

Determination of Selenium(IV) Using o-Phenylenediamine by Differential Pulse Polarography/Interference of Metal Ions

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A new sensitive and selective pulse polarographic method for the determination of Se(IV) next to interfering ions is described. This method is based on the highly sensitive peak formed by the reaction of Se(IV) with o-phenylenediamine in Britton-Robinson buffer solution (pH 2.5) at -0.08 V vs. SCE. The new peak due to the Se(IV)/o-PDA complex not only prevents the interference of Pb(II), Cd(II) and Sn(II) for selenium, but also increases its sensitivity. A linear calibration graph is obtained for Se(IV) at a concentration of 5.0×10^{-8} to 6.8×10^{-5} M with a correlation coefficient of 0.9988. The proposed method showed good reproducibility and accuracy with a relative standard deviation of 5.5% and relative error of -5.6% for the determination of 5.0×10^{-8} M Se(IV) next to 5.0×10^{-7} M Pb(II). There is no serious interference from some ions when present at levels more than 50 times that selenium and no need for separation or pre-concentration procedures, which are tedious, time-consuming and polluting.

Key Words: Selenium determination, o-phenylenediamine, Interference's problem, Polarography

Introduction

Determination of selenium in biological and environmental samples is usually difficult due to its trace or ultra-trace quantities, pre-concentration stages, destruction of organic matrices by acid digestion and oxygen plasma combustion followed by separation from interfering metal ions such as ion exchange separation, solvent extraction or hydride generation. Selective separation of selenium is particularly important in the determination of small amounts of the element in complex materials. These are all time consuming procedures and losses of selenium are also possible. It is therefore very important to accomplish methods with minimal interference.

In the electroanalytical determination of selenium, the most serious interfering elements were indicated to be copper, lead, cadmium and tin due to their surface reaction with selenium on a mercury drop electrode^{1,2}. In some voltammetric studies, such as anodic stripping voltammetry (ASV)³ and cathodic

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stripping voltammetry (CSV) ^{4,5}, it was stated that the addition of Se(IV) to a sample containing ions such as lead, cadmium or tin had a diminishing effect on their peak heights, which would lead to erroneous results. The same kind of interference was also observed in differential pulse polarographic (DPP) ²studies, a phenomenon not mentioned before in polarographic works, and was attributed to the formation of an intermetallic compound. The new peak belonging to the intermetallic compound was used for the quantitative determination of Se(IV). However, this procedure includes converting all the selenium to intermetallic form and needs therefore an indirect procedure resulting in extra-ions in the solution. In addition, when selenium and more than one interfering ion are found in the same medium, the procedure fails and therefore a new solution for this kind of interference problem must be proposed.

Since the piaszelenols formed by the reaction of selenium(IV) with such compounds as 3,3'-diaminobenzidine^{6,7}, 2,3-diaminonaphthalene^{8,9} or 4,5-dichloro-o-phenylenediamine¹⁰ can be used for the determination of selenium by spectrophotometric methods and by the adsorptive stripping voltammetry¹¹⁻¹⁴ based on the adsorption of selenium(IV) complex with aromatic diamines on the mercury electrode, o-phenylenediamine (o-PDA) was thought to overcome interference by metal ions, particularly lead(II), cadmium(II) and tin(II).

In the present work, it was shown that, when selenium and o-phenylenediamine were present together, a new polarographic peak belonging to the Se(IV)/o-PDA complex compound appeared. The aim of this study was to propose an alternative pulse polarographic method for the determination of Se(IV) in the presence of heavy metal ions such as Pb(II), Cd(II) and Sn(II), which takes the advantage of this new peak formed between Se(IV) and o-PDA, and describes a more sensitive and selective procedure avoiding interfering ions without any separation procedure.

Materials and Methods

Apparatus

A PAR model 174A polarographic analyser system, equipped with a PAR mercury drop timer, was used. A Kalousek electrolytic cell with a reference-saturated electrode (SCE), separated by a liquid junction, was used in a 3 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 pulse amplitude of 50 mV.

Reagents

All chemicals used were analytical-reagent grade (Merck). 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 HNO₃ 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 absences of impurities.

