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Differential Pulse Polarographic Determination of Selenium(IV) Using 3,4-Diaminobenzoic Acid

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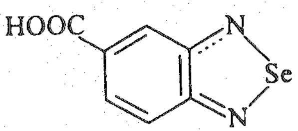
In the polarographic determination of Se(IV), the most serious interfering elements were indicated to be Pb(II) and Cd(II) due to their surface reaction with selenium on mercury drop electrode. Since the piazselenols formed by the reaction of Se(IV) with 5-carboxy-1,1,3-benzoselenadiazole (4-carboxypiazselenol), differential pulse polarography based on the adsorption of 4-carboxy piazselenol on the mercury electrode gave a very sensitive peak at –0.12 V (*vs.* SCE) and this overcame interference by Pb(II) and Cd(II). 4-Carboxy piazselenol was reduced as the adsorbed compound and the peak current was large enough to have better sensitivity than the ordinary reduction process for Se(IV). The proposed method based on this new peak showed good reproducibility and accuracy with a relative standard deviation of 1.19% and relative error of +0.80% for the determination of 5.0×10^{-6} M Se(IV) next to 1.0×10^{-5} M Pb(II). There is a linear relationship between the differential pulse polarography peak current and the Se(IV) concentration over the range 1.0×10^{-7}–1.0×10^{-4} M with a correlation coefficient of 0.9958. The method was applied to synthetic samples containing known amounts of Se(IV) next to known amounts of interfering ions with different ratios and probabilities.

Key Words: Selenium(IV) determination, 3,4-Diaminobenzoic acid, Polarography.

INTRODUCTION

All the aromatic *o*-diamines can be employed as very sensitive and selective reagents for the extraction-spectrophotometric and voltammetric determination of selenium. In acid solutions (pH 1–2) selenious acid reacts with *para*-substituted (4-methyl, 4-chloro, 4-nitro) *o*-phenylenediamine to form benzoselenodiazoles and all these compounds can be extracted by toluene[1]. Piazselenols formed by the reaction of selenium(IV) with such compounds as 3,3′-diaminobenzidine[2, 3], 2,3-diaminonaphthalene[4, 5] and 4,5-dichloro-*o*-phenylenediamine[6] can be used for the determination of selenium by spectrophotometric methods. A coloured or fluorescent piazselenol is formed when selenium(IV) reacts with an aromatic *o*-diamine, 3,3′-diaminobenzidine is based on this type, where a relatively basic piazselenol is obtained which can be extracted only if the pH of the solution is high. Speciation of Se(VI) and Se(VI) were performed by the reaction with

4,5-dichloro-*o*-phenylenediamine using gas chromatography (GC-MS)[7] and inductively coupled plasma atomic emission spectrometry (ICP-AES)[8]. The condensation reactions of Se(IV) with 3,4-diaminobenzoic acid and 4-bromo-1,2-phenylenediamine have been studied by means of UV spectra and a mechanism for their structure proposed[9].



Tetravalent selenium can also be determined using polarographic[10] or voltammetric techniques[11, 12] by the peaks of piazselenols formed when aromatic *o*-diamines were added to Se(IV) containing solution. In our previous work, a new sensitive and selective polarographic method for the determination of selenium(IV) was described and the new peak due to the Se(IV)/*o*-phenylenediamine not only prevented the interference of Pb(II), Cd(II) and Sn(II) for selenium, but also increased its sensitivity[10].

In the electroanalytical determination of Se(IV), the most serious interfering elements were indicated to be Cu(II), Pb(II), Cd(II) and Sn(II) due to their surface reaction with selenium on mercury drop electrode[13]. It was stated that the addition of Se(IV) to a sample containing ions such as Cu(II), Pb(II), Cd(II) and Sn(II) had a diminishing effect on their peak heights, which would lead to erroneous results. This kind of interference observed in polarographic studies was attributed to the formation of intermetallic compounds.

