

## Electrochemical behaviour of selenium(IV) during electrolysis by square-wave voltammetry after deposition on a hanging mercury drop electrode

VALENTIN MIRČESKI, SIMKA PETROVSKA-JOVANOVIĆ, KORNELIJA STOJANOVA and  
BLAGOJA JORDANOSKI

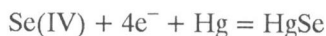
*Institute of Chemistry, Faculty of Science, The "Sv. Kiril i Metodij" University, Arhimedova 5, 91000 Skopje,  
Macedonia*

(Received 22 November 1993, revised 29 March 1994)

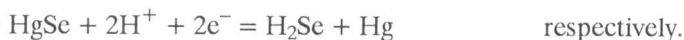
Square-wave voltammetry, one of the more advanced electroanalytical techniques, was used to investigate the electrochemical behaviour of selenium(IV) after deposition on the surface of a hanging mercury drop electrode (HMDE). The effect of deposition time and parameters of the excitation signal on the SW peak of selenium are discussed. It was found that the best defined SW peak of selenium(IV) was obtained using the following square wave signal parameters: frequency of 100 Hz, amplitude of 20 mV and scan increment of 2 mV. Using these experimental conditions and a deposition time of 60 s, selenium(IV) can be quantitatively determined in solution in the concentration range  $8.5 \times 10^{-7}$  to  $5.6 \times 10^{-6}$  mol dm<sup>3</sup>.

The importance of selenium in soils, plants and biological systems has led to the development of various analytical methods<sup>1-12</sup> for its determination at low concentrations.

Polarographic investigations have shown that selenium(IV) gives up to three polarographic waves, depending on the pH of the solutions. Christian *et al.*<sup>13</sup> studied the polarographic behaviour of selenium(IV) in various supporting electrolytes and reported two polarographic waves in 0.1 mol dm<sup>-3</sup> hydrochloric acid medium, at -0.01 and -0.54 V vs. SCE, corresponding to the reactions:



and



Only the latter reaction is reversible.

The methods used for the determination of electroactive components at trace level are cathodic or anodic stripping voltammetry.<sup>14</sup> The process of stripping the compound from the surface of the working electrode can be performed by different voltammetry techniques. The methods mainly used for the determination of

selenium(IV) at trace levels are cathodic or anodic differential pulse stripping voltammetry.<sup>1,4,9</sup>

The present work uses square-wave voltammetry (SWV) for the determination of selenium(IV) after deposition of the surface of a HMDE. Literature data about square-wave voltammetry of selenium(IV) does not exist.

Square-wave voltammetry is one of the more sensitive and most advanced electroanalytical techniques<sup>15-17</sup> and using it the electrolysis of the solutions takes only a few seconds. So, the investigation of the selenium(IV) using this technique is of great importance.

The aim of the present work was to investigate the electrochemical behaviour of selenium(IV) during electrolysis by SW voltammetry after deposition on the hanging mercury drop electrode (HMDE) surface.

## EXPERIMENTAL

### *Instrumentation*

An EG&G Princeton Applied Research microprocessor-based polarographic analyzer (PAR Model 384B) equipped with PAR Model 303A static mercury drop electrode and a PAR Mode 305 stirrer was used to record all SW voltammograms. The electrode compartment consisted of a hanging mercury drop (HMDE), a silver-silver chloride (saturated KCl), and a platinum wire as the working, reference, and auxiliary electrodes, respectively. Deposition of the selenium(IV) onto the mercury electrode with a middle surface area was achieved by using a slow stirring rate. The solutions were degassed with highly purified nitrogen at the start of each experiment and a flow of nitrogen was maintained over the solution during the experiment to prevent oxygen interference. All experiments were performed at room temperature.

### *Reagents and other conditions*

All the chemicals used were of analytical reagent grade. Redistilled water was used.

The nitrogen used for oxygen removal from the solutions was deoxygenated by passage through acidic vanadium(II) chloride solutions. The purging time was 10 min.

Stock solutions of selenium(IV) were prepared from pure selenium,<sup>18</sup> standardized by known methods,<sup>19</sup> and further diluted as required.

The interference of Cu, Cd, Pb, Zn, Co, and Ni ions were also investigated at a constant concentration of selenium(IV). The concentration of these ions present in the selenium(IV) solutions was within the allowed concentration of the same ions in drinking water, which are presented in Table I.