A 0.1 M standard stock solution of Se(IV) was prepared by dissolving 1.1977 g of SeO₂ in 100.0 mL of hot water. Then 0.1 M lead(II) and cadmium(II) solutions were prepared by dissolving their nitrate salts in water. A 0.1 M standard stock solution of tin(II) was prepared by dissolving 2.2663 g of SnCl₂·2H₂O in

100.0 mL of 6.0 M HCl solution. A 0.05 M o-PDA solution was prepared freshly by dissolving 0.5408 g of o-PDA in 100.0 mL of ethanol, and 1.0×10^{-3} , 1.0×10^{-4} and 1.0×10^{-5} M working solutions were prepared by daily dilution.

Britton-Robinson (B-R) buffer solution was prepared in such a way that 2.3 mL of glacial acetic acid, 2.7 mL of phosphoric acid and 2.4720 g of boric acid dissolved by dilution with water to 1.0 L. Then 50.0 mL portions of this solution were taken and the desired pH was adjusted to between 2.0 and 5.0 by addition of an appropriate amount of 2.0 M NaOH.

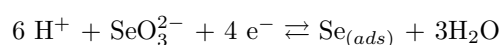
Polarographic determination

A 10.0 mL volume of supporting electrolyte (B-R buffer solution) in a polarographic cell was de-aerated by a stream of nitrogen gas (99.999%) for 3.0 min; then, according to need, 50-200 μ L of 1.0×10^{-3} , 1.0×10^{-4} or 1.0×10^{-5} M Pb(II), Cd(II), Sn(II) and o-PDA solutions were added. Polarograms were recorded by scanning the potential in the negative potential direction from +0.10 V to about -1.20 V at a scan rate of 5 mV/s and pulse amplitude of 50 mV.

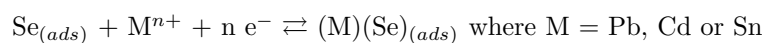
Results and Discussion

Interference of lead(II), cadmium(II) and tin(II) on selenium(IV)

During the differential pulse polarographic determination of selenium, when Se(IV) was added onto some ions such as lead(II), cadmium(II) or tin(II) (or the addition of metal ions onto Se(IV)), it was observed that the metal ion's peaks were diminished while a new peak appeared at a more positive potential than for the mentioned ions and Se(IV) (Figures 1b-d). This observation is attributed to intermetallic compound formation between selenium and the ions present. The peak is brought about by a reduction in the interfering ions, which afterwards forms an intermetallic compound with selenium adsorbed on the mercury drop surface. For the product resulting due to this kind of interference, the following mechanism was proposed²



and



Because of this interference, care must be taken in the polarographic determination of the selenium and mentioned ions when they are found in the same solution. In other words, without considering this kind of interference, most electroanalytical determinations in solutions that contain both Se(IV) and at least one of these ions will be wrong. In our earlier work^{1,2}, the proposed method for the determination of selenium in the presence of interfering metal ion needs to convert all selenium to intermetallic form by adding an excess of one of the interfering ions and therefore needs an indirect procedure resulting in extra-ions in the sample. In addition, when selenium and more than one interfering ion are found in the same medium (PbSe, CdSe and SnSe intermetallic peaks are at about the same potentials) another method for this kind of interference must be proposed. Therefore, an alternative method was recommended resulting in a new free peak for the determination Se(IV) (Figures 1e-f). Since the complex formation of Se(IV) with aromatic diamines is well known^{10,13}, the new peak must belong to the Se(IV)/o-PDA complex. On the other hand, the scope of this

work was only its application for selenium determination next to interfering ions.

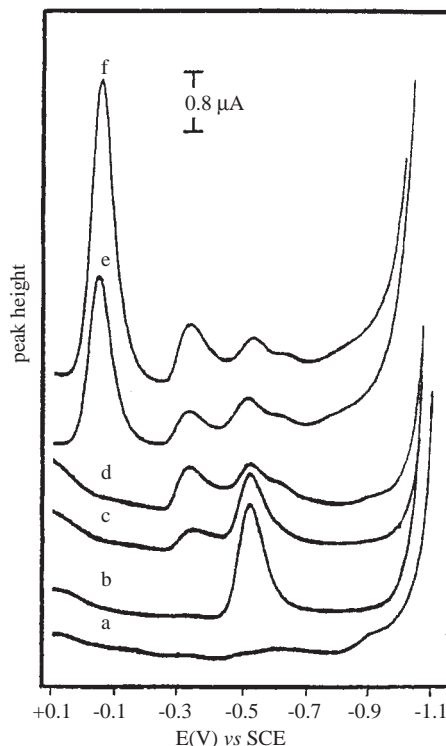


Figure 1. Effect of selenium(IV) addition on Cd(II) and determination of selenium(IV) using Se(IV)/o-PDA peak. (a) 10.0 mL of B-R buffer solution (pH 2.51) (b) a + 1.50×10^{-5} M Cd(II) (c) b + 5.0×10^{-6} M Se(IV) (d) c + 5.0×10^{-6} M Se(IV) (e) d + 1.0×10^{-3} M o-PDA (f) e + 1.0×10^{-5} M Se(IV).

