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Short communication

Interference between selenium and some trace elements during polarographic studies and its elimination

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Abstract

When selenite was added into solutions of some ions such as copper, lead, cadmium, zinc, chromium and arsenic their DPP peak decreased. This kind of interference was observed in all acids and in wide range of pH values, causing at least 50% error when both ions (the ion present and selenite) were in similar quantities. It was found that this interference was not taking place at pH 8.5 in the presence of large amounts of selenite. A synthetic sample containing these elements in 10^{-5} M in the presence of 50 times selenite has been analyzed at pH 8.5 without any interference. The detection limit in this medium was 3×10^{-7} M for cadmium and lead, 1×10^{-6} M for copper and zinc and it was 3×10^{-7} M for selenite.

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1. Introduction

For the determination of trace elements among many methods electroanalytical methods are preferred because of their sensitivity and selectivity feature. In our differential pulse polarographic (DPP) study for the trace element determination we found strong interference between selenite and some ions [1]. In some voltammetric studies such as ASV [2] and CSV [3,4] it was mentioned that addition of selenite to a sample containing ions such as copper, lead and cadmium, had a diminishing effect on their peak heights which would lead to erroneous results. Thorough investigation revealed formation at the mercury electrode surface of an intermetallic compound between selenium and the elements present [3,5]. For rain water analysis DPP was used and [6] it was observed that the peak of cadmium and lead decreased about 10% by the addition of selenite and selenite peak decreased 40%. This kind of interference was attributed to an intermetallic compound formation [1] and the new peak formed has been used for the quantitative determination of selenite in blood [7] using DPP. During our polarographic studies for the determination of tin, strong interference was observed when selenium was present in the same solution, which made their correct determination impossible. However, our further studies have shown that this interference can be used for the trace determination of tin by the addition of large amount of selenite and using the newly formed peak [8]. Interference was observed when ASV and CSV methods were used for the determination of As, Se, Cu, Pb and Cd in sea water [9], but it was eliminated by standard addition method.

The aim of the present work was to investigate the pH dependence of the interference between selenite and some ions and the optimum conditions for minimum amount of interference.

2. Experimental

2.1. Apparatus

A PAR Model 174 A polarographic analyzer system, equipped with a PAR mercury drop timer, was used. A

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Kalusek electrolytic cell with reference saturated calomel electrode (SCE), separated by liquid junction, was used in three-electrode configuration. The natural drop time of mercury electrode was in the range of 2–3 s (2.4 mg s^{-1}). A platinum wire was used as a counter electrode. The polarograms were recorded with a Linseis LY 1600 X-Y recorder. The polarograms were recorded under the conditions of a drop life of 1 s, a scan rate of 5 mV s^{-1} and pulse amplitude of 50 mV.

2.2. Reagents

All of the reagents used were of analytical-reagent grade (proanalysis). Triply distilled water was used in the preparation of all solutions. Solutions of 10^{-3} M and more dilute ones were prepared before every use in order to avoid the aging process of solution.

The mercury used in the dropping mercury electrode was obtained from Merck (Darmstadt, Germany). Contaminated mercury was cleaned by passing it successively through dilute HNO_3 (3.0 M) and water columns in the form of fine droplets by using a platinum sieve. The collected mercury was dried between sheets of filter paper. Before use, a DPP polarogram of this mercury was recorded in order to confirm the absence of impurities.

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 (85%) and 2.47 g of boric acid dissolved by dilution with water to 1.0 l; 50 ml portions of this solution were taken, and the pH was adjusted by the addition of an appropriate amount of 2.0 M NaOH to the desired value.

