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CHRONOPOTENTIOMETRIC STRIPPING ANALYSIS OF SELENIUM USING MERCURY FILM ELECTRODE

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The influence of the most important experimental factors in chronopotentiometric stripping analysis (CSA) of selenium(IV) using mercury film working electrode was examined. Interferences of copper, iron and lead were investigated as well. The possibility of avoiding prolonged deaeration of the solution was examined by applying medium exchange modification of the technique, where the dissolution of the deposit was performed in calcium-chloride solution. Detection limits obtained for the modification of the CSA with prior deaeration and medium exchange modification were 0.4 $\mu g/dm^3$ and 1.15 $\mu g/dm^3$, respectively.

Accuracy of the defined techniques has been confirmed by analysing reference material (RM 8436) - wheat durum flour.The results obtained by applying both modifications of the technique showed a very good agreement of total selenium content with declareted value.

KEY WORDS: selenium, chronopotentiometric stripping analysis, mercury film electrode

INTRODUCTION

Selenium is a trace element which naturally occurs in soils, water and metal minerals, but industrial processes like the glass and electronic industries, as well as copper mines, can also influence its enviormental content and distribution.

Selenium naturally exists in several oxidation states, in both inorganic and organic forms. The inorganic selenium species most frequently found in water and soils are selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}). Several organoselenium compounds have been identified in biological samples (animals, plants, microorganisms) with direct Se-C

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bond, including methylated compounds, selenoaminoacids, selenoproteins and their derivatives.

Biochemical and metabolic role of selenium, which is considered essential element for plants, animals and humans, is rather complex (1). Selenium forms an integral part of the enzimes glutathione-peroxidase (1), iodothyronine deiodinase, thyoredoxin reductase (2), metalloproteines, fatty and binding proteins (3), selenoproteine P (4) and many other proteins.

Selenium is considered as an antioxidant nutrient due to the activity of glutathione-peroxidase, which reduces the concentration of free radicals formed during various metabolic reactions. Free radicals are implicated in many diseases. Diseases where low selenium is implicated range from nutritional disorder like protein energy malnutrition to generation diseases such as cancer, cardiovascular diseases and cataract (5).

Selenium compounds also inhibit the toxic effect of heavy metals such as lead, arsenic, cadmium, mercury and tin via to the formation of their stable selenides (6). On the other hand, at higher concentrations selenium is toxic (7).

The development of a reliable technique to study speciation of selenium in environmental and biological samples requires the understanding of the biochemical cycle, mobility and uptake of selenium, as well as its toxicity. The problems in selenium determination are associated with its low concentration, considering the fact that significant errors may arise by losses of volatile compounds, instability of some chemical species, contamination, etc.

The low content of selenium in biological samples demands high-sensitivity analytical methods for its determination. A number of methods have been developed for the determination of selenium. Some of them involve the reaction between selenium(IV) and aromatic diamine to obtain a piazselenol, which is determined by fluorimetry (8,9). Other implies gas chromatography (10-12) or hydride generation (13, 14).

Among the electroanalytical techniques for selenium determination stripping voltammetry is most commonly used. The method is highly sensitive, accurate and simple, and inexpensive at that. Cathodic stripping voltammetry with hanging mercury drop electrode as the working electrode is the most often used electroanalytical method for determining traces of selenium in biological samples. Selenium is accumulated at an electrode surface by electroreduction, either in the form of mercury-selenide (15-17) or intermetallic compounds such as copper-selenium (18, 19).

Selenium can also be determined by cathodic stripping voltammetry after adsorptive collection in the form of complex with 3,3´-diaminobenzidine on a hanging mercury drop electrode (20).

Anodic stripping voltammetry can be applied only in connection with solid electrodes, e.g. gold electrode (21).

In addition to stripping voltammetry, the stripping techniques that appeared to be useful for selenium determination with a detection limit down to ppb levels are the reductive potentiometric stripping analysis (PSA) (22) and CSA (23, 24).

Chronopotentiometric stripping analysis is an electroanalytical technique which has been less frequently applied for selenium determination. Hence, the aim of this work was to define optimal experimental conditions for CSA of selenium on model solutions using common electrochemical cell and mercury film electrode as the working electrode. In the case of CSA, deaeration of the analysed solution is necessary since oxygen can

influence the dissolution process of mercury-selenide formed at the working electrode. Because of that, two modifications of CSA were considered and compared. One involves prior deaeration of the analysed solution, and the other, so-called medium-exchange technique, is performed by the dissolution of the deposit in another medium, in which oxygen is poorly dissolved.