The Se(IV)/o-PDA peak not only prevents the interference for selenium but also increases its sensitivity. To investigate this situation thoroughly, solutions of various compositions were prepared and DPP peaks were observed under different conditions.

Effect of concentration of o-PDA on the selenium(IV) peak

When a 100 μ L 1.0×10^{-3} M selenite solution was added to 10.0 mL of B-R buffer solution (pH 2.5) and a polarogram was recorded, a reduction peak for selenium at -0.53 V was observed. When successive additions of o-PDA solution to this solution were made, a new peak at about -0.08 V appeared, as can be seen in Figure 2. This new peak was observable only when Se(IV) and o-PDA were present together, which means that the Se(IV)/o-PDA complex reduced at the mercury electrode. On the other hand, when there was only o-PDA in the B-R buffer solution (pH 2.5), no peak was observed. The height of the Se(IV)/o-PDA peak current depends on the o-PDA concentration and reaches a maximum value at about 1.0×10^{-3} M o-PDA. Since further addition of o-PDA had nearly no effect, 1.0×10^{-3} M o-PDA was used throughout the study.

Effects of acids, pH and time on the selenium(IV)/ o -PDA peak

Different kinds of acids such as HClO_4 , H_2SO_4 , HNO_3 and B-R buffer solutions were used to investigate the effects of supporting electrolytes and pH on the new peak (Figure 3). Although the sensitivity of

the Se(IV)/o-PDA peak was nearly unchanged in HClO₄, H₂SO₄ and HNO₃ (pH 1), a very small peak for selenium could be observed in HNO₃ due to the reaction of HNO₃ with mercury. The maximum peak current for Se(IV)-PDA at pH 2.51 can be explained by the formation of HSeO₃⁻ (pK_a 2.7). Therefore the optimum pH was about 2.5 and was used for further studies (Figure 4a).

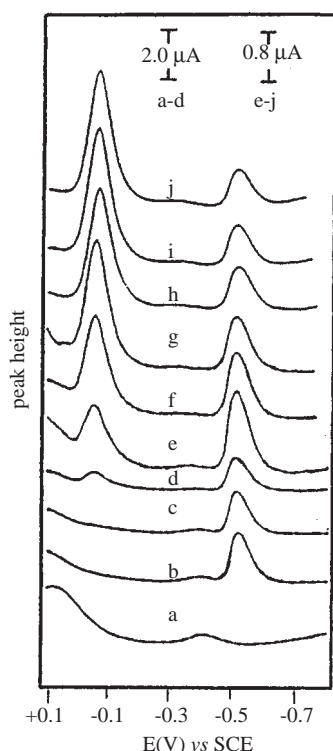
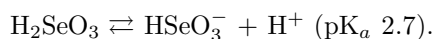


Figure 2. Effect of concentration of o-PDA on the selenium(IV) peak. (a) 10.0 mL of B-R buffer solution (pH 2.51) (b) a + 1.0 × 10⁻⁵ M Se(IV) (c) b + 1.0 × 10⁻⁵ M o-PDA (d) c + 1.0 × 10⁻⁴ M o-PDA (e) d magnified 2.5 times (f) e + 1.0 × 10⁻⁴ M o-PDA (g) f + 2.0 × 10⁻⁴ M o-PDA (h) e + 5.0 × 10⁻⁴ M o-PDA (i) e + 1.0 × 10⁻³ M o-PDA (j) e + 5.0 × 10⁻³ M o-PDA.