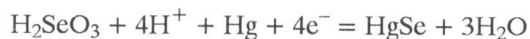
The supporting electrolyte was 0.1 mol dm<sup>-3</sup> HClO<sub>4</sub>.

During the deposition step the solutions were stirred using a magnetic stirrer. A quiescent period of 15 s was allowed, and then the SW polarograms were recorded.

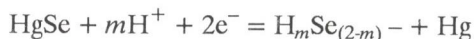
The solutions were polarographed in the potential range from 0.05 to -0.08 V. The deposition potential was 0.05 V.

## RESULTS AND DISCUSSION

Square-wave voltammetry of solutions of selenium(IV) after deposition on the surface of HMDE gives up to two SW peaks. The peak potential of the first one is about -0.01 V and of the second about -0.59 V. The second peak is larger and more convenient for analytical tracing. These peaks are most probably the result of the following electrode reactions, postulated by Adeloju *et al.*,<sup>20-24</sup> for the cathodic stripping process of selenium(IV):



for the first, and



for the second peak.

The peak current ( $I_p$ ) and peak potential ( $E_p$ ) of the second SW peak of selenium(IV) depend mainly on the concentration of selenium in the solution, the deposition time and the concentration of the supporting electrolyte. Experiments were performed at perchloric acid with concentrations of 0.10 and 1.00 mol dm<sup>-3</sup>. The peak shape is well defined in both cases, but the peak current is almost two times higher in 0.10 mol dm<sup>-3</sup> perchloric acid. Considering the background current 0.10 mol dm<sup>-3</sup> perchloric acid is also more convenient for investigation purposes. Hence, for the following experiments 0.10 mol dm<sup>-3</sup> perchloric acid was chosen as the supporting electrolyte.

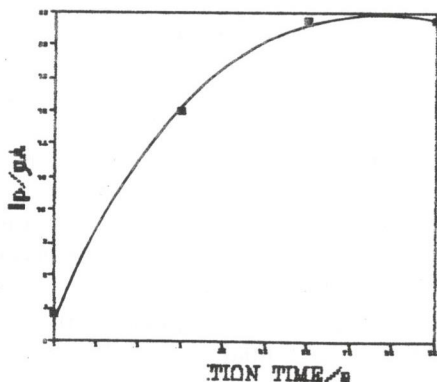


Fig. 1. Effect of the deposition time on the peak of selenium(IV). Concentration of selenium(IV)  $6 \times 10^{-6}$  mol dm<sup>-3</sup>; frequency 100 Hz; amplitude 20 mV and scan increment 2 mV.

The effect of deposition time on the peak current was investigated of constant selenium(IV) concentration in the solutions. From Fig. 1 it can be seen that the peak current initially increases with increasing deposition time. However, after 60 s, the deposition time on longer effects the peak current. It is obvious that a deposition time of 60 s is sufficient for saturation of the HMDE surface.

For a reversible electrode reaction, in which both the reactant and product of the reaction are adsorbed on the HMDE surface, the frequency of the applied SW signal influences only the peak current.<sup>15,16</sup> In the case of selenium(IV), the peak current increases linearly with increasing frequency (Fig. 2). It has to be mentioned that frequency is one of the factors which determine the reversibility of an electrode process. At very high frequencies, a reversible process can be transformed into an irreversible one. This results in disturbed peak shapes. For this reason, a frequency of 100 Hz was chosen for further investigations, because at this value the SW peak of selenium(IV) has the best defined peak shape. The frequency does not influence the peak potential which is in accordance with theoretical predictions.

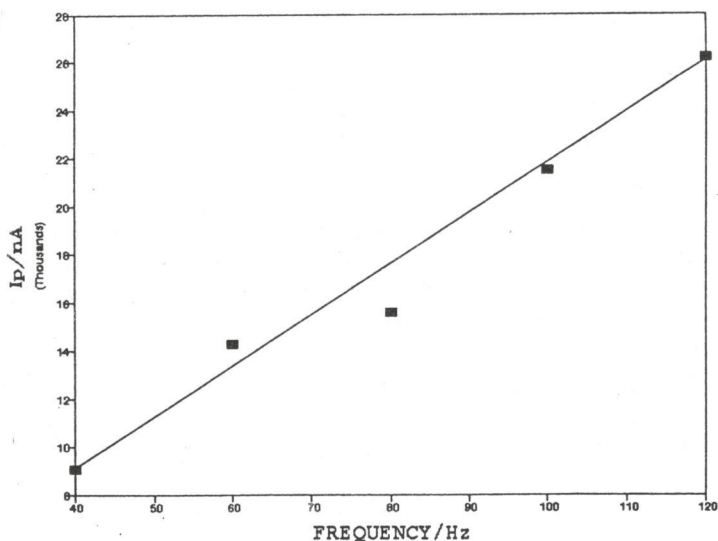


Fig. 2. Dependence of the selenium peak current on the frequency of the applied SW signal. All other parameters as in Fig. 1.