EXPERIMENTAL

Instrumentation and chemicals

Experiments were carried out using a computerized system for electrochemical stripping analysis produced by Elektrouniverzal, Leskovac and the Faculty of Technology, Novi Sad (25,26). Mercury film deposit at glassy carbon disc electrode was used as a working electrode. As a counter electrode served a platinum wire (φ 0.7 mm, l=7 mm) and the reference was the Ag/AgCl, KCl (3.5 mol/dm^3) electrode.

Stock solution of 2 g/dm^3 selenium(IV) was prepared by dissolving sodium-selenite pentahydrate p.a. purity, Merck, in a 0.1 mol/dm^3 hydrochloric acid and kept in a poly-ethylene bottle in the dark. Working solutions of 8 mg/dm^3 and 80 mg/dm^3 selenium(IV) were obtained by diluting the stock solution with double distilled water. Solutions containing 8 mg/dm^3 of selenium(IV) were prepared daily and those containing 80 mg/dm^3 of selenium(IV) once in a month.

Extra purity nitrogen, which was additionally purified by passing through pyrogalol and double distilled water, was used for dearation.

Copper(II), iron(III) and lead(II) solutions were prepared by diluting "Titrisol" solutions with double distilled water.

Calcium-chloride solution was obtained by dissolving calcium-chloride byhidrate (Zorka) in a 0.2 mol/dm^3 hydrochloric acid.

All vessels were washed with detergent, nitric acid (1:1) and rinsed with distilled and double distilled water, to eliminate traces of metals.

Procedure for CSA of selenium

Working electrode was formed by the electrodeposition of a mercury film in a separate acidic solution containing mercury(II) ions with constant current (50 μA) at a glassy carbon disc electrode. Prior to the film formation, the glassy carbon surface was wiped first with filter paper drenched with acetone and then with distilled and double distilled water.

According to the results of previous investigation (27), hydrochloric acid was used as an appropriate supporting electrolyte for selenium determination by CSA. The prepared sample was acidified with hydrochloric acid to obtain the acid concentration of 0.2 mol/dm^3, and then degassed by passing nitrogen for ten minutes (modification of the CSA with deaeration). The measurements were made after a preconcentration (deposition) step, in which the solution was stirred and the working electrode held at an appropriate potential for a certain time. After a rest period of 10 s, the deposit of mercury-selenide was dissolved by applying constant reductive current.

In the procedure with medium exchange the analysed solution was replaced with calcium-chloride solution during the last few seconds of the rest period.

Sample digestion

The sample of reference material (RM 8436) - durum wheat flour sample was dried at 85°C for 4 hours in a 1-cm layer, because the selenium content (1.23±0.09 mg/kg) is declared for a dry sample. After transferring the sample (3 g) to a 100-cm^3 quartz Kjeldahl flask, 20 cm^3 of nitric acid, 10 cm^3 of perchloric acid and 15 boiling pearls were added. The sample was heated at 75°C until dark nitrogen oxides fumes were completely removed. Heating was continued at 150°C until the solution became clear and colorless.

Reduction of the hexavalent selenium

After the sample digestion it was necessary to reduce the hexavalent selenium to tetravalent, since only selenium(IV) exhibits electrochemical activity. During the digestion in strong mineral acids, Se^0 and Se^{2-} are oxidized to Se^{4+}. The reduction of selenium(VI) was performed under strong reductive conditions. Perchloric acid was evaporated first, using a glass tube connected with a water vacuum pump, which enabled its complete removal evolution for only 7 minutes. Dry residue was dissolved in 5 cm^3 of 5 mol/dm^3 hydrochloric acid and heated for 15 minutes at 75°C, in order to reduce selenium(VI) to selenium(IV). The solution was then filtered and transferred quantitatively to a 100-cm^3 glass flask with double-distilled water.

RESULTS AND DISCUSSION

In order to define optimal conditions for the CSA of selenium, the influence of mercury film thickness, supporting electrolyte concentration, electrolysis potential, electrolysis time and dissolution current were investigated. The dependence of the analytical signal on the selenium concentration and metal interferences was investigated as well.

In the medium-exchange technique, the concentration of added hydrochloric acid in calcium-chloride solution, calcium-chloride concentration, and the dependence of the analytical signal on the selenium concentration were investigated.