Since the piazselenols formed by the reaction of Se(IV) with aromatic *o*-diamines are commonly used[2–6] for the determination of Se(IV) by spectrophotometric methods, differential pulse polarography (DPP) based on the adsorption of 2,1,3-benzoselenadiazole-5-carboxylic acid (4-carboxy piazselenol) on the mercury electrode was thought to give a very sensitive peak and overcome interference by metal ions, particularly Pb(II), Cd(II). In the present work, a new polarographic peak was observed when only Se(IV) and 3,4-diaminobenzoic acid were present together and this new peak belonging to 4-carboxy piazselenol compound not only prevented the interference of Pb(II) and Cd(II) for selenium, but also increased its sensitivity.

EXPERIMENTAL

A PAR model 174-A polarographic analyzer system, equipped with a PAR mercury drop timer, was used. A Kalousek electrolytic cell with reference-saturated electrode (SCE), separated by liquid junction, was used in a three-electrode configuration. The counter electrode was platinum wire. The natural drop time of the mercury electrode was in the range 2–3 s (2.37 mg/s). The polarograms were recorded with a Linseis LY 1600 X–Y recorder. DP polarograms were recorded under the conditions of a drop life of 1 s, a scan rate of 5 mV/s and a pulse amplitude of 50 mV.

Triply distilled water was used for the preparation of all solutions and at other stages of analysis. The mercury (pro-analysis) was obtained from Merck

(Damstadt, Germany). Contaminated mercury was cleaned by passing it successively through dilute HNO_3 and water columns in the form of fine droplets. The collected mercury was dried between sheets of filter paper. Before use, a differential pulse polarogram of this mercury was recorded in order to confirm the absence of impurities.

A 0.1 M standard stock solution of Se(IV) was prepared by dissolving 1.1096 g of SeO_2 in 100.0 mL hot water. 0.1 M lead(II) and cadmium(II) solutions were prepared by dissolving 3.3120 g $Pb(NO_3)_2$ and 3.0847 g $Cd(NO_3)_2 \cdot 4H_2O$ in 100 mL water. A 0.01 M 3,4-diaminobenzoic acid solution was prepared freshly by dissolving 0.1522 g 3,4-diaminobenzoic acid in 50.0 mL of ethanol and diluting up 100 mL by water. 1.0×10^{-3} and 1.0×10^{-4} M working solutions were prepared by daily dilution.

Britton-Robinson (B-R) buffer solution was prepared in such a way that 2.3 mL glacial acetic acid, 2.7 mL phosphoric acid and 2.4720 g boric acid dissolved by dilution with water to 1.0 L. 50.0 mL portions of this solution were taken and the desired pH was adjusted between 2.5 and 5.5 by addition of appropriate amount of 2.0 M NaOH.

Polarographic determination

A 10.0 mL volume of supporting electrolyte (B-R buffer, pH = 3.02) in a polarographic cell was deaerated by a stream of nitrogen gas (99.999%) for 3.0 min; then according to the need 50–200 μL 1.0×10^{-3}, 1.0×10^{-4} or 1.0×10^{-5} M Se(IV), Pb(II), Cd(II) and 3,4-diaminobenzoic acid solutions were added. Polarograms were recorded by scanning the potential in the negative potential direction from +0.05 V to about −1.20 V at a scan rate of 5 mV/s and pulse amplitude of 50 mV.

RESULTS AND DISCUSSION

Interference's problem of Se(IV) in the presence of Pb(II) or Cd(II)

In polarographic work, when Pb(II) or Cd(II) was added on to Se(IV) [or addition of Se(IV) on to Cd(II) or Pb(II)], Se(IV) peak was diminished while a new peak appeared at a more positive potential than the mentioned ions and Se(IV) (Figs. 1b–c). This was attributed to an intermetallic compound formation between selenium and the ions present. The peak is brought about by a reduction of interfering ions, which afterwards forms an intermetallic compound with selenium adsorbed on the mercury drop surface. For the product resulting due to the this kind of interference, the following mechanism was proposed[13].

$$6H^+ + SeO_3^{2-} + 4e^- \rightleftharpoons Se_{(ads)} + 3H_2O$$

$$Se_{(ads)} + M^{2+} + ne^- \rightleftharpoons (M)(Se)_{(ads)} \quad \text{where } M = Pb \text{ or } Cd$$

Without considering this kind of interference, polarographic determination in solutions that contain both Se(IV) and at least one of these ions would be wrong. Because of this interference, care must be taken in the polarographic determination of the selenium and mentioned ions when they are present in the same solution. Therefore, an alternative method must be recommended for the determination of Se(IV) in the presence of Pb(II) or Cd(II) or both.