3. Results and discussion

During our DPP polarographic studies when selenite was added into a solution containing some elements such as copper, lead, cadmium, arsenic and zinc their peak height decreased and a new peak appeared at more positive potentials than the ion in the solution. As can be seen from Fig. 1, at pH 2 cadmium ion had a peak at −0.58 V, when selenite ion was added cadmium peak decreased and a new peak appeared at −0.36 V (curve c). With additions of selenite, while cadmium peak was continuously decreasing, the new peak was increasing. But then its increase became nearly constant. The amount of selenite used until this time was about 5 moles per one mole of cadmium at this pH. The decrease of cadmium peak during first additions was large, the peak decreased nearly 50% when same amount of selenite was added (curve c). The new peak formation was attributed to the formation of an intermetallic compound, formed between selenium and the ion present by a Somer mechanism [1]. It was formulated for cadmium as follows:

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

$$Se_{ads} + Cd^{2+} + 2e^- \rightleftarrows CdSe_{ads}$$

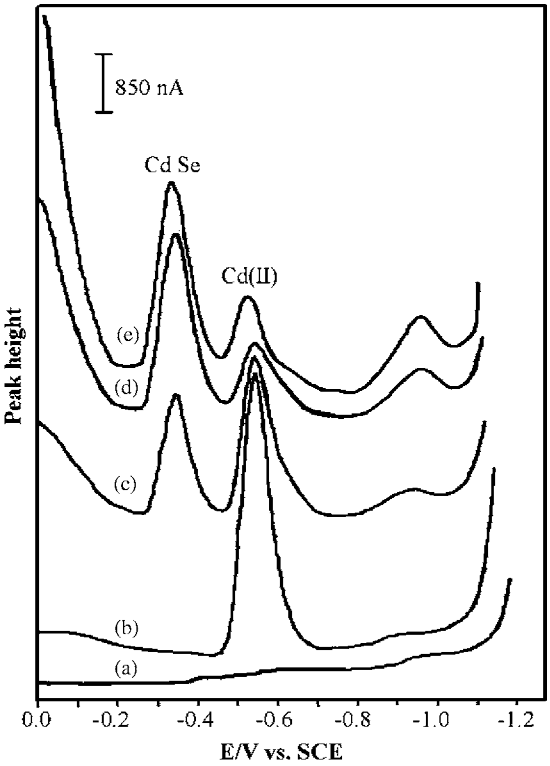

Fig. 1. Effect of Se(IV) on Cd(II) ions: (a) 10.0 ml, 1.0 M HAc/Ac^- buffer (pH 2.0); (b) a + 0.1 ml, 1 × 10^{-3} M Cd(II); (c) b + 0.1 ml, 1 × 10^{-3} M Se(IV); (d) c + 0.1 ml, 1 × 10^{-3} M Se(IV); (e) d + 0.2 ml, 1 × 10^{-3} M Se(IV).

As can be seen because of this interference it will be impossible to determine the above-mentioned ions in the presence of selenite correctly. For this purpose the behavior of these ions has to be followed in different media, where the interference can be eliminated.

3.1. The behavior in $HClO_4$ solution

The polarographic behavior of Cd, Pb, Zn, Cu, As and Se has been studied in various concentrations of $HClO_4$. For this purpose, first for each ion DPP polarograms were taken in 2, 1 and 0.1 M $HClO_4$ solutions and then selenite was added. During the additions of selenite the peak under consideration was decreasing and a new peak at more positive potentials was forming. At first the height of the new peak was continuously increasing by the additions of selenite, then it became nearly constant and its height depended on the amount of the ion present before the addition of selenite. This peak was used for the determination of the ion under consideration after addition of large amounts of selenite [7,8]. The change of peak potentials of the ions investigated and the new peak after addition of selenite with acid concentration have been summarized in Table 1. The peak obtained in the presence of selenium and cadmium is represented by CdSe and the same representation was used for the other ions present. Zinc could not be observed at this high

Table 1
Effect of acid concentration on peak potentials, V vs. SCE

	2 M $HClO_4$	1 M $HClO_4$	0.1 M $HClO_4$
Se(IV)	−0.11	−0.08	−0.04
	−0.40	−0.42	−0.47
Cd(II)	−0.59	−0.57	−0.55
CdSe	−0.36	−0.35	−0.30
Pb(II)	−0.39	−0.37	−0.34
PbSe	−0.32	−0.30	−0.28
Zn(II)	No peak	No peak	–
ZnSe	No peak	No peak	–
As(III)	−0.56	−059	−0.66
	−0.69	−0.70	−0.75
	−0.84	−0.85	−0.90
AsSe	−0.30	−0.31	−0.37

acidity (1 and 2 M acid) because of preceding hydrogen reduction peak. It was not possible to observe copper peak at this high acidity because of the first peak of selenium at about −0.11 V.