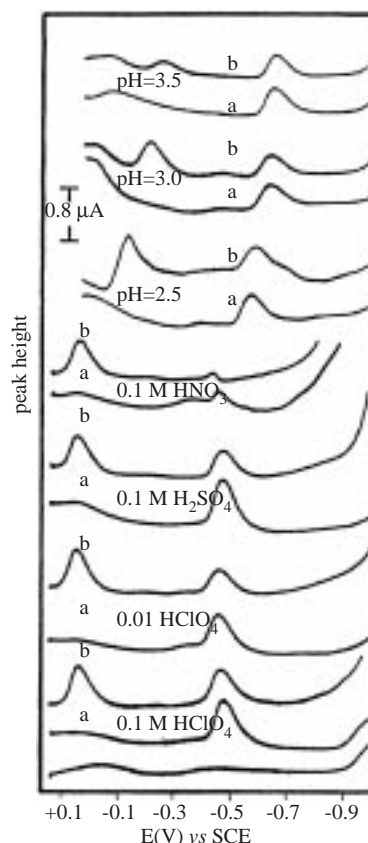
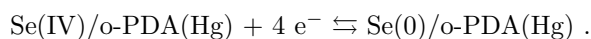


Figure 3. Effect of different kinds of acids (HClO₄, H₂SO₄, HNO₃) and pH (B-R buffer solution) on the o-PDA peak (a) 5.0 × 10⁻⁶ M Se(IV), (b) a + 1.0 × 10⁻³ M o-PDA.

It was observed that the reduction potentials of both Se(IV) and Se(IV)/o-PDA complex shifted to a more negative potential with increasing pH. This fact is an indication that the peak at -0.08 V is due to the formation of the Se(IV)/o-PDA, and subsequent reduction of the Se(IV)/o-PDA complex,



A similar reduction process was also proposed for selenium complexes on a mercury electrode^{13,15}. In order to determine the time dependence for Se(IV)/o-PDA formation, polarograms of 5.0 × 10⁻⁶ M Se(IV) in the presence of 1.0 × 10⁻³ M o-PDA were recorded between 1 and 12 min (Figure 4b). The peak current of Se(IV)/o-PDA increased until about 5 min and then remained constant due to the stable complex formation.

This was because of the relatively slow reaction between Se(IV) and o-PDA for the completion of the complex formation reaction. The optimum time for the complex formation was chosen as 5 min for further studies.

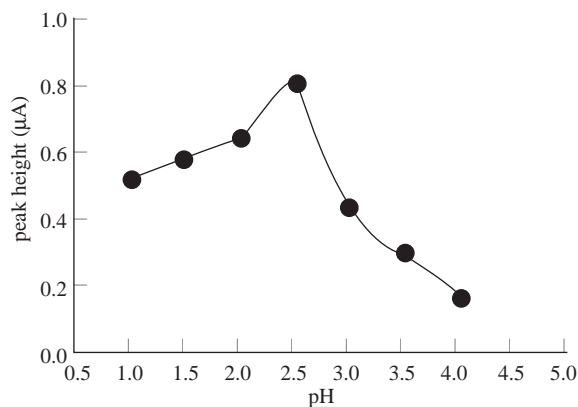


Figure 4a. Effect of the pH on the Se(IV)/o-PDA peak [5.0×10^{-6} M Se(IV); 1.0×10^{-3} M o-PDA].

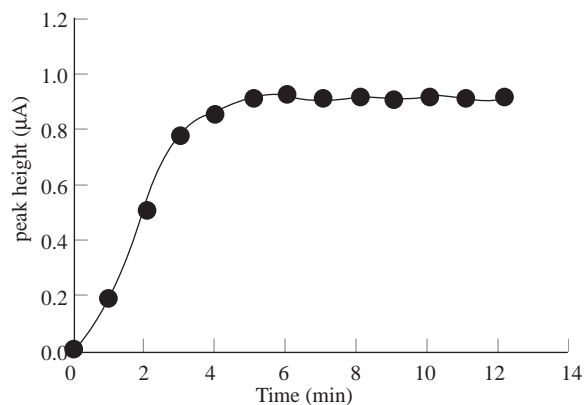


Figure 4b. Effect of time on the formation of Se(IV)/o-PDA peak [10.0 mL of B-R buffer solution (pH 2.51); 5.0×10^{-6} M Se(IV); 1.0×10^{-3} M o-PDA].