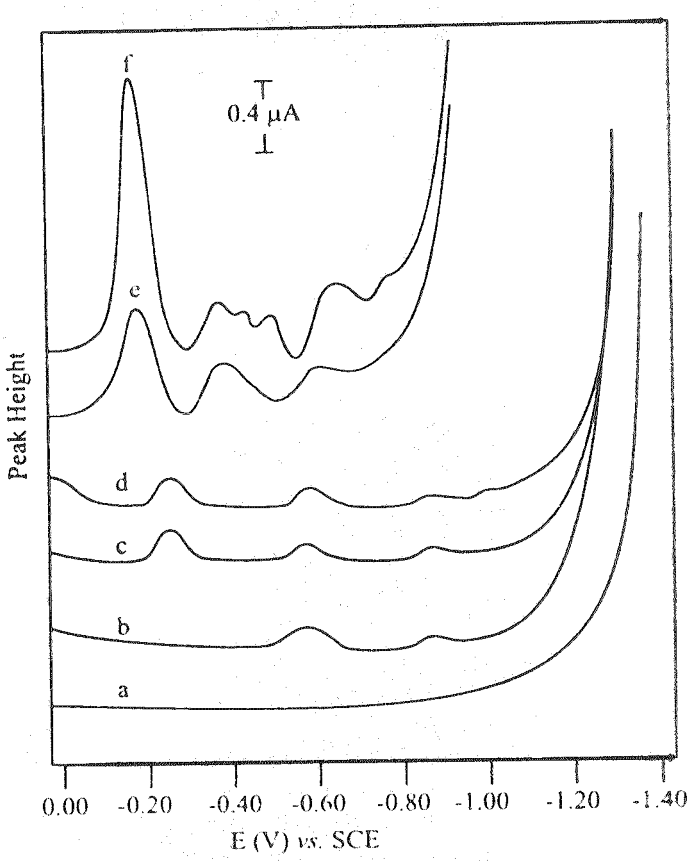


Fig. 1. Effect of the Pb(II) addition on to Se(IV) solution and formation of 4-carboxy piazselenol peak. (a) 10.0 mL of pH = 3.02 B-R buffer solution, (b) a$^+$ 1.0×10^{-5} M Se(IV), (c) b$^+$ 1.0×10^{-5} M Pb(II) (d) c$^+$ 1.0×10^{-5} M Se(IV), (e) d$^+$ 1.0×10^{-3} M 3,4-diamino benzoic acid, (f) e$^+$ 4.0×10^{-5} M Se(IV)

Polarographic work for 4-carboxy piazselenol

During the polarographic determination of selenite, the selenite peak appeared at about –0.62 V (*vs.* SCE) in 10.0 mL of pH = 3.02 B-R buffer solution. However, when lead(II) solution (or cadmium) was added on to this solution, the peak at –0.62 V decreased and a new peak at –0.33 V appeared as can be observed in Fig. 1c. As seen from Fig. 1d, the standard addition of Se(IV) on to this solution would lead to erroneous results and because of this phenomenon, most of the electroanalytical determinations in solutions which contain both selenite and at least one of these ions would be wrong. When additions of 3,4-diamino benzoic acid solution on to this solution were made, a new peak at about –0.12 V appeared, as can be seen in Fig. 1e. This new peak was observable when only Se(IV) and 3,4-diamino benzoic acid were present together, which means 4-carboxy piazselenol reduced at mercury electrode. The peak height was proportional to the standard Se(IV) additions and can be used for quantification of Se(IV) (Fig. 1f). On the other hand, when there was only 3,4-diaminobenzoic acid in the B-R buffer solution (pH = 3.02), no peak was observed.