Modification of CSA with sample deaeration

Mercury film thickness influences directly the amount of the mercury-selenide formed. The influence of mercury film thickness on the selenium analytical signal was investigated by varying the electrolysis time from 60 s to 420 s (film thickness from ~31 to 226 nm) in the solutions with 60 $\mu g/dm^3$ of selenium(IV). The applied electrolysis potential was -0.15 V, electrolysis time 60 s, dissolution (reduction) current 3 μA and the stirring rate 4000 r.p.m. On the basis of the reproducibility and height of the analytical signal, an electrolysis time of 300 s was adopted as adequate, wich corresponded

to a 163-nm film thickness, assuming a 100% electrolysis efficiency. Only 2-3 analyses with the prior solution deaeration could be performed with such mercury film.

Concentration of the supporting electrolyte. The role of supporting electrolyte is very important because of the pH and conductivity adjustment of the analysed solution and minimization of the migration current. The influence of supporting electrolyte concentration was examined under the same experimental conditions as in the previous experiment, in the concentration range of hydrochloric acid 0.1-1 mol/dm^3. Applying the same criterion, 0.2 mol/dm^3 hydrochloric acid was chosen as optimal. It was noticed that increase in the increasing hydrochloric acid concentration produced a shift of the potential of mercury-selenide dissolution to more positive values. For example, in 0.1 mol/dm^3 hydrochloric acid mercury-selenide dissolved at -520 mV, while in 1 mol/dm^3 hydrochloric acid the selenium analytical signal appeared at -460 mV.

Stirring rate in the electrolysis step influences the diffusion layer thickness and thus the amount of the deposit formed. An the increase of the stirring rate resulted, normally, in an enhanced analytical signal for selenium. The stirring rates employed ranged from 1000 r.p.m. to 6000 r.p.m. The rate of 6000 r.p.m. resulted in a low reproducibility of the analytical signal because of the mechanical damage of the electrode surface. The rate of 4000 r.p.m. was accepted as satisfactory regarding the height and reproducibility of the selenium analytical signal. The number of analyses that could be performed with one mercury film at the chosen stirring rate was 10-11.

Electrolysis potential. In order to obtain sharp and well-defined dissolution signal of mercury-selenide, the determination of the appropriate electrolysis potential (E_{el}) is of great importance.

The examined electrolysis potential was in the range from -0.05 V to -0.3 V. The results are shown in Table 1.

Table 1. Dependence of the selenium analytical signal on the electrolysis potential

E_{el} (V)	τ (s)	S (s)	KV (%)
- 0.05	1.09	0.15	13.8
- 0.10	0.98	0.05	4.68
- 0.15	0.97	0.08	8.67
- 0.20	0.75	0.18	24.10
- 0.25	0.35	0.01	3.78
- 0.30	0.22	0.02	7.83

Dissolution times (τ) for each potential, shown in Table 1, represents an average value of five analyses using the same mercury film. Reproducibility, expressed as standard deviation and coefficient of variation (KV), is also shown. Dissolution time decreased at more negative potentials, probably because of the smaller amount of mercury(II) ions available for the reaction. The highest analytical signal for selenium was obtained by applying the electrolysis potential of -0.05 V, but with poor reproducibility. Best reproducibility was obtained applying the electrolysis potential of -0.1 V and -0.15 V. The electrolysis potential of -0.1 V was selected because the selenium analytical signal was slightly higher.

Electrolysis time. Dependence of the selenium analytical signal on the electrolysis time (t_{el}) was investigated in selenium(IV) solutions of 60 μg/dm^3 and 10 μg/dm^3. The results are shown in Fig. 1. The given τ values represent averages of five analyses performed at different mercury films.

