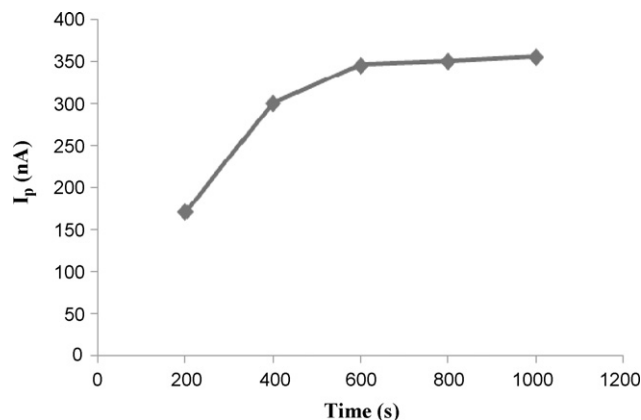
After adsorption of  $\text{Se-I}_2$  on TMFE, the solution was replaced with  $10 \text{ mL}$  of deaerated  $\text{HCl}$  solution. Fig. 3b shows the dependence of peak current on hydrochloric acid concentration as supporting electrolyte during stripping process.

### 3.3. Effect of protein and its concentration on adsorption of $\text{Se-I}_2$

Interaction of selenium compounds and iodine with proteins is well known [28–30]. Fig. 4 shows that the presence of bovine albumin affects seriously the adsorption process and increases the peak current about three-fold and peak potential is shifted about  $24 \text{ mV}$  to more negative. The highest peak current was achieved when the protein is  $0.04 \text{ mg mL}^{-1}$ . Higher concentrations of albumin decrease the cathodic current during stripping (Fig. 4). This can be explained by assuming that the higher thickness of protein prevents the adsorption of  $\text{Se-I}_2$  on mercury film and electron transfer will be difficult. The lower amount of protein brings about a broadening of the cathodic peak during stripping. This is because the TMFE is not completely covered by protein and subsequently some  $\text{Se-I}_2$  is adsorbed directly on to the mercury. Some poly-ol compounds like gelatin were studied as surface-active materials. In this case the increase in adsorption was also observed but the results were not reproducible.

### 3.4. Effect of mercury film thickness, rotating rate of electrode, adsorption time and oxygen removal

The thickness of mercury film was studied by varying the electrolysis time before adsorption process. The mercury ion concentration was kept at  $1 \times 10^{-3} \text{ M}$  constant, but the electrolysis time was varied ( $60, 90, 120, 150$  and  $180 \text{ s}$ ). By increasing the



**Fig. 5.** Dependence of peak current of  $50 \text{ ng mL}^{-1}$  Se(IV) in  $0.4 \text{ M HCl}$  and  $0.1 \text{ M KI}$  and  $0.04 \text{ mg mL}^{-1}$  albumin on adsorption time.

mercury film thickness, the adsorption of  $\text{Se-I}_2$  first increases and then decreases. The best results were obtained at  $120 \text{ s}$ . At higher times of electrolysis or higher film thickness, the centrifugal force applied by rotating disc electrode causes the deformation of mercury film surface and subsequently decreases the adsorption of  $\text{Se-I}_2$ . On the other hand the decreasing electrolysis time, means that the glassy carbon electrode surface will not be completely covered by mercury film and consequently  $\text{Se-I}_2$  will not be adsorbed. The rotating rate also can deform mercury film surface during adsorption process. In this study, the best electrode rotating rate was found to be  $1800 \text{ rpm}$ . The adsorption time for a range of Se(IV) concentration ( $2\text{--}50 \text{ ng mL}^{-1}$ ) were studied. The results of measurements showed that the best adsorption time is between  $7$  and  $10 \text{ min}$  for various amounts of Se(IV) concentrations used in the analytical curve (Fig. 5). In agreement with other results about oxygen effect in voltammetric measurements, the results showed that adsorption was decreased in the presence of oxygen about  $30\text{--}40\%$ . The best time for deaeration was found to be  $5 \text{ min}$ .