As can be seen because of this interference it is not possible to determine the quantities of these elements correctly in this medium.

3.2. Behavior in acetate buffer at various pH values

The behavior of the above-mentioned ions was studied in the presence of selenite at various pH values of 2, 3, 4 and 5. The results are given in Table 2. As can be seen the same interference was observed for Pb, Cd, Zn, Cu and As(III) ions, but not for Cr(III) and Cr(VI). Zinc peak could not be observed at pH 2 and 3 because of hydrogen reduction peak, but at pH 4 and 5 zinc and ZnSe peaks were possible to observe. There was no interference of copper at pH 4 and 5, the new peak of CuSe could only be observed at lower pH values. As was observed in Fig. 1 the peak of the corresponding ion decreased about 50% by the addition of selenite. Since this interference will take place for many ions and will cause large errors in the determinations, its elimination is very important. One solution might be the addition of EDTA, which would form complex with the ion and may eliminate this effect. However, when selenite was added into a solution containing the EDTA complex of ion, the complex decomposed and the intermetallic compound formation took place, indicating that the interference is stronger than the EDTA complex.

Table 2
Effect of pH on peak potentials V vs. SCE

	pH 2	pH 3	pH 4	pH 5
Se(IV)	−0.47	−0.58	−0.62	−0.65
		−1.10	−1.13	−1.22
Pb(II)	−0.36	−0.37	−0.40	−0.40
PbSe	−0.30	−0.30	−0.33	−0.34
Cd(II)	−0.58	−0.56	−0.56	−0.56
CdSe	−0.36	−0.34	−0.32	−0.32
Zn(II)	–	–	−0.92	−1.0
ZnSe	–	–	−0.55	−0.61
As(III)	−0.47		−0.90	
	−0.75		−1.16	
	−0.90		−1.35	
	−1.05			
AsSe	−0.32	–	−0.50	–
Cu(II)	−0.12	−0.12	−0.08	−0.08
CuSe	−0.05	−0.08	No peak	No peak
Cr(III)	–	–	−1.00	−0.91
Cr(III)Se	–	–	No peak	No peak
Cr(VI)	No peak	No peak	−0.48	
	–		−0.95	

The intermetallic compound formation must be a reversible reaction since same behavior was observed for the reverse reaction that is when one of the above-mentioned ions was added into a selenite solution the new peak appeared at the same potential.

When the increase of the new peak became nearly constant during continuous additions of selenite, the number of moles of selenite used for one mole of ion present is calculated. It was found that the number of moles of selenite depended of pH. The results obtained for cadmium and lead are given in Table 3. As can be seen while 0.6 moles of selenite was needed for one mole of lead at pH 2, it was 2.4 moles at pH 5. On the other hand while 5 moles of selenite was needed for one mole of cadmium at pH 2, 13 moles of selenite was used at pH 5. The pH dependence is because of the ease of reduction of selenite at lower pH values.

As can be concluded from the pH dependence, the interference weakens at high pH values. Thus, it may be possible to find conditions at high pH values where no interference will take place. For this purpose the interference studies are made at pH 8.5.

3.3. Behavior at pH 8.5 in acetate and BR buffer

The above given experiments were repeated at pH 8.5 in acetate solution and in BR buffer. As can be seen from Table 4 no interference was observed for Cd, Pb, Zn, Cu, As(III) and Cr(III). However, it is interesting to note that while interference was observed for Cr(VI) in acetate solution, there was no interference in BR buffer. This must be due to some reactions between Cr(VI) and buffer components. The above given results are indicating the possibility of trace element determinations in the presence of selenite at pH 8.5 without any interference.