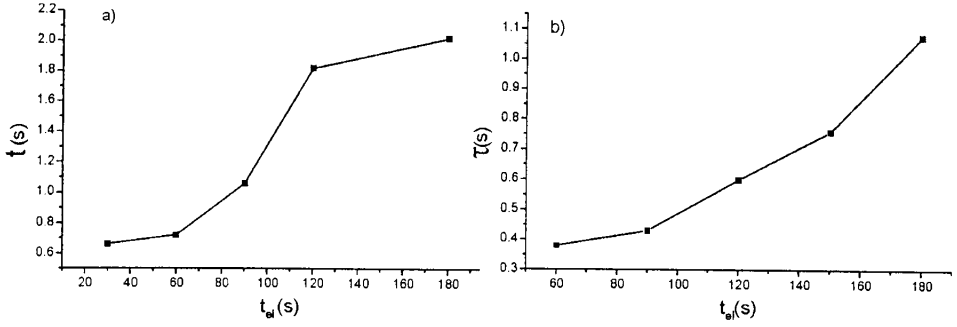

Fig. 1. Dependence of the selenium analytical signal on the electrolysis time
a) C_m = 60 μg/dm^3; i = 3 μA b) C_m = 10 μg/dm^3; i = 1.8 μA

In both cases (10 μg/dm^3 and 60 μg/dm^3) longer electrolysis time resulted in a higher determination sensitivity, though the increase was moderate in the solutions of 10 μg/dm^3 of selenium. Longer electrolysis time in the solutions of 60 μg/dm^3 of selenium caused saturation of the working electrode and curving of the mentioned dependence (Fig. 1a). The content of 10 μg/dm^3 of selenium was insufficient to cause such an effect (Fig. 1b).

Dissolution current is one of the most important experimental conditions in chronopotentiometric stripping analysis. Its influence was investigated in the solutions containing 60 μg/dm^3 and 10 μg/dm^3 of selenium(IV) and varied from -2.2 μA to -4.2 μA for the higher and from -1.5 μA to -2,6 μA for lower selenium contents. Dependence of the analytical signal (dissolution time) on the dissolution current obtained in the solution containing 10 μg/dm^3 of selenium is shown in Fig. 2. Each value of the analytical signal represents an average of five analyses on different mercury films.

The decrease of the dissolution current caused an approximately exponential increase of the selenium analytical signal for both lower and higher selenium content. A dissolution current lower than 2.2 μA was insufficient to dissolve the deposit obtained from the solution containing 60 μg/dm^3 of selenium and caused distortion of the analytical signal (inflection point was not well defined), while the higher dissolution current of 4.2 μA caused significant decrease of the signal. Similarly, currents higher than 2.6 μA caused a decrease of the determination sensitivity in the solutions containing 10 μg/dm^3 of selenium.

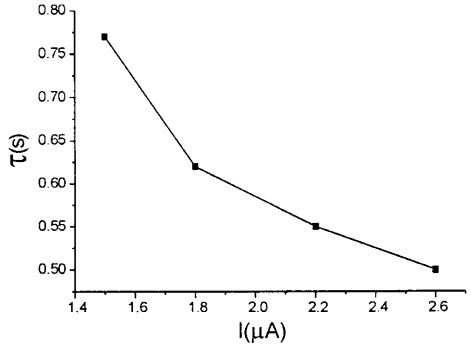

Fig. 2. Dependence of the selenium analytical signal on the dissolution current
C_m = 10 μg/dm^3; t_{el} = 90 s

Since the reproducibility of the analytical signal was not satisfactory because of the differences in the mercury film formation (each examination series was performed at a different mercury film) the reproducibility could not be accepted as a criterion for selecting an appropriate dissolution current. For that purpose the dependence of I· τ on I was used, and the results obtained for the solution containing 10 μg/dm^3 of selenium are shown in Fig. 3.

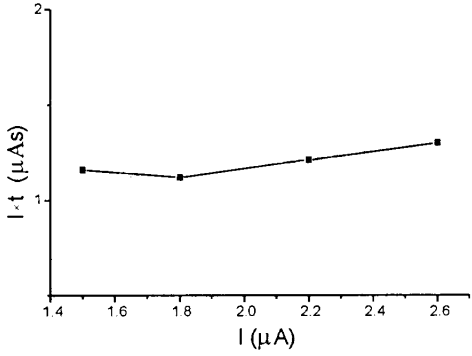

Fig. 3. Dependence of I·τ on I (C_m= 10 μg/dm^3)

Considering the current range where the I· τ product is approximately constant, for selenium solutions of 60 μg/dm^3 the optimal dissolution current was in the range 3.0-4.2 μA and for selenium solutions of 10 μg/dm^3 in the range from 1.5 μA to 2.2 μA.

The dependence of the analytical signal on the selenium concentration was examined for two content ranges: 20-60 μg/dm^3 and 100-140 μg/dm^3. The results obtained for the content range 20-60 μg/dm^3 are presented in Fig. 4.