Determination of selenium(IV) in the presence of lead(II), cadmium(II) and tin(II)

When Se(IV) and some metal ions such as lead(II), cadmium(II) and tin(II) were present together, a strong interference was observed depending on the concentration ratios of the ions present. If the Se(IV) concentration was lower than that of metal ions, 2 peaks were observed in acidic media, one corresponding to free metal ions at -0.55 V (Cd^{2+}) and the second to an intermetallic compound between Se(IV) and metal ion at about -0.33 V (Figure 1c). When standard additions of Se(IV) were made to this solution, the peak for the metal ion decreased as the peak at -0.33 V increased (Figure 1d). Since the reduction of the metal ion occurred in both of these peaks and all the selenium was in intermetallic form, they had to be analysed individually. When we added 1.0×10^{-3} M PDA to this solution, a new peak at about -0.08 V corresponding to Se(IV)/o-PDA complex was obtained (Figure 1e). Since the new peak responded quantitatively to Se(IV) additions (Figure 1f), it gave an advantage for selenium determination in spite of strong interference due to metal ions such as lead(II), cadmium(II) and tin(II).

When the Se(IV) concentration was higher than that of metal ions, 2 peaks were observed: one corresponded to free Se(IV) at about -0.53 V and the other to an intermetallic compound between the metal ion and selenium at -0.33 V. After the standard additions of Se(IV) were made to this solution, the peak at -0.53 V increased but it was not possible to determine Se(IV) from this increment since one part of Se(IV) was reduced to the intermetallic compound (at -0.33 V). In order to solve this problem 1.0×10^{-3} M PDA was added to this solution and a new peak at about -0.08 V corresponding to Se(IV)/o-PDA complex was obtained. After standard additions of Se(IV), its determination was achieved from the quantitative increments of the new peak without any interfering effects.

When the molar ratio of Se(IV) and metal ions in the solution was equal to one, a larger peak at -0.33 V belonging to the intermetallic compound and a very small peak at -0.53 V for Se(IV) still existed (because

of the equilibrium reaction between Se(IV) and metal ions). After the addition of 1.0×10^{-3} M *o*-PDA, the new peak at about -0.08 V appeared and gave good qualitative increments upon standard Se(IV) addition (Figure 5).

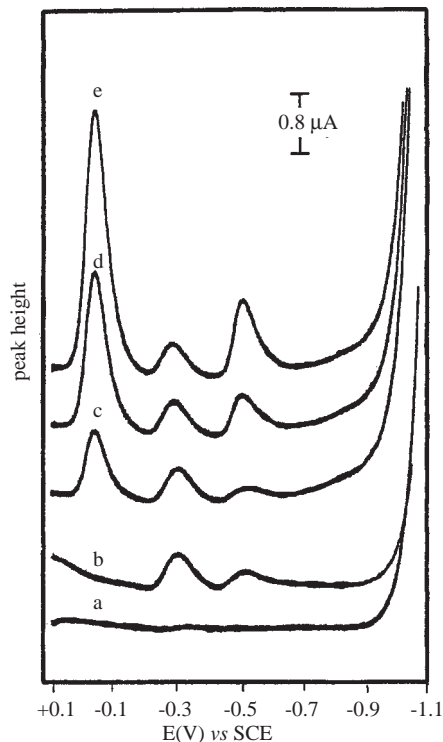


Figure 5. Determination of 5.0×10^{-6} M Se(IV) in the presence of 5.0×10^{-6} M Pb(II) using Se(IV)/*o*-PDA peak. (a) 10.0 mL of B-R buffer solution (pH 2.51) (b) a + 5.0×10^{-6} M Se(IV) and 5.0×10^{-6} M Pb(II) (c) b + 1.0×10^{-3} M *o*-PDA (d) c + 5.0×10^{-6} M Se(IV) (e) d + 5.0×10^{-6} M Se(IV).