Table 3
Number of moles of selenite used for one mole of Cd and Pb at varying pH

	pH 2	pH 3	pH 4	pH 5
CdSe	−0.36 V	−0.34 V	−0.32 V	−0.32 V
	5 Se(IV)	5 Se(IV)	8 Se(IV)	13 Se(IV)
PbSe	−0.30 V	−0.30 V	−0.33 V	−0.34 V
	0.6 Se(IV)	0.6 Se(IV)	1.4 Se(IV)	2.4 Se(IV)

Table 4
Behavior of ions at high pH values, potentials, V vs. SCE

	pH 8.5	pH 8.5[a]
Se(IV)	−1.65	−1.76
Cd(II)	−0.60	−0.53
CdSe	No peak	No peak
Pb(II)	−0.42	−0.36
PbSe	No peak	No peak
Zn(II)	−0.94	−0.95
ZnSe	No peak	No peak
Cu(II)	−0.06	−0.07
CuSe	No peak	No peak
Cr(III)	−1.50	–
Cr(III)Se	No peak	–
Cr(VI)	−0.30	−0.25
–	−1.59	−1.66
Cr(VI)Se	−0.15	–
As(III)	–	−1.65
AsSe	–	No peak

[a] B.R buffer.

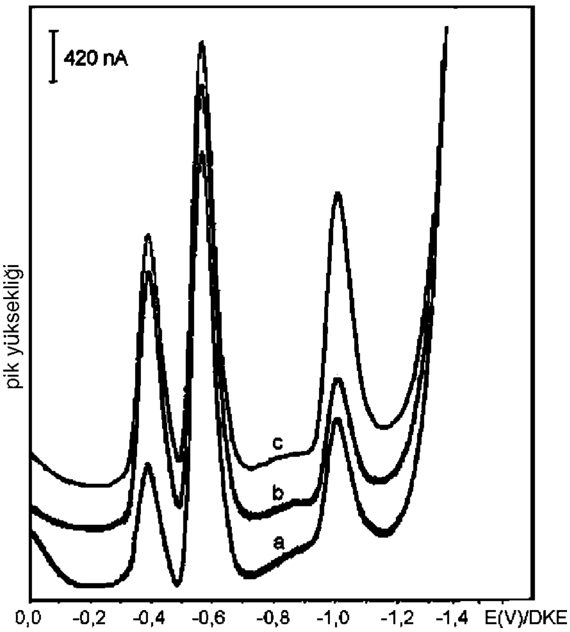

Fig. 2. Determination of lead and zinc in a synthetic sample containing 50 times of selenite: (a) 10 ml, 0.1 M NaAc (pH 8.5) + Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}(each 10^{-5} M) + 5 × 10^{-4} M Se(IV); (b) a + 0.1 ml, 1 × 10^{-3} M Pb(II); (c) b + 0.1 ml, 1 × 10^{-3} M Zn(II).

The amount of selenite next to the ion will also be important, thus, each element has to be determined in a medium where known concentrations of selenite are present. Each ion was first determined in the presence of 1, 10 and 50 times of selenite. Then three solutions containing Cd, Pb, Cu, Zn and Cr(VI) each in 10^{-5} M concentration were prepared. Each solution contained selenite in 1, 10 and 50 times of the mentioned ions. There was no interference for Cd, Pb and Cu even in the presence of 100 times of selenite. However, because of the very large selenite peak (about −1.5 V) the other ions could not be observed at this high concentration of Se(IV), they could be determined in the presence of 50 times of selenite. Fig. 2 is given as an example for the determination of lead and zinc in the presence of copper, cadmium and selenite. As can be seen all these ions appear at different potentials in this medium, which enables their determination without any interference. Selenite peak appears at about −1.6 V, but because of its high concentration it is out of scale. Copper peak on the other hand is at more positive potentials, which can be determined as given in Section 3.2. The results are summarized in Table 5 with their standard deviations. Here for each ion pooled standard deviations have been used.