The obtained results correspond to those obtained by examining the electrolysis time influence, which is to be expected because a longer electrolysis time is analogous to a higher selenium concentrations. For lower concentration range, the obtained dependence is linear but for the higher one it is polynomial (n=2). Therefore, for the concentrations of

of selenium >60 μg/dm^3 the method of calibration curve is recommended. Standard addition method is proposed for lower selenium concentrations, but its application causes a slight increase of the results due to the intercept at dissolution time axis.

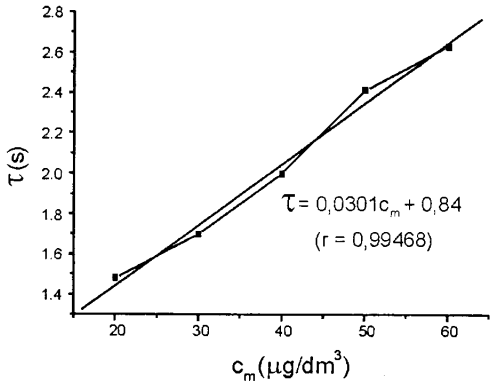

Fig. 4. Dependence of the analytical signal of the selenium concentration
E_{el} = -0.1 V; t_{el} = 90 s; i = 1.8 μA

Metal interferences. Influence of copper on the selenium analytical signal was examined in the solutions of 40 μg/dm^3 of selenium(IV) by increasing the copper(II) concentration. It was concluded that the copper content which could be present in the solution without influencing the height and sharpness of the selenium analytical signal, increases with the selenium content increase. Interference could not be defined by the Cu/Se concentration ratio. When the concentration of the copper(II) reached 2.5 mg/dm^3 the mercury film electrode was blocked because of the formation of a copper electrode, considering the fact that selenium and copper form an inetrmetallic compound Cu(Hg)Se.

Influence of iron(III) on the selenium analytical signal was examined in the solutions of 40 μg/dm^3 of selenium(IV) by varying the ratio Fe:Se from 1:1 to 500:1. Iron(III) did not influence the selenium signal till the ratio Fe:Se=200:1. With the increase of iron(III) concentration, the potential of the working electrode shifted to the positive values, due to the strong oxidative effect of Fe(III).

Under the given experimental conditions the lead chronopotentiometric wave appeared at a similar potential as the selenium one. Starting from the lead/selenium concentration ratio of 1:1, two close waves were observed. In the ratio Pb:Se<50:1, lead did not influence the selenium signal, but at higher concentrations chronopotentio-metric wave of lead overlapped with the selenium wave, so that selenium could not be determined.

Detection time. The criterion used to determine the detection limit was the concentration of selenium(IV) that at an electrolysis time of 600 s produced signal of at least 0.4 s. After defining the optimal experimental conditions for the CSA modification with deaeration and analysis of the blank solution (0.2 mol/dm^3 hydrochloric acid), the obtained detection limit was 0.4 μg/dm^3.

Hydrochloric acid concentration in calcium-chloride solution. Influence of the hydrochloric acid concentration in calcium-chloride solution was investigated in the range 0.05-1.0 mol/dm^3. The concentrations higher than 0.1 mol/dm^3 caused broadening of the selenium chronopotentiometric wave. Sensitivity of the selenium determination was significantly lower using hydrochloric acid concentrations higher or equal to 0.3 mol/dm^3. Therefore, the hydrochloric acid concentration of 0.05 mol/dm^3 was adopted as the optimal one, as the analytical signal was sharp, well defined and provided the highest determination sensitivity.

Calcium-chloride concentration. One of the most important experimental conditions for medium exchange modification of the CSA was calcium-chloride concentration. Its influence was investigated using the solutions of 60 μg/dm^3 of selenium(IV) in the concentration range from 1.0 mol/dm^3 to 5.1 mol/dm^3. Results are shown in Table 2.

Table 2. Dependence of the selenium analytical signal on the calcium-chloride concentration

c (CaCl) (mol/dm^3)	τ (s)	S (s)	KV (%)
2	3.95	0.39	9.8
3	2.59	0.11	4.1
4	1.98	0.27	14.4
5.1	0.27	0.11	38.9

The concentration of calcium chloride of 1.0 mol/dm^3 caused broadening of the chronopotentiogram due to the high concentration of dissolved oxygen. With increase of the calcium-chloride concentration, the selenium analytical signal decreased significantly. The concentration of 2.0 mol/dm^3 was adapted as optimal, since the signal was highest and the reproducibility (KV=9.8%) was satisfactory.

