

## ELECTROANALYTICAL INVESTIGATION OF TUNGSTEN IN HYDROCHLORIC ACID USING SQUARE-WAVE VOLTAMMETRY

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The square-wave voltammetry (SWV) is a technique that can be used for determination of tungsten in microamounts. The method is based upon a quasi-reversible reduction reaction of W(V) to W(III) in hydrochloric acid ( $c(\text{HCl}) = 6 \text{ mol dm}^{-3}$ ), which was chosen by our measurements as the best supporting electrolyte. The best results were achieved at the following experimental conditions: initial potential of  $-0.550 \text{ V}$ , final potential of  $-0.850 \text{ V}$ , frequency of  $100 \text{ Hz}$ , square-wave amplitude of  $0.04 \text{ V}$  and potential increment of  $2 \text{ mV}$ . The well-defined cathodic peak, which occurs at a potential of approximately  $-0.700 \text{ V}$ , can be used to determine the tungsten in the range of  $2.0 \cdot 10^{-6} \text{ mol dm}^{-3}$  to  $8.3 \cdot 10^{-5} \text{ mol dm}^{-3}$ . In order to apply the proposed method for the determination of tungsten in some samples, the influence of several potentially interfering ions (Pb, Cd, Cu, Ni, Co, Zn and Fe) is investigated. The experimental results showed that it is necessary to eliminate the interference by Pb(II) and Cd(II) ions when they are present in large quantities (higher or equal to the W(VI) concentration in the cell).

**Key words:** tungsten; SWV; electroanalytical investigation

### INTRODUCTION

According to data in the literature, the electroanalytical methods used for determination of W(VI) in mineral raw materials and composite nuclear fuels are: differential pulse polarography [1], adsorptive polarographic techniques [2–4], and the alternating current polarography [5–6]. Some authors have used SW-polarography to determine tungsten in the molybdenum [7], where the minimal detection level is  $3 \cdot 10^{-5} \text{ mol dm}^{-3}$ .

The square-wave voltammetry technique [8, 9] is a new version of the SW-polarography, invented by Barker [10–13]. In our previous work [14], SWV was applied for determination of Mo(VI). In fact, SWV has proven itself as one of the most superior techniques for analysis of some essential systems (e.g. all kinds of water, food and biological samples), regarding the reliability, the speed, and the cost. As a working electrode, the

SWV uses a single hanging mercury drop (HMDE), compared to the polarographic techniques, where a dropping mercury electrode is used for the same purpose.

Besides, the entire SW-voltammogram can be recorded in few seconds on a single hanging drop, taking into account that with the polarographic techniques a few minutes are necessary. The sensitivity of the square-wave determination is its advantage over most of the polarographic techniques, because of its ability to discriminate between faradaic and the capacitive current.

The aim of this work is to develop a voltammetric method for determination of tungsten in microamounts. To achieve the desired goal, direct current polarography (DCP), cyclic voltammetry (CV), and square-wave voltammetry (SWV) have been used.

## EXPERIMENTAL

*Reagents*

The solution of  $\text{H}_2\text{WO}_4$  ( $c = 0.01 \text{ mol dm}^{-3}$ ) was prepared (by making a solution of  $\text{H}_2\text{WO}_4$  in  $0.2 \text{ mol dm}^{-3}$  NaOH) and standardized with EDTA [15]. The working solution of W(VI) was made with an appropriate diluting. Solutions of hydrochloric acid ( $c = 10 \text{ mol dm}^{-3}$ ) and of sodium hydroxide ( $c = 2 \text{ mol dm}^{-3}$ ) were made from commercial reagents. All the reagents were of analytical purity. The solutions of the metals were made with analytically pure nitrate and chloride salts (Merck), and were then standardized using known methods, and diluted when needed.

In the preparation of all the solutions, and their standardization, a twice distilled water was used.

*Instrumentation*

The polarographic analyzer PAR Model 384 B, combined with a static mercury drop electrode (SMDE), Model 303, was used during our experiments. The three-electrode system includes a hanging mercury dropping electrode (HMDE) as a working electrode, Ag/AgCl (with saturated KCl) as a reference electrode, and a platinum wire as counter electrode.