During our polarographic studies for the determination of Se(IV), strong interference was also observed when tin(II) was present in the same solution, which made its correct determination impossible. This fact is also very important, since both of these ions may be present with great probability in the same sample. However, our further studies have shown that the determination of Se(IV) using the new peak formed with *o*-PDA is possible. Tin(II) has either 1 or 2 peaks, depending on the pH of the solution (Figure 6). In 0.1 M HClO₄ or HNO₃, it has only 1 peak at about -0.40 V, which corresponds to its reduction, and at pH values higher than 2, it has 2 peaks: 1 for the oxidation of tin(II) to tin(IV) at about -0.12 V and the other at about -0.44 V for its reduction. When a small amount of Se(IV) was added to a solution containing tin(II) (pH 2.5), a new peak at -0.36 V appeared (Se-Sn) while the peak for tin(II) at -0.44 V decreased and a small peak for Se(IV) also became observable (Figure 6c). The standard Se(IV) addition for its determination would give us an incorrect result since it annihilated the tin(II) peak by shifting toward Sn-Se formation (Figure 6d). After the addition of 1.0×10^{-3} M *o*-PDA to this solution, the new peak appeared for Se/*o*-PDA at about -0.08 V (Figure 6e). The selenium determination was achieved from a good qualitative increment upon standard Se(IV) additions (Figure 6f).

Similar results were also observed for solutions containing lead(II), cadmium(II) and selenium(IV)

(Figure 7) or lead(II), cadmium(II), tin(II) and selenium(IV). As shown in Figure 7, when there was more than one interfering ion next to selenium, the determination of selenium would be more difficult without this method since CdSe, PbSe and SnSe intermetallic peaks appeared together at about -0.33 V as a broad peak. 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, and the amounts of Se(IV) found using the advantage of this new peak are given in Table 1 along with their relative standard deviations (90% confidence level) and relative errors.

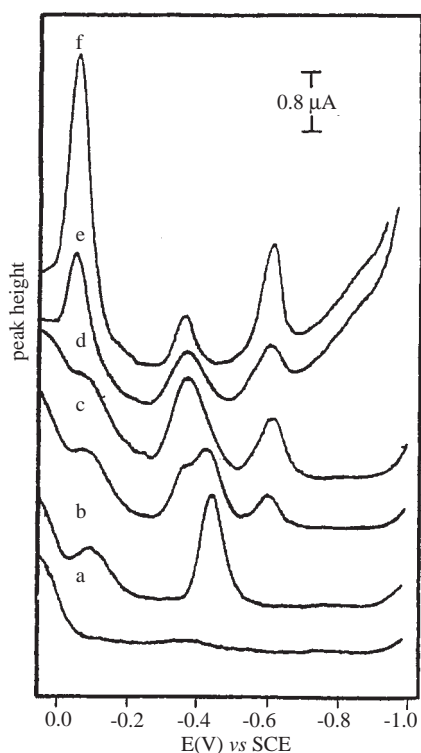


Figure 6. Effect of selenium(IV) addition on tin(II) and determination of selenium(IV) using Se(IV)/o-PDA peak. (a) 10.0 mL of B-R buffer solution (pH 2.51) (b) a + 2.0×10^{-5} M Sn(II) (c) b + 5.0×10^{-6} M Se(IV) (d) c + 5.0×10^{-6} M Se(IV) (e) d + 1.0×10^{-3} M o-PDA (f) e + 2.0×10^{-5} M Se(IV).

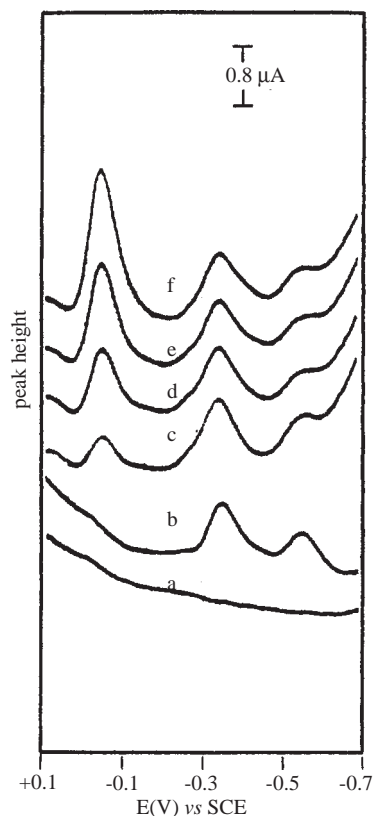


Figure 7. Determination of 5.0×10^{-7} M selenium(IV) in the presence of 1.5×10^{-6} M Pb(II) and 1.5×10^{-6} M Cd(II) using Se(IV)/o-PDA peak. (a) 10.0 mL of B-R buffer solution (pH 2.51) (b) a + 5.0×10^{-7} M Se(IV); 1.5×10^{-6} M Pb(II); 1.5×10^{-6} M Cd(II) (c) b + 1.0×10^{-3} M o-PDA (d) c + 5.0×10^{-7} M Se(IV) (e) d + 5.0×10^{-7} M Se(IV) (f) e + 5.0×10^{-7} M Se(IV).