The square-wave amplitude has a great influence on the peak current and peak potential. Variation of the amplitude from 20 to 80 mV causes an increase in the peak current followed by a shifting of the peak to more positive potentials and an increase in the half-width of the peak. This phenomena is also predicted by the theory of square-wave voltammetry of adsorbed reactants.<sup>15</sup>

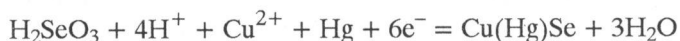
Varying the value of the potential increment of the SW signal have a minor influence of the peak current and potential.

The performed investigations have shown that the best experimental conditions for a well-defined SW peak of Se(IV) are: deposition time 60 s, frequency 100 Hz, SW amplitude 20 mV and potential increment 2 mV.

The results of the interference studies are shown in Table I.  $\Delta E_p$  is the differences between the peak potential of the pure selenium(IV) solution and the peak potential of selenium(IV) in the presence of the metal ions.  $\Delta I_p$  is the percentage reduction of the peak current in the presence of metal ions.

The diverse cations mostly influence the shape of the peak and the peak current. The interference by metal ions may occur through the formation of intermetallic compounds with selenium.<sup>1,9,11</sup>

The interference by copper ions can be described by the reaction:



The formation of such compound is in accordance with the splitting of the peak in addition of the appearance of a new peak at positive potentials (Fig. 3). The presence of zinc ions has a similar influence on the SW peak of selenium(IV).

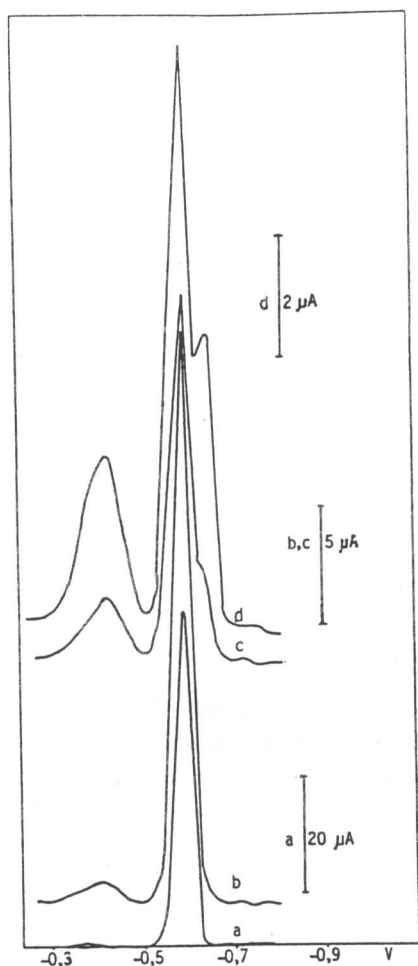


Fig. 3. Effect of the addition of  $\text{Cu}^{2+}$  cations on the SW peak of selenium(IV). a) SW peak of pure selenium(IV) b) selenium(IV) and  $6.9 \times 10^{-8} \text{ mol dm}^{-3} \text{ Cu}^{2+}$  c) Selenium(IV) and  $6.9 \times 10^{-7} \text{ mol dm}^{-3} \text{ Cu}^{2+}$  d) selenium(IV) and  $6.9 \times 10^{-6} \text{ mol dm}^{-3} \text{ Cu}^{2+}$ . All other parameters as in Fig. 1.

The electrochemical behaviour of selenium(IV) during electrolysis by SW voltammetry in the presence of some ions, is in accordance with the results obtained by DP polarography.<sup>11</sup> We did not obtain the expected effects of Pb, however, significant Zn-effects were observed. The differences in the effects of the metal ions between this and previous investigations, are most probably the result of the different deposition potential.