Because piazselenol formations of Se(IV) with aromatic diamines are well known[2–6], the new polarographic peak appeared when only Se(IV) and 3,4-diamino benzoic acid are found in the same solution which must belong to the corresponding piazselenol. This new peak not only prevents the interference for selenium but also increases its sensitivity. On the other hand, the aim of this work is not to clarify the structure of this piazselenol but only to apply for selenium determination next to interfering ions.

Effect of concentration of 3,4-diamino benzoic acid

The effect of the concentration of 3,4-diamino benzoic acid on the peak height of the corresponding piazselenol was shown in Fig. 2, where successive additions of 3,4-diamino benzoic acid solution up to 3.0×10^{-3} M were made to 10 mL of 1.0×10^{-5} M Se(IV) solutions at pH 3.02 and stood for 1 h. The peak current of the 4-carboxy piazselenol depends on the 3,4-diamino benzoic acid concentration and reaches a maximum value at about 1.0×10^{-3} M 3,4-diamino benzoic acid. The further addition of 3,4-diamino benzoic acid has nearly no effect and 1.0×10^{-3} M 3,4-diamino benzoic acid was used throughout the study.

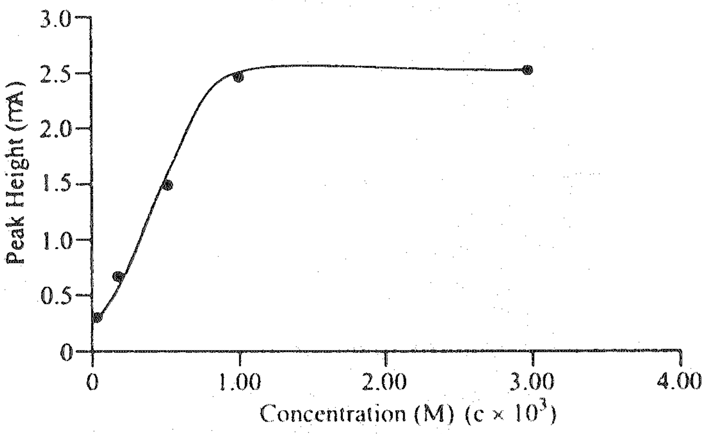


Fig. 2. Effect of the concentration of 3,4-diamino benzoic acid on the peak height of the 4-carboxy piazselenol peak (1.0×10^{-5} M Se(IV) solutions at pH = 3.02 and 1 h standing time)

Effect of standing time after mixing Se(IV) with 3,4-diamino benzoic acid to form 4-carboxypiazselenol

Fig. 3 shows the effect of the standing time after 1.0×10^{-5} M Se(IV) and

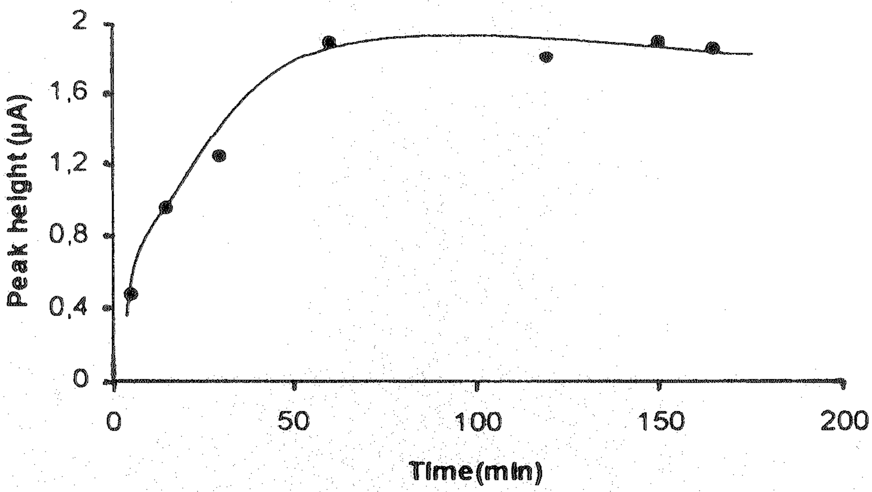


Fig. 3. Effect of the standing time on the peak current of 4-carboxy piazselenol (1.0×10^{-5} M Se(IV) and 1.0×10^{-3} M 3,4-diamino benzoic acid in 10.0 mL B-R buffer solution, pH = 3.02)