The dissolved oxygen was removed from the solutions by passing highly refined nitrogen through the cell, for a period of 4 minutes (sufficient time to remove the oxygen). Afterwards nitrogen was passed over the solutions during the measurements. All the experiments were performed at a room temperature ( $T = 20 \text{ }^\circ\text{C} \pm 0.5 \text{ }^\circ\text{C}$ ).

## RESULTS AND DISCUSSION

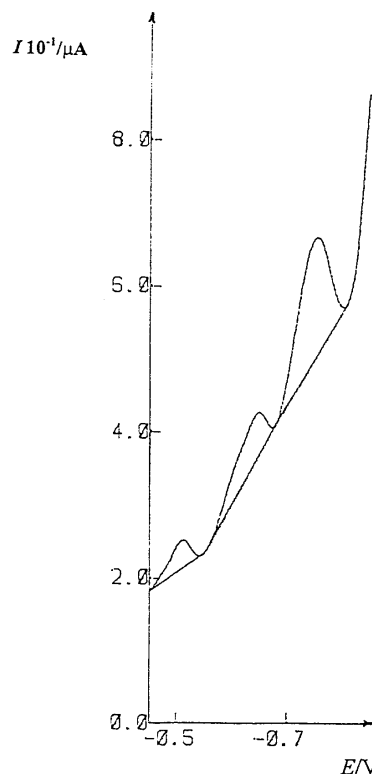
*Choice of the supporting electrolyte*

Since it is known that the nature and the concentration of the supporting electrolyte influence the voltammetric behaviour, four acids were investigated: HCl,  $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ .

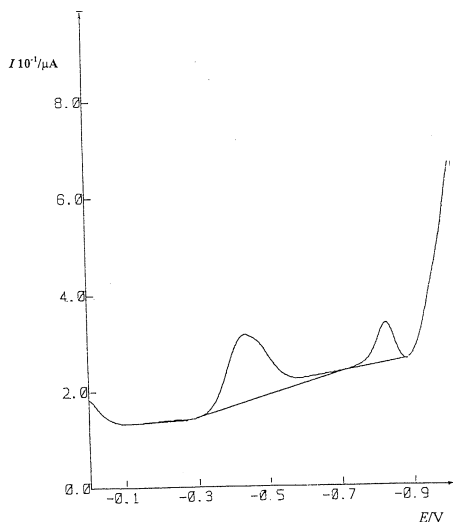
In  $\text{H}_2\text{SO}_4$  with  $c(\text{H}_2\text{SO}_4) = 1 \text{ mol dm}^{-3}$ , three peaks are observed when  $c(\text{W(VI)}) = 1 \cdot 10^{-4} \text{ mol dm}^{-3}$ , with remarkable currents as is presented in Fig. 1. Peaks are not detectable at lower concentrations of W(VI). Overlapping of the peaks is observed at higher concentration of tungsten. So,  $\text{H}_2\text{SO}_4$  isn't suitable for SWV determination of W(VI).

In the presence of  $\text{H}_3\text{PO}_4$  as a supporting electrolyte ( $c = 9.0 \text{ mol dm}^{-3}$ ), two peaks are observed (Fig. 2). The decrease of the tungsten concentration results in the decrease of the peaks heights. At high tungsten concentration ( $c(\text{W(VI)}) = 1 \cdot 10^{-4} \text{ mol dm}^{-3}$ ), two peaks with small currents are recorded, and because of that,  $\text{H}_3\text{PO}_4$  isn't convenient for SW-voltammetric determination of W(VI).

In the presence of  $\text{HClO}_4$  ( $c = 1 \text{ mol dm}^{-3}$ ), one peak is observed but it is with very small current ( $I_p = 338 \text{ nA}$ ) at higher concentration of W(VI) ( $c = 1.0 \cdot 10^{-3} \text{ mol dm}^{-3}$ ). At lower tungsten concentration it is hard to observe.