### 3.5. Interferences of cations and anions

Interferences of various kinds of anions like  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Br}^-$  which exist freely in hydrochloric acid solution ( $0.4 \text{ M}$ ) were studied. The anion concentration was  $10\text{--}100$  times of Se(IV) concentration ( $30 \text{ ng mL}^{-1}$ ). They have no effect on the peak current. The effect of some cations like  $\text{Mn(II)}$ ,  $\text{Fe(III)}$ ,  $\text{Co(II)}$ ,  $\text{Cu(II)}$ ,  $\text{Zn(II)}$ ,  $\text{Cd(II)}$ ,  $\text{Hg(II)}$ ,  $\text{Pb(II)}$ ,  $\text{Al(III)}$  and  $\text{Ag(I)}$  were also studied. The concentration range of these cations was  $30\text{--}500 \text{ ng mL}^{-1}$  and Se(IV)  $30 \text{ ng mL}^{-1}$ . The effects were different. Some of these cations like  $\text{Mn(II)}$ ,  $\text{Hg(II)}$ ,  $\text{Cd(II)}$  and  $\text{Ni(II)}$  have no effect on adsorption of  $\text{Se-I}_2$ . Some others like  $\text{Cu(II)}$ ,  $\text{Fe(III)}$  and  $\text{Co(II)}$  cause a decrease of peak current during stripping at high concentrations ( $500 \text{ ng mL}^{-1}$ ).  $\text{Pb(II)}$  and  $\text{Al(III)}$  decreased the peak current about  $50\%$  at more than  $300 \text{ ng mL}^{-1}$ . Only  $\text{Zn(II)}$  at above  $300 \text{ ng mL}^{-1}$  causes an increase in peak current but this effect was not reproducible. Because of the interference of cations, real samples were mixed with strong acidic catex. As a result, the positive and negative interference effects of cations were eliminated (see Section 3.7).

### 3.6. Analytical curve

Seven  $10 \text{ mL}$  solutions containing  $2, 5, 10, 20, 30, 40$  and  $50 \text{ ng mL}^{-1}$  of Se(IV) and appropriate amount of iodide,  $\text{HCl}$  and bovine albumin were prepared and voltammograms were recorded (Fig. 6). Fig. 7 shows that the dependence of peak current on

**Table 1**  
The amount of Se(IV)<sup>a</sup> and Se(VI)<sup>b</sup> (ng mL<sup>-1</sup>) in natural waters obtained by different methods.

Sample	Ads. DPCSV		DPCSV		HG-AAS		ICP-AES	
	Se(IV)	Se(VI)	Se(IV)	Se(VI)	Se(IV)	Se(VI)	Se(IV)	Se(VI)
Anzali lagoon	0.75 ± 0.04	0.22 ± 0.02	0.9 ± 0.05	0.18 ± 0.02	0.69 ± 0.03	0.31 ± 0.03	0.78 ± 0.05	0.30 ± 0.02
Caspian Sea <sup>c</sup>	0.46 ± 0.05	0.11 ± 0.03	0.51 ± 0.04	0.14 ± 0.01	0.51 ± 0.05	0.1 ± 0.01	0.55 ± 0.04	0.04 ± 0.01
Kiashahr Lagoon	0.24 ± 0.04	0.08 ± 0.03	– <sup>e</sup>	–	–	–	0.31 ± 0.02	0.04 ± 0.01
Urmia Lake	0.82 ± 0.03	0.24 ± 0.03	0.78 ± 0.05	0.20 ± 0.01	0.79 ± 0.03	0.22 ± 0.02	0.86 ± 0.06	0.19 ± 0.02
Bandar Abbas <sup>d</sup>	0.16 ± 0.04	0.07 ± 0.03	–	–	–	–	0.21 ± 0.03	–

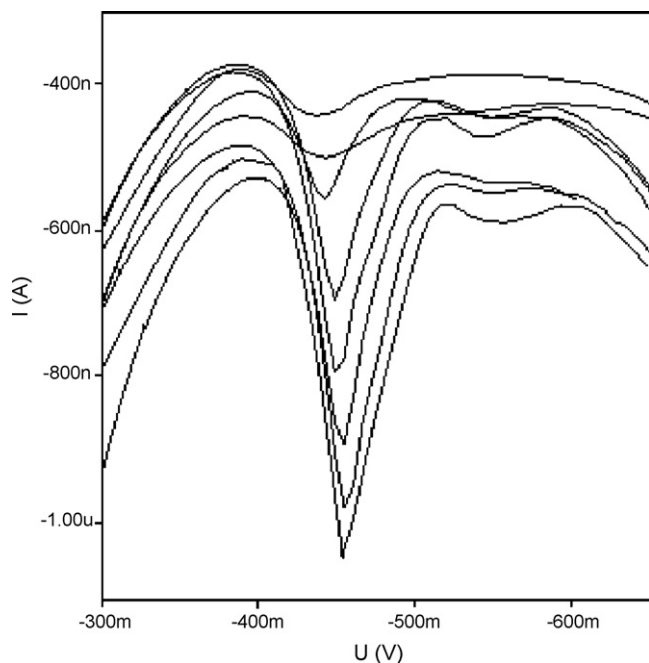
<sup>a</sup> The results are reported after correction by preconcentration factor.