1.0×10^{-3} M 3,4-diamino benzoic acid were mixed in 10.0 mL B-R buffer solution (pH = 3.02). In order to try the time dependence for 4-carboxy piazselenol formation, some polarograms were recorded at definite times during 3 h. The peak current of 4-carboxy piazselenol was increased until about 1 h and remained constant due to the stable piazselenol formation. This was because of the relatively slow reaction between Se(IV) and 3,4-diamino benzoic acid for the completion of the piazselenol formation. Optimum time for this formation was chosen as 1 h for further study.

Effect of pH on the peak potentials and currents for Se(IV) and 4-carboxy piazselenol

The effects of pH on the peak potentials and currents for Se(IV) alone and 4-carboxy piazselenol acid are summarized in Table-1. As seen in Table-1, reduction potentials of Se(IV) and 4-carboxy piazselenol both shifted to more negative potential with increasing pH. Most probably, therefore, the reduction process in the new peak should contain the reduction of Se(IV). Since 3,4-diamino benzoic acid was proved to be electro-inactive, this fact is an indication that the peak at –0.12 V is due to the formation and subsequent reduction of the 4-carboxy piazselenol.

$$\text{Se(IV)/DABA(Hg)} + 4e^- \rightleftharpoons \text{Se(0)/DABA(Hg)}$$

(3,4-diamino benzoic acid = DABA)

TABLE-1
EFFECT OF THE pH ON THE PEAK POTENTIALS AND CURRENTS FOR Se(IV) AND 4-CARBOXY PIAZSELENOL

pH	4-carboxypiazselenol E(V) *vs.* SCE	4-carboxypiazselenol current (μ A)	Se(IV) E(V) *vs.* SCE	Se(IV) current (μA)
2.50	–0.04	2.36	–0.56	1.12
3.00	–0.12	2.72	–0.62	1.20
3.50	–0.18	1.36	–0.64	0.76
4.00	–0.20	0.52	–0.65	0.76
4.52	–0.20	0.28	–0.67	0.32
5.00	–0.20	0.48	–0.70	0.28
5.57	–0.20	0.56	–0.70	0.29

As shown in Fig. 4, the maximum peak current for 4-carboxy piazselenol (2.0×10^{-5} M Se(IV) and 1.0×10^{-3} M 3,4-diamino benzoic acid) obtained at pH = 3.02 can be explained with the formation of $HSeO_3^-$ ($pK_a = 2.7$). At low pH values, on the other hand, $HSeO_3^-$ is not present in significant amount which leads to a very low current. Therefore the optimum pH was found to be about 3.02 and used for further study. The peak current for 4-carboxy piazselenol was much more higher than the corresponding Se(IV), especially at pH 3.02. Since the 4-carboxy piazselenol was reduced as the adsorbed compound, the peak current was large enough to have better sensitivities than the ordinary reduction process for Se(IV).