Influences of co-existing ions on the selenium (IV)/ o-PDA peak

The effect of the possible interference from some metal ions, such as Pb(II), Cd(II), Zn(II), Sb(III), Ni(II), Mo(VI), Cr(III) and As(III), were investigated at a concentration of 5.0×10^{-6} M Se(IV) and 1.0×10^{-3} M o-PDA. The co-existing ions were taken as 10, 20 and 50-fold molar excesses of Se(IV) and the results are summarised in Table 2. The values show the ratio of peak currents in the presence of the co-existing ions to that in their absence (by percentage). According to the results 20-fold of Pb(II), Cd(II), Zn(II), Ni(II), Cr(III) and probably As(III) exert nearly no influence on the determination of selenium. However,

at higher concentrations of co-existing ions some influence was observed except for Zn(II) and Cr(III). Due to the overlapping of the peak potentials for Cu(II) and Se(IV)/o-PDA, the influence of the copper was so enormous that it exceeds the original peak by more than 200-fold.

Table 1. Determination of selenium(IV) next to interfering ions with different ratios and probability in synthetic samples.

Synthetic sample(M)	Se(IV) found (M) ($\bar{x} \pm t^{\alpha}.s/\sqrt{n}$)	R.S.D ^b (%)	Relative error(%)
5.0 x 10 ⁻⁶ Se(IV) : 5.0 x 10 ⁻⁶ Pb(II)	(4.81 ± 0.21) x 10 ⁻⁶	4.4	-3.8
5.0 x 10 ⁻⁸ Se(IV) : 5.0 x 10 ⁻⁷ Pb(II)	(4.72 ± 0.26) x 10 ⁻⁸	5.5	-5.6
5.0 x 10 ⁻⁷ Se(IV) : 2.5 x 10 ⁻⁶ Pb(II)	(5.09 ± 0.34) x 10 ⁻⁷	6.7	+1.8
5.0 x 10 ⁻⁷ Se(IV) : 5.0 x 10 ⁻⁷ Pb(II)	(4.75 ± 0.12) x 10 ⁻⁷	2.5	-5.0
3.0 x 10 ⁻⁶ Se(IV) : 5.0 x 10 ⁻⁷ Pb(II)	(3.12 ± 0.20) x 10 ⁻⁶	6.4	+4.0
1.5 x 10 ⁻⁶ Se(IV) : 5.0 x 10 ⁻⁷ Cd(II)	(1.43 ± 0.04) x 10 ⁻⁶	2.8	-4.7
3.0 x 10 ⁻⁵ Se(IV) : 5.0 x 10 ⁻⁶ Cd(II)	(3.11 ± 0.17) x 10 ⁻⁵	5.5	+3.7
1.0 x 10 ⁻⁵ Se(IV) : 1.5 x 10 ⁻⁵ Cd(II)	(1.04 ± 0.05) x 10 ⁻⁵	4.8	+4.0
5.0 x 10 ⁻⁷ Se(IV) : 5.0 x 10 ⁻⁷ Cd(II)	(4.74 ± 0.26) x 10 ⁻⁷	5.5	-5.2
5.0 x 10 ⁻⁷ Se(IV) : 1.5 x 10 ⁻⁶ Cd(II)	(4.65 ± 0.33) x 10 ⁻⁷	7.1	-7.0
3.0 x 10 ⁻⁵ Se(IV) : 1.0 x 10 ⁻⁵ Sn(II)	(3.16 ± 0.07) x 10 ⁻⁵	2.2	+5.3
1.0 x 10 ⁻⁵ Se(IV) : 2.0 x 10 ⁻⁵ Sn(II)	(0.95 ± 0.03) x 10 ⁻⁵	3.2	-5.0
1.0 x 10 ⁻⁵ Se(IV) : 1.0 x 10 ⁻⁵ Sn(II)	(0.98 ± 0.02) x 10 ⁻⁵	2.0	-2.0
5.0 x 10 ⁻⁷ Se(IV) : 2.0 x 10 ⁻⁷ Pb(II): 2.0 x 10 ⁻⁷ Cd(II)	(5.28 ± 0.35) x 10 ⁻⁷	6.6	+5.6
5.0 x 10 ⁻⁷ Se(IV) : 5.0 x 10 ⁻⁷ Pb(II): 5.0 x 10 ⁻⁷ Cd(II)	(5.25 ± 0.42) x 10 ⁻⁷	8.0	+5.0
5.0 x 10 ⁻⁷ Se(IV) : 1.5 x 10 ⁻⁶ Pb(II): 1.5 x 10 ⁻⁶ Cd(II)	(4.68 ± 0.39) x 10 ⁻⁷	8.3	-6.4
2.8 x 10 ⁻⁵ Se(IV) : 4.7 x 10 ⁻⁶ Pb(II) : 4.7 x 10 ⁻⁶ Cd(II)	(2.97 ± 0.22) x 10 ⁻⁶	7.4	+6.1
{ 5.0 x 10 ⁻⁶ Se(IV) : 1.0 x 10 ⁻⁵ Pb(II): 1.0 x 10 ⁻⁵ Cd(II) : 1.0x10 ⁻⁵ Sn(II) }	(4.57 ± 0.33)x10 ⁻⁶	7.2	-8.6