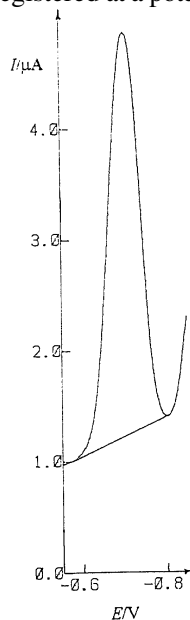
**Fig. 1.** SW voltammogram of W(VI) with  $c = 10^{-4} \text{ mol dm}^{-3}$  in  $\text{H}_2\text{SO}_4$  ( $c = 1.0 \text{ mol dm}^{-3}$ ),  $\nu = 100 \text{ Hz}$ ,  $a = 0.02 \text{ V}$ ,  $\Delta E = 2 \text{ mV}$



**Fig. 2.** SW voltammogram of W(VI) with  $c = 10^{-4} \text{ mol dm}^{-3}$  in  $\text{H}_3\text{PO}_4$  ( $c = 9.0 \text{ mol dm}^{-3}$ ),  $\nu = 100 \text{ Hz}$ ,  $a = 0.02 \text{ V}$ ,  $\Delta E = 2 \text{ mV}$

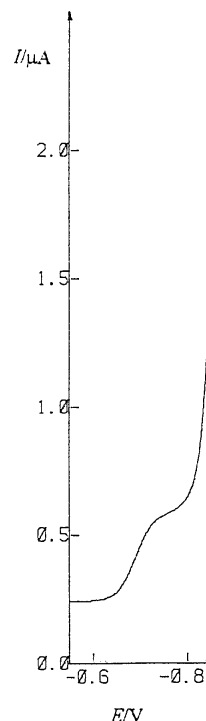
A single peak with nice shape and high current for lower concentration of tungsten ( $c(\text{W(VI)}) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ ) in HCl is recorded, in comparison with the peaks recorded in the other supporting electrolytes ( $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$  and  $\text{H}_3\text{PO}_4$ ) at significantly higher tungsten concentration. Besides, hydrochloric acid gave a lower blank than the others and was chosen for use.

In the SW-voltammogram as is presented in Fig. 3 a peak is registered at a potential of  $-0.704 \text{ V}$ .



**Fig. 3.** SW voltammogram of tungsten  $c(\text{W(VI)}) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ ,  $\nu = 100 \text{ Hz}$ ,  $a = 0.04 \text{ V}$ ,  $\Delta E = 2 \text{ mV}$ ,  $c(\text{HCl}) = 6 \text{ mol dm}^{-3}$

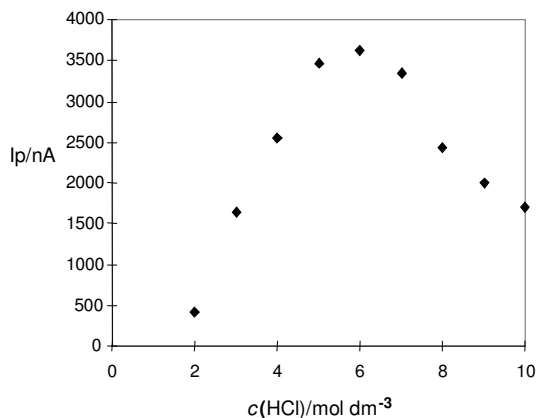
The value of the peak potential is approximately equal to the half-wave potential ( $E_{1/2} = -0.690 \text{ V}$ ), from the DC polarogram (Fig. 4). According to the literature [16] at this potential the reduction of the W(V) ions to W(III) ions appears, which will be further evaluated. At the same time, the reduction of W(VI) to W(V) should appear at a potential more positive than  $0.4 \text{ V}$  [16] was not registered by us, because the voltammograms were recorded in the area of more negative potentials.