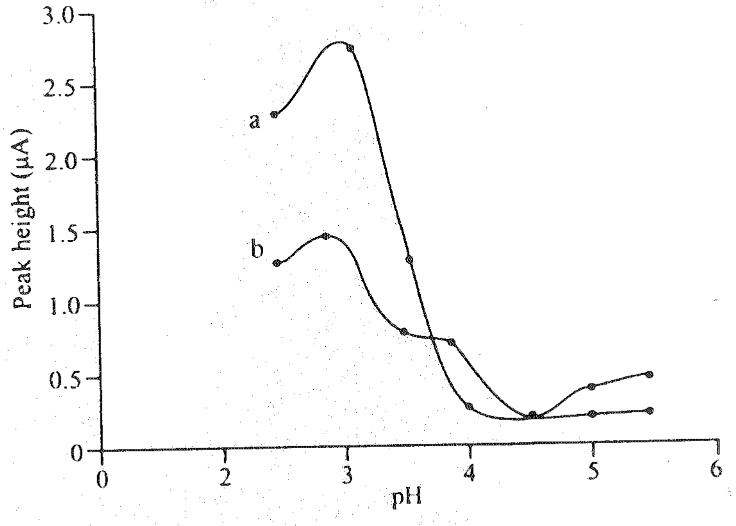


Fig. 4. Effect of pH on the peak current of (a) 4-carboxy piazselenol (2.0×10^{-5} M Se(IV) and 1.0×10^{-3} M 3,4-diamino benzoic acid, (b) 2.0×10^{-5} M Se(IV) (1 h standing time at each pH))

Analyical application of the method to synthetic samples

In order to check the accuracy of the method, synthetic samples containing known amounts of Se(IV) next to interfering ions with different ratios and probability were prepared. The polarogram for a solution containing 5.0×10^{-6} M Se(IV) and 2.5×10^{-6} M Pb(II) exhibited two peaks in 10.0 mL pH 3.02 solution and selenium is found in both of the peaks (Fig. 5b). The first peak at about –0.33 V corresponds to Pb-Se intermetallic peak and the second one at about –0.62 V is the remaining Se(IV) peak since it exceeds lead. In this case, the correct determination of Se(IV) using direct standard addition will not be possible in the presence of second ion. Consequently, none of them will have the own true peak height of Se(IV). In spite of this fact, the standard Se(IV) addition was made to this synthetic solution (5.0×10^{-6} M Se(IV) next to 2.5×10^{-6} M Pb(II) in 10.0 mL pH 3.02) as if we had not known this strong interference effect (Figs. 5c–e). Since the Se(IV) peak at –0.62 V did not represent the total selenium (some selenium at –0.33 V together with lead), the calculations from the direct standard additions of Se(IV) would give enormous errors up to –35.0% for a mixture of 5.0×10^{-6} M Se(IV) and 2.5×10^{-6} M Pb(II).

Fig. 6 shows the determination of Se(IV) in synthetic solution of 5.0×10^{-6} M Se(IV) and 2.5×10^{-6} M Pb(II), but with the only exception of using the advantage of the new peak of 4-carboxy piazselenol appearing after the addition of 1.0×10^{-3} M 3,4-diamino benzoic acid on to this solution. The Se(IV) determination was achieved from a good quantitative increment of the appeared peak of 4-carboxy piazselenol at –0.12 V, upon the standard Se(IV) addition **(Fig. 6c–e)**. The proposed method showed good reproducibility and accuracy with a relative