The detection limits in this medium are also calculated and it was 3 × 10^{-7} for cadmium and lead, and 1 × 10^{-6} M for copper and zinc.

Although no interference was observed for the above-mentioned ions at HAc-Ac^{-}, pH 8.5, there was interference for Cr(VI) (−0.30 V) in the presence of selenite and a new peak appeared after selenite addition at −0.15 V which corresponds to CrSe intermetallic compound. For the determination of Cr(VI) this peak at −0.15 V has been used in the presence of 10 times of selenite. In a sample containing all

Table 5
Determination of trace elements in a synthetic sample, in the presence of selenite (each element in 1 × 10^{-5} M concentration)

	E_{peak} (V)	Se(IV) present	Formula (M)($\bar{x} \pm \frac{z\sigma}{\sqrt{N}}$)	% error	Experiment number
Cd(II)	−0.53	1 × 10^{-5}	(1.01 ± 0.05) × 10^{-5}	+1	6
	−0.53	1 × 10^{-4}	(1.00 ± 0.04) × 10^{-5}	0	8
	−0.53	5 × 10^{-4}	(0.96 ± 0.07) × 10^{-5}	−4	3
Pb(II)	−0.36	1 × 10^{-5}	(0.99 ± 0.05) × 10^{-5}	−1	6
	−0.36	1 × 10^{-4}	(1.02 ± 0.04) × 10^{-5}	+2	7
	−0.36	5 × 10^{-4}	(0.95 ± 0.06) × 10^{-5}	−5	3
Zn(II)	−0.94	1 × 10^{-5}	(0.95 ± 0.08) × 10^{-5}	−5	3
	−0.94	1 × 10^{-4}	(1.02 ± 0.06) × 10^{-5}	+2	6
	−0.94	5 × 10^{-4}	(0.99 ± 0.07) × 10^{-5}	−1	3
Cu(II)	−0.29	1 × 10^{-5}	(0.95 ± 0.08) × 10^{-5}	−5	3
	−0.29	1 × 10^{-4}	(1.02 ± 0.06) × 10^{-5}	+2	6
	−0.29	5 × 10^{-4}	(0.99 ± 0.07) × 10^{-5}	−1	3
Se(IV)	−1.65	1 × 10^{-5}	(0.96 ± 0.06) × 10^{-5}	−3	3

z: Confidence interval, 90%.

the above given elements and Cr(VI) in 1.0×10^{-5} M concentration its quantity was found to be as $(1.12 \pm 0.12) \times 10^{-5}$ M in a 95% confidence interval.

4. Conclusion

Because of the interference between selenite and many ions their determination will not be accurate. It is found that this interference takes place in acidic solutions and also at pH values between 2 and 5. In this work it is shown that this interference can be eliminated at pH 8.5. Under these conditions it was possible to determine copper, cadmium, lead, zinc and selenite (each 10^{-5} M) in the presence of 50–100 times of selenite with great accuracy. The detection limit was 3×10^{-7} M for cadmium and lead, 1×10^{-6} M for copper and zinc and it was 3×10^{-7} M for selenite.

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References

[1] R. Inam, G. Somer, Anal. Sci. 14 (1998) 399–403.

[2] H. Aydın, G. Somer, Anal. Sci. 5 (1989) 89–94.

[3] S.B. Adeloju, A.M. Bond, M.H. Briggs, C.H. Hughes, Anal. Chem. 55 (1983) 2076–2082.

[4] W. Holak, J. Specchio, Analyst 119 (1994) 2179–2182.

[5] G. Somer, M.S. Karacan, Electroanalysis 6 (1994) 527–530.

[6] L. Vos, Z. Komy, G. Reggers, E. Roekens, R. Van Grieken, Anal. Chim. Acta 184 (1986) 271–280.

[7] R. Inam, G. Somer, Talanta 46 (1998) 1347–1355.

[8] G. Ekmekci, R. Inam, G. Somer, Anal. Sci. 16 (2000) 1151–1155.

[9] C. Locatelli, G. Torsi, J. Electroanal. Chem. 509 (2001) 80–89.