**Fig. 4.** DC-polarogram of tungsten with  $c(\text{W(VI)}) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ ,  $c(\text{HCl}) = 6 \text{ mol dm}^{-3}$

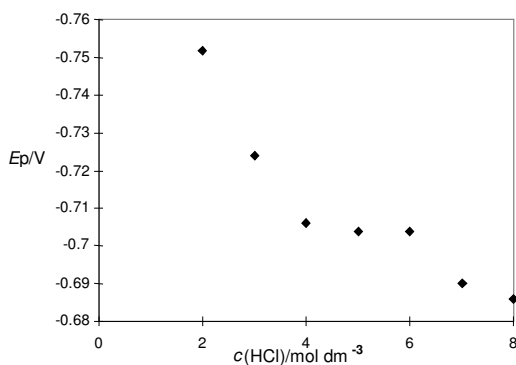
#### Optimization of the voltammetric response

Fig. 5 shows the dependence of peak current ( $I_p$ ) of W(VI), on the concentration of the hydrochloric acid. Peak current increases with the increase of the hydrochloric acid concentration up to  $6.0 \text{ mol dm}^{-3}$  and then, with the further increase of HCl concentration, the decrease of the heights of the peaks are observed. That is why the HCl with a concentration of  $6.0 \text{ mol dm}^{-3}$  is chosen as the supporting electrolyte for the following experiments.



**Fig. 5.** Influence of the concentration of supporting electrolyte on the peak current of tungsten:  $c(\text{W(VI)}) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ ,  $\nu = 100 \text{ Hz}$ ,  $a = 0.04 \text{ V}$ ,  $\Delta E = 2 \text{ mV}$

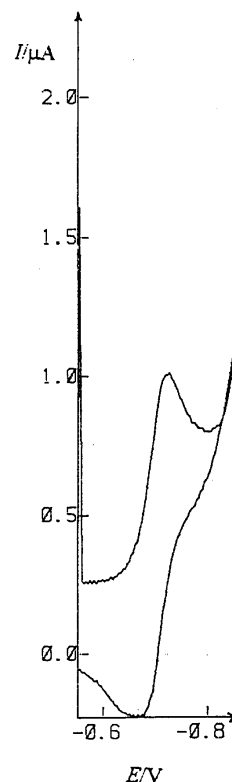
The results from the experiments have shown that with the increase of the concentration of HCl, the potential of the evaluated peak moves towards more positive values (Fig. 6). Both the potential of the peak and the peak current are dependent on the concentration of the supporting electrolyte, which indicates that the hydrogen ions are involved in the electrode process. This statement corresponds to the previous investigations made by other polarographic techniques for W(VI) in acidic solutions [2, 4].



**Fig. 6.** Influence of the concentration of supporting electrolyte on the peak potential of tungsten:  $c(\text{W(VI)}) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ ,  $\nu = 100 \text{ Hz}$ ,  $a = 0.04 \text{ V}$ ,  $\Delta E = 2 \text{ mV}$

The cyclic voltammetry is used to investigate the reversibility of the second electrode process. The presence of a cathodic and anodic peak in the cyclic voltammogram (Fig. 7) indicates a quasi-

reversible electrode reaction in which the process of oxidation (anodic direction) is slightly weaker than the process of reduction (cathodic direction). The cathodic wave, which is much higher than the respective anodic wave, is more appropriate for analytical use.



**Fig. 7.** Cyclic voltammogram of tungsten with  $c(\text{W(VI)}) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ , scan rate =  $400 \text{ mV s}^{-1}$ ,  $c(\text{HCl}) = 6 \text{ mol dm}^{-3}$

#### *Influence of the instrumental parameters*

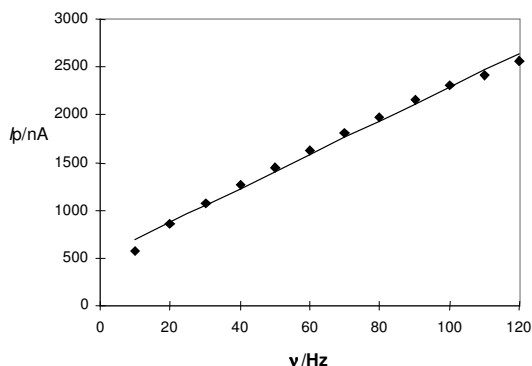
When the optimal experimental conditions were defined in order to get the best defined peak in SWV determination of tungsten, the influence of the frequency of the square-wave amplitude as well as the potential increment on the peak current is investigated. All the examinations were performed with a constant concentration of W(VI) in the cell, which equaled  $4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ , in the presence of HCl ( $c = 6 \text{ mol dm}^{-3}$ ).