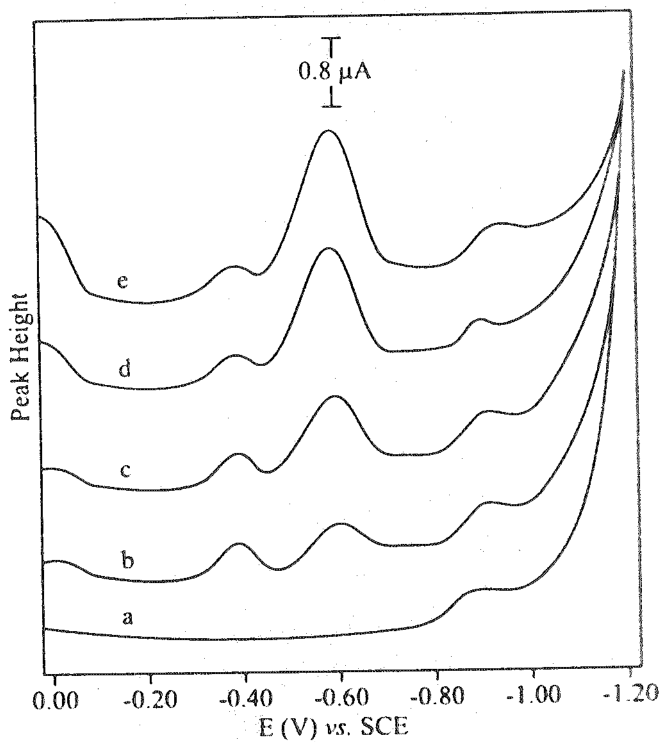


Fig. 5. Determination of Se(IV) without considering interference effect in the synthetic sample containing 5.0×10^{-6} M Se(IV) and 2.5×10^{-6} M Pb(II) (1 h standing time at pH = 3.02). (a) 10.0 mL of pH = 3.02 B-R buffer solution, (b) a^{+} 5.0×10^{-6} M Se(IV) and 2.5×10^{-6} M Pb(II), (c) b^{+} 5.0×10^{-6} M Se(IV), (d) c^{+} 5.0×10^{-6} M Se(IV), (e) d^{+} 5.0×10^{-6} M Se(IV)

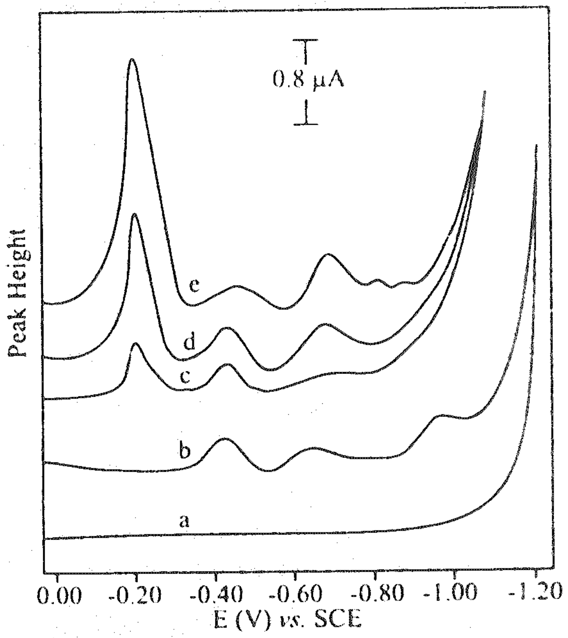


Fig. 6. Determination of Se(IV) in synthetic sample containing 5.0×10^{-6} M Se(IV) and 2.5×10^{-6} M Pb(II) using the advantage of 4-carboxy piazselenol peak (1 h standing time at pH = 3.02). (a) 10.0 mL of pH = 3.02 B-R buffer solution, (b) a^{+} 5.0×10^{-6} M Se(IV) and 2.5×10^{-6} M Pb(II), (c) b^{+} 1.0×10^{-3} M 3,4-diamino benzoic acid, (d) c^{+} 5.0×10^{-6} M Se(IV), (e) d^{+} 5.0×10^{-6} M Se(IV)

standard deviation of 1.94% and relative error of –7.40% for the determination of 5.0×10^{-6} M Se(IV) next to 2.5×10^{-6} M Pb(II). The other results in synthetic samples containing known amounts of Se(IV) next to interfering ions with different ratios and probabilities were given in Table-2.

TABLE-2
DETERMINATION OF Se(IV) NEXT TO INTERFERING IONS IN SYNTHETIC SAMPLES USING 4-CARBOXY PIAZSELENOL

Synthetic samples	$C_{Se(IV)}$ (M) $(\bar{\chi} \pm s)^*$	R.S.D.* (%)	Relative Error (%)
5×10^{-6} M Se(IV); 1.0×10^{-5} M Pb(II)	$(5.04 \pm 0.06) \times 10^{-6}$	1.19	+0.80
5×10^{-6} M Se(IV); 5.0×10^{-6} M Pb(II)	$(5.08 \pm 0.39) \times 10^{-6}$	7.68	+1.60
5×10^{-6} M Se(IV); 2.5×10^{-6} M Pb(II)	$(4.63 \pm 0.09) \times 10^{-6}$	1.94	–7.40
5×10^{-6} M Se(IV); 1.0×10^{-5} M Cd(II)	$(4.87 \pm 0.06) \times 10^{-6}$	1.23	–2.60
5×10^{-6} M Se(IV); 5.0×10^{-6} M Cd(II)	$(4.75 \pm 0.11) \times 10^{-6}$	2.32	–5.00
5×10^{-6} M Se(IV); 2.5×10^{-6} M Cd(II)	$(4.60 \pm 0.28) \times 10^{-6}$	6.10	–8.00
5×10^{-6} M Se(IV); 5.0×10^{-6} M Pb(II); 5.0×10^{-6} M Cd(II)	$(4.64 \pm 0.06) \times 10^{-6}$	1.29	–7.20
5×10^{-6} M Se(IV); 2.5×10^{-6} M Pb(II); 2.5×10^{-6} M Cd(II)	$(4.61 \pm 0.06) \times 10^{-6}$	1.30	–7.80
5×10^{-6} M Se(IV); 1.0×10^{-6} M Pb(II); 1.0×10^{-5} M Cd(II)	$(4.67 \pm 0.07) \times 10^{-6}$	1.49	–6.60