It is well known that the effects of ions present can be eliminated by adding EDTA in the solutions.<sup>11,25</sup> It must be taken into consideration that the presence of EDTA in higher concentration can lead to negative effects. Namely, the free molecules of EDTA, as well as the complex formed with the metal ions can be accumulated on the HMDE surface and inhibit the main electrode process.

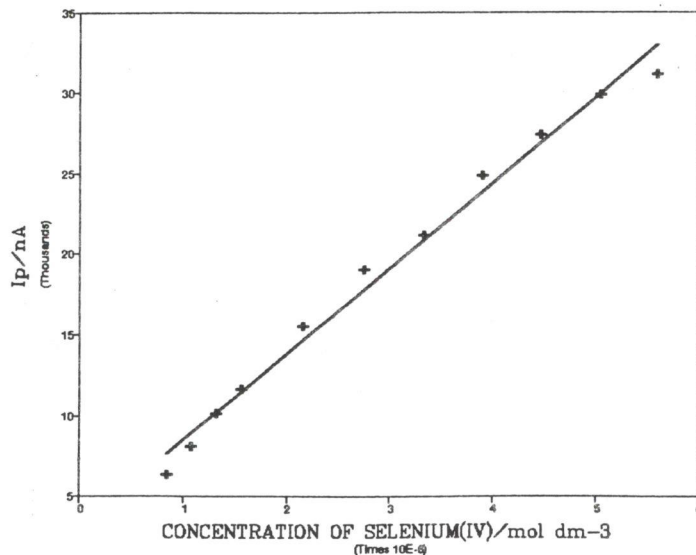


Fig. 4. Calibration curve for selenium(IV) in the concentration range from  $8.5 \times 10^{-7}$  to  $5.6 \times 10^{-6}$  mol dm<sup>-3</sup>. Deposition time 60 s; frequency 100 Hz; amplitude 20 mV; scan increment 2 mV.

As already mentioned, the height of the SW peak of selenium(IV) is dependent on the concentration of selenium(IV). Linear dependence between peak current and the Se(IV) concentration occurs within the range from  $8.5 \times 10^{-7}$  to  $5.6 \times 10^{-6}$  mol dm<sup>-3</sup> (Fig. 4). The calibration curve was constructed in the presence of all the investigated metal ions with their middle concentration shown in Table I and equimolar quantities of EDTA.

TABLE I. Effect of the metal cations on the SW peak of Se(IV). All other parameters as in Fig. 1.

Metal	$c/\text{mol dm}^{-3}$	$\Delta E_p/\text{mV}$	$\Delta I_p/\%$
Cu <sup>2+</sup>	$6.9 \times 10^{-8}$	0	16.8
	$6.9 \times 10^{-7}$ *	8	46.8
	$6.9 \times 10^{-6}$	14	65.8
Cd <sup>2+</sup>	$4.7 \times 10^{-9}$	0	12.0
	$4.7 \times 10^{-8}$ *	0	47.1
	$4.7 \times 10^{-7}$	4	69.8
Pb <sup>2+</sup>	$7.3 \times 10^{-8}$	0	/
	$7.3 \times 10^{-7}$ *	0	/
	$7.3 \times 10^{-6}$	0	9.8

TABLE I. Cont.

Metal	$c/\text{mol dm}^{-3}$	$\Delta E_p/\text{mV}$	$\Delta I_p/\%$
$\text{Zn}^{2+}$	$4.7 \times 10^{-6}$	0	12.3
	$4.7 \times 10^{-5}^*$	4	47.1
	$4.7 \times 10^{-4}$	42	69.8
$\text{Co}^{2+}$	$4.7 \times 10^{-7}$	0	/
	$4.7 \times 10^{-6}^*$	0	1.1
	$4.7 \times 10^{-5}$	0	7.8
$\text{Ni}^{2+}$	$6.4 \times 10^{-8}$	2	/
	$6.4 \times 10^{-7}^*$	2	0.5
	$6.4 \times 10^{-6}$	2	1.5

\* allowed concentration in drinking water / no reduction in the peak current

All these results enabled us to develop a complete analytical method for the determination of selenium(IV) in solutions as well as in natural materials.