<sup>b</sup> The difference between total amount of Se and Se(IV) is attributed to Se(VI).

<sup>c</sup> South shore of Caspian Sea.

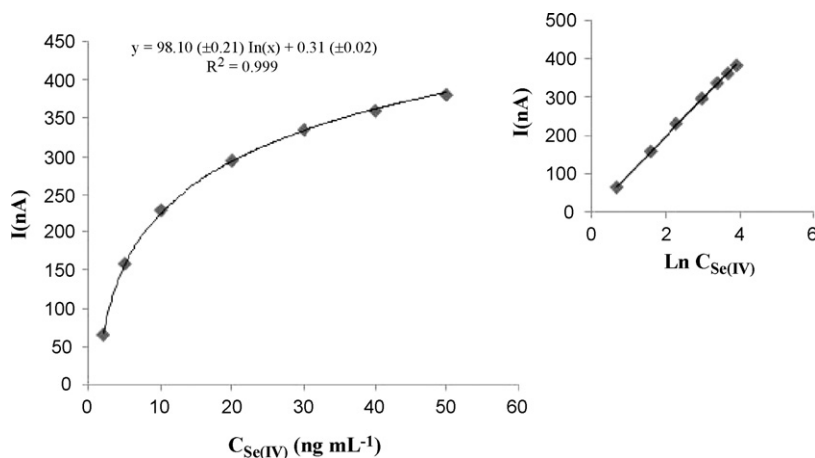
<sup>d</sup> North shore of Persian Gulf.

<sup>e</sup> The amount of selenium is below of detection limit of applied method.



**Fig. 6.** Voltammograms of standard solutions of 0, 2, 5, 10, 20, 30, 40 and 50 ng mL<sup>-1</sup> Se(IV) in 0.4 M HCl and 0.1 M KI and 0.04 mg mL<sup>-1</sup> albumin at 600 s adsorption time.

concentration of Se(IV) is logarithmic and it seems that the adsorption isotherm obeys the Frumkin equation. Five blank solutions were prepared and background cathodic currents were measured. After determination of standard deviation for background currents,



**Fig. 7.** Calibration curve of Se(IV) in optimum condition: 0.1 M KI, 0.4 M HCl, 0.04 mg mL<sup>-1</sup> albumin and adsorption time of 600 s, dependence of peak current during stripping on Se(IV) concentration (Frumkin equation). Inset figure shows dependence of peak current on  $\ln C_{\text{Se(IV)}}$ .

limit of detection was calculated by multiplying standard deviation by 3 plus background current. According to this, the detection limit was 0.37 ng mL<sup>-1</sup> [31].

### 3.7. Application to natural waters

Natural waters were sampled from some internationally registered lagoons and lakes South and South Western Caspian Sea (named in Ramsar convention of wetland), Caspian Sea and Bandar Abbas shore (North Persian Gulf) from different depths. 500 mL of every sample was acidified with 5 mL of HCl 5 M and slowly evaporated to 50 mL. Because of the high salinity of samples (for example, Urmia Lake is one of the most saline lakes in the world); the samples became saturated and precipitated during evaporation. Therefore the samples were filtered by Buchner's funnel and the filtrates were adjusted to 50 mL for analysis. For determination of Se(IV) a 10 mL solution of concentrated sample was mixed with 20 mL of acidic catex resin (Dowex 50X-100) to eliminate interferences of cations. The high salinity of waters causes the high viscosity and subsequently lower mass transfer rate during adsorption; therefore all measurements were carried out by three standard additions (5, 10, 20 ng mL<sup>-1</sup>). Every measurement was repeated three times. Table 1, shows the obtained results after applying the correction factor for preconcentration.