*R.S.D.: Relative Standard Deviation, n: number of experiment (3)

Influences of some coexisting ions

The influences of some cations such as Cd(II), Co(II), Cr(III), Ni(III), Pb(II) and Zn(II) on 4-carboxy piazselenol peak were investigated in 10.0 mL pH = 3.02 solution containing 1.0×10^{-5} M Se(IV) and 1.0×10^{-3} M 3,4-diamino benzoic acid. The coexisting ions were taken as 10, 20 and 50-fold molar excess of Se(IV) and the results were summarized in Table-3.

TABLE 3
EFFECT OF THE COEXISTING IONS FOR THE PEAK CURRENT OF 4-CARBOXY PIAZSELENOL*

Concentration (M)	Cd(II)	Co(II)	Cr(III)	Ni(II)	Pb(II)	Zn(II)
1.0×10^{-4}	100	91	100	109	100	100
2.0×10^{-4}	100	118	100	109	90	100
5.0×10^{-4}	100	127	100	109	82	100

*Se(IV): 1.0×10^{-5} M; 3,4-Diamino benzoic acid: 1.0×10^{-3} M

The results were taken as the ratio of peak currents in the presence of the co-existing ions to that in their absence (by percentage). As seen in Table-3, while

10, 20 and 50-fold of Cd(II), Zn(II), Cr(II) have no effect, Co(II) and probably Ni(II) exert slight influence in the positive way for the determination of selenium using 4-carboxy piazselenol peak. However, at higher concentrations of Pb(II) ions, 4-carboxy piazselenol peak was decreased which would lead us to some negative systematic error.

Calibration curve

When 1 h of standing time has elapsed out after mixing Se(IV) with 1.0×10^{-3} M 3,4-diamino benzoic acid in 10.0 mL pH 3.02 solution to form 4-carboxypiazselenol, followed by a potential scan of 5 mV/s in the negative potential direction from +0.05 V to about −1.2 V (*vs.* SCE), there is a linear relationship between the DPP peak current (I) and the Se(IV) concentration (C) over the range $1.0 \times 10^{-7} - 1.0 \times 10^{-4}$ M with a correlation coefficient of 0.9958.

$$I = 1.34 \times 10^{5}\,C + 1.7 \times 10^{-2} \quad (\text{I in } \mu\text{A, C in molarity})$$

The proposed method showed good reproducibility and accuracy with a relative standard deviation of 1.19% and relative error of +0.80% for the determination of 5.0×10^{-6} M Se(IV) next to 1.0×10^{-5} M Pb(II). The relative standard deviation and relative error for the determination of 5.0×10^{-6} M Se(IV) next to 1.0×10^{-5} M Cd(II) were 1.23% and −2.60% and for triple mixture of 5.0×10^{-6} Se(IV) next to 1.0×10^{-5} M Pb(II) and 1.0×10^{-5} M Cd(II), were 1.49% and −6.60%, respectively.

This method, which could be used for the direct determination of Se(IV) using the advantage of 4-carboxy piazselenol peak by differental pulse polarography, has proved to be satisfactory, and can even be used in the analysis of the biolgoical sample containing complex mixture of metals. There is no need for separation and pre-concentration procedures, which are tedious, time-consuming and also polluting.

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