## ИЗВОД

## ЕЛЕКТРОХЕМИЈСКО ПОНАШАЊЕ СЕЛЕНА(IV) ПРИ ЕЛЕКТРОЛИЗИ SW ВОЛТАМЕТРИЈОМ, ПОСЛЕ ДЕПОЗИЦИЈЕ НА ВИСЕЋОЈ ЖИВИНОЈ КАПИ

ВАЛЕНТИН МИРЧЕСКИ, СИМКА ПЕТРОВСКА-ЈОВАНОВИЋ, КОРНЕЛИЈА СТОЈАНОВА и БЛАГОЈА ЈОРДАНОВСКИ  
Институт за хемију, Природно-математички факултет Универзитет "Св. Кирил и Методиј", Архимедова 5, 91000 Скопје,  
Македонија

Квадратно-таласна волтаметрија (SWV) као једна од модернијих електроаналитичких метода искоришћена је за проучавање електрохемијског понашања селена(IV) после таложења на површини висеће живине капи (HMDE). Дискутовани су ефекти параметара SW сигнала, као и утицај времена таложења на положај и висину SW пика селена(IV) добијен при следећим параметрима SW сигнала: фреквенцији од 100 Hz, амплитуди од 20 mV и потенцијалном инкрименту од 2 mV. При овим експерименталним условима и времену таложења од 60 s, селен(IV) може да буде квантитативно одређиван у растворима концентрације од  $8,5 \times 10^{-7}$  до  $5,6 \times 10^{-6}$  mol dm<sup>-3</sup>.

(Примљено 22. новембра 1993, ревидирано 29. марта 1994)

## REFERENCES

1. G. Henze, P. Monks, G. Tolg, F. Umland, E. Weisling, *Fresenius Z. Anal. Chem.* **1-6** (1969) 295
2. O. J. Kronborg, E. S. Steinnes, *Analyst* **100** (1975) 835
3. P. N. Vijan, G. R. Wood, *Talanta* **22** (1976) 1
4. B. L. Dennis, J. L. Moyers, G. S. Wilson, *Anal. Chem.* **48** (1976) 1611
5. G. P. Bound, S. Forbes, *Analyst* **103** (1978) 176
6. G. Schwedt, A. Schwarz, *J. Chromatog.* **160** (1978) 309
7. M. Verlinden, H. Deelstra, E. Andriaessens, *Talanta* **28** (1981) 637
8. C. McCrory-Joy, J. M. Rosamilia, *Anal. Chim. Acta* **142** (1982) 231

9. S. B. Adeloju, A. M. Bond, M. H. Briggs, H. C. Hughes, *Anal. Chem.* **55** (1983) 2076
10. T. Ferri, R. Morabito, B. M. Petronio, E. Pitti, *Talanta* **36** (1989) 1259
11. B. V. Trivedi, N. V. Thakkara, *ibid.* **36** (1989) 786
12. A. M. Shafiqul Alam, O. Vittori, M. Porthault, *Analytica Chim. Acta* **87** (1976) 437
13. G. D. Christian, E. C. Knoblock, W. C. Purdy, *Anal. Chem.* **35** (1963) 1128
14. R. Calvoda, M. Copanica, *Pure and Appl. Chem.* **61** (1989) 97
15. J. G. Osteryoung, K. A. Osteryoung, *Anal. Chem.* **57** (1973) 101A
16. M. Lovrić, S. Komoski-Lovrić, R. W. Murray, *Electrochim. Acta* **33** (1988) 739
17. M. Lovrić, S. Komoski-Lovrić, *J. Electroanal. Chem.* **248** (1988) 239
18. L. M. Dennis, J. P. Koller, *J. Am. Chem. Soc.* **41** (1919) 949
19. G. Sharlo, *Metody analitičeskoj khimii*. Kolichestvennyi analiz neorganicheskih soedinenii, Khimiya, Moskva, 1966, p. 786 (Russ. transl.)
20. S. B. Adeloju, A. M. Bond, H. C. Hughes, *Anal. Chim. Acta* **148** (1985) 59
21. G. P. Bound, S. Forbes, *Analyst* **103** (1978) 176
22. J. J. Lingane, L. W. Niedrach, *J. Am. Chem. Soc.* **71** (1949) 169, 303
23. G. D. Christian, J. Buffleand W. Haerdi, *J. Electroanal. Chem.* **109** (1980) 187
24. P. Deldime, P. J. Hartman, *Anal. Lett.* **13** (1980) 105
25. E. Temmerman, Verbelek, *J. Electroanal. Chem.* **19** (1968) 423.