For determination of Se(VI), all samples were digested with UV lamp for 2 h at pH 9 [25,32]. The difference between the results in this case and the results from Se(IV) is attributed to the amount of Se(VI) (see Table 1). DPCSV after electrochemical preconcentration of Se(IV) on TMFE was also applied for comparison. Film of mercury was formed in situ. 0.5 mL of Hg(II) ( $1 \times 10^{-3}$  M) was added to 10 mL preconcentrated sample containing 1 M HCl. Because all



**Table 2**

The amount of Se(IV)<sup>a</sup> and Se(VI)<sup>b</sup> (ng mL<sup>-1</sup>) of Caspian Sea and Persian Gulf in different depth.

Depth (m)	Caspian Sea		Persian Gulf	
	Se(IV)	Se(VI)	Se(IV)	Se(VI)
0.5–1	0.46 ± 0.03	0.11 ± 0.02	0.16 ± 0.03	0.07 ± 0.02
4	0.47 ± 0.04	0.15 ± 0.03	0.17 ± 0.04	0.11 ± 0.03
20	0.36 ± 0.04	0.18 ± 0.03	0.13 ± 0.03	0.20 ± 0.03
50	0.25 ± 0.03	0.25 ± 0.03	0.14 ± 0.03	0.27 ± 0.04

<sup>a</sup> The results are reported after correction by preconcentration factor.

<sup>b</sup> The difference between total amount of Se and Se(IV) is attributed to Se(VI).

**Table 3**

Analysis of NIST certified reference materials, Se(IV).

Certified value (ng mL <sup>-1</sup> )	Determined value (ng mL <sup>-1</sup> )
12.0 ± 0.1	11.95 ± 0.15

solutions were premixed with catex, the cathodic stripping was carried out in the same solution. Standard addition method was also used in this method. Table 1, shows the results. To make sure of the reliability of the offered method all sample after preconcentration were analyzed by ICP-AES [33] and AAS after hydride generation [34]. Standard addition was used for determination of selenium and obtained results are shown in Table 1.

The obtained results show that the amount of selenium in Anzali lagoon is higher than other places in the Caspian Sea. This is because river estuaries, which pass various factories, empty into this lagoon. The level of Se(IV) in Kiashahr lagoon, which is nearly virgin area and is only surrounded by rice fields, is lower. The highest depth of Anzali, Kiashahr lagoon and Urmia Lake is 20, 15 and 6 m respectively. Therefore samples from these places are just surface water (0.5–1 m). Table 2 shows the dependence of Se(IV) and Se(VI) concentration on depth. For Caspian Sea, the total amount of selenium is nearly constant by depth (0.5–0.6 ng mL<sup>-1</sup>), but the ratio between Se(IV) and Se(VI) is changing. Bandar Abbas port is encountered with heavy traffic of various kinds of ships and wastewater from refineries. Dependence of selenium concentration with depth shows an increase in level of Se(VI) on increasing depths (Table 2).

One-way ANOVA test revealed no significant difference at confidence limit of 0.05 between results obtained from methods used for analyze samples.

The validation of reported method was checked analyzing NIST reference standard material its total content of selenium is in the range of analytical curve (simulated natural water (SRM 1463e) certified at 12.0 ± 0.1 ng mL<sup>-1</sup>). This standard material was analyzed according to the procedure describing in Section 3.7. There was good agreement between certified and determined value. The results are shown in Table 3.

#### 4. Conclusion

Control of selenium amount is important for today's life. Some employed methods for this purpose are expensive and have their own complications. The offered method in this paper is sensitive, reliable and simple. The novelty of this method is the effect of bovine albumin on the adsorptive accumulation of Se-I<sub>2</sub> and consequently lowering the detection limit (0.37 ng mL<sup>-1</sup> or 4.6 pmol mL<sup>-1</sup>) which is comparable with DPSCV (0.0005–0.1 ng mL<sup>-1</sup>), ICP-AES (0.055–1.2 ng mL<sup>-1</sup>) and HG-AAS (0.05–0.1 ng mL<sup>-1</sup>) [14]. This method can be used for determination of selenium in natural waters, which often have a high salinity, and drink waters. The presence of surface-active material is not a serious problem in this method provided that their concentration is

low. Unfortunately there are no reliable data for selenium amount in south bank of Caspian Sea to compare with the obtained results, but the amount of total selenium in Persian Gulf (Bandar Abbas) is forty times more than total selenium in Indian Ocean reported in 1977 [3].

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