Dependence of the analytical signal on the selenium concentration. Applying the electrolysis potential of -0.1 V, electrolysis time of 120 s and dissolution current of 3 μA, the experiment was conducted in same manner and in the same concentration range as in the case with the CSA modification with prior deaeration. Furthermore, the obtained results are similar as well (Fig. 5).

On the basis of the obtained results, calibration curve method can be proposed for the selenium determination in a wider concentration range and higher selenium concentrations because the application of standard addition method caused a determination error due to a considerable intercept at the dissolution time axis.

The detection limit obtained for the medium-exchange modification of CSA, applying the same criterion as in the previous modification, was 1.12 μg/dm^3.

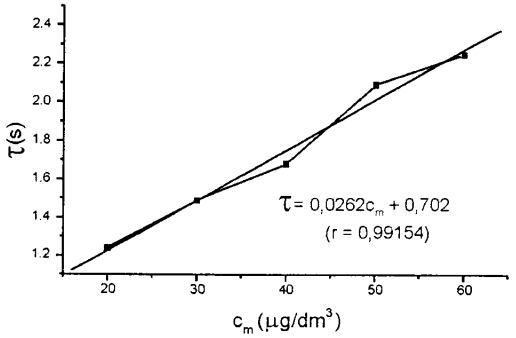

Fig. 5. Dependence of the analytical signal on the selenium concentration (medium-exchange) t_{el} = 120 s; i = 3 μA

Accuracy of the CSA modifications. After digesting the reference sample (RM 8436) and reduction of the hexavalent selenium, samples were analysed applying both CSA modifications using the following experimental conditions: electrolysis potential -0.1 V, electrolysis time 120 s, dissolution current 3 μA for medium exchange modification, and electrolysis potential -0.1 V, electrolysis time 180 s, dissolution current 1.8 μA for the modification with prior deaeration. The results are shown in Table 3.

Table 3. Results of selenium determination in the reference sample RM 8436

Sample	CSA whith deaeration (mg/kg)	Medium exchange CSA (mg/kg)
1	1.32	1.25
2	1.31	1.15
3	1.31	1.29
4	1.26	1.40

Selenium contents obtained using the CSA modification with deaeration were in the declarated range (1.23±0.09 mg/kg). The contents determined applying the medium exchange modification of CSA were also in the declarated range except for the content of 1.40 mg/kg, which differed by 0.08 mg/kg.

CONCLUSIONS

The modifications of CSA developed in this work allow fast and simple determination of selenium. Medium exchange modification of CSA has certain advantages comparing to the modification with prior deaeration of the analysed solution. Using medium exchange technique, prolonged period of deaeration, as well as the risk of contamination of the analysed solution by deaeration gas is avoided. Nevertheless, when a higher sensitivity is needed, the modification with deaeration is recommended. Another advantage of the medium exchange modification for routine analysis is that one mercury film can be used for 10-15 analyses, while in the case of the modification with deaeration, only 2-3 analyses can be performed because of the mercury film damage caused by nitrogen

bubbles. The proposed relative method for the determination by both modifications is the calibration curve method.

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ХРОНОПОТЕНЦИОМЕТРИЈСКА СТРИПИНГ АНАЛИЗА СЕЛЕНА ПОМОЋУ ТАНКОСЛОЈНЕ ЖИВИНЕ ЕЛЕКТРОДЕ

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Испитан је утицај најзначајнијих експерименталних фактора хронопотенциометријске стрипинг анализе (HSA) селена на танкослојној живиној електроди. Размотрене су и интерференције од стране неких метала као што су бакар, гвожђе и олово. Испитана је могућност избегавања дуготрајног процеса деаерације раствора применом модификације основне електроаналитичке технике код које се растварање депозита изводило у раствору калцијум хлорида, у коме је растворљивост кисеоника мала. Одређене су границе детекције за модификацију HSA уз претходну деаерацију и модификацију са заменом основног раствора од 0,4 $\mu g/dm^3$, односно 1,12 $\mu g/dm^3$.

Исправност дефинисаних метода потврђена је анализом референтног материјала (RM 8436) пшеничног дурум брашна, у коме је укупан садржај селена одређен применом обе модификације основне технике показао врло добро слагање са декларисаним садржајем.

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