^a 90% confidence interval, n = 4 ; ^b Relative standard deviation.

Table 2. Influence of co-existing ions for the peak current of Se(IV)/o-PDA in 5.0 μM Se(IV).

Concentrations of co-existing ions (μM)	Co-existing ions and their influence on signal ratio (%)								
	Pb(II)	Cd(II)	Zn(II)	Sb(III)	Ni(II)	Mo(VI)	Cr(III)	As(III)	Cu(II)
50	101	103	106	96	100	111	100	100	>200
100	105	107	106	85	104	115	105	108	>200
250	108	113	106	81	112	115	105	108	>200

Analytical features

The results presented made it possible to specify the optimum conditions for the DPP determination of Se(IV) using o-PDA. Since the formation of the Se(IV)/o-PDA complex is relatively slow, the reaction mixture was left for 5 min (at about 20 °C) and then polarograms were recorded at the end of this period. B-R buffer solution with a pH ~ 2.5 and 100-1000-fold molar excess of o-PDA against Se(IV) were suitable. Under these conditions, a linear relationship holds between the peak height of the reduction of Se(IV)/o-PDA and the concentration of Se(IV) in the range of 5.0 x 10⁻⁸ to 6.8 x 10⁻⁵M Se(IV). The statistical data for the calibration line for this range was as follows: slope 9.57 x 10⁴μA/M, intercept 1.08 x 10⁻³μA and

correlation coefficient 0.9988 ($I = 9.57 \times 10^4 C + 1.08 \times 10^{-3}$; I in μA , C in molarity). The proposed method showed good reproducibility and accuracy with a relative standard deviation of 5.5% and a relative error of -5.6% for the determination of 5.0×10^{-8} M Se(IV) next to 5.0×10^{-7} M Pb(II). Without using this method based on the complex peak of Se(VI)/o-PDA, selenium determination by direct standard additions of Se(IV) would give enormous errors up to -44.5% for a mixture of 5.0×10^{-6} M Pb(II) and 1.0×10^{-5} M Se(IV) and -66.0% for 5.0×10^{-6} M Cd(II) and 1.5×10^{-5} M Se(IV). The greatest advantage for the determination of Se(IV) by means of Se(VI)/o-PDA is not only its high sensitivity but also its capability for the separation of selenium from interfering components. Although analysis by atomic absorption spectroscopy has been shown to be a quick and simple method using the hydride vapour generation technique¹⁶, there are also a number of factors generally overlooked, such as interferences, matrix effects and losses through volatilisation at high temperature. The limit of detection is also poor compared to voltammetric methods. Other accessible techniques such as X-ray fluorescence (XRF), and atomic emission spectroscopy with inductively coupled plasma excitation (AES-ICP) are very expensive and often do not offer sufficient sensitivity or selectivity at trace to ultra trace concentration. According to some previous electroanalytical studies, selenium interferes with the determination of lead, copper or cadmium^{3,5} and separation procedures of Se with organic solvents are usually needed¹⁷.

This method could be used for direct the determination of selenium by differential pulse polarography. It has proved to be satisfactory, even in the analysis of biological samples containing a complex mixture of metals. There is no need for separation or pre-concentration procedures, which are tedious, time-consuming and polluting.

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