The influence of the frequency ( $\nu$ ) on the peak current of the tungsten is shown in Fig. 8. There is linear dependence between the peak current and the frequency between 20 Hz and 100 Hz.

The equation, which depicts this linear dependence between  $I_p$  and  $\nu$  is as follows:

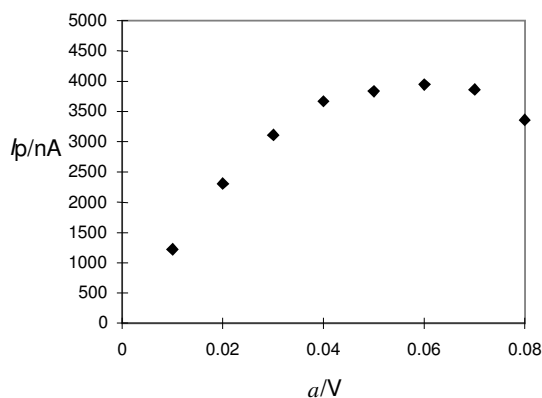
$$I_p / \text{nA} = 17.7 \nu / \text{Hz} + 519.0$$

For the frequency of 100 Hz, a peak with well defined shape and high current is recorded. That value is chosen as optimal for further examinations.



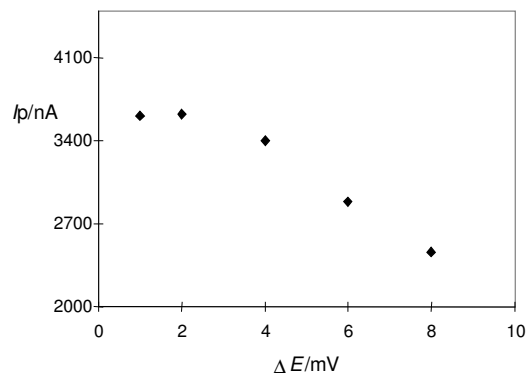
**Fig. 8.** Influence of the frequency on the peak current of tungsten:  $c(\text{W(VI)}) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ ,  $a = 0.02 \text{ V}$ ,  $\Delta E = 2 \text{ mV}$ ,  $c(\text{HCl}) = 6 \text{ mol dm}^{-3}$

The influence of the square-wave amplitude on the peak current of W(VI) is shown on the Fig. 9. The experiments were performed at various amplitudes, starting with 0.01 V and up to 0.08 V. The diagram indicates that the height of the peak increases at the beginning, following the increasing of the SW-amplitude ( $a$ ), and then a plateau is reached at about 0.04 V, and this value was chosen as an optimal SW-amplitude and used in all of the further researches.



**Fig. 9.** Influence of the amplitude on the peak current of tungsten:  $c(\text{W(VI)}) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ ,  $\nu = 100 \text{ Hz}$ ,  $\Delta E = 2 \text{ mV}$ ,  $c(\text{HCl}) = 6 \text{ mol dm}^{-3}$

The Fig. 10 shows the influence of the potential increment ( $\Delta E$ ) on the current of the tungsten SW-peak. With the increase of the potential increment from 1 mV to 2 mV a slight increase of the peak current can be noticed. Further increase of the increment, with a step of 1 mV results in decreasing of  $I_p$ . The potential increment of 2 mV is chosen as optimal and is used in the further experiments.



**Fig. 10.** Influence of the pot. increment on the peak current of tungsten:  $c(\text{W(VI)}) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ ,  $\nu = 100 \text{ Hz}$ ,  $a = 0.04 \text{ V}$ ,  $c(\text{HCl}) = 6 \text{ mol dm}^{-3}$

The examinations above have shown that as the best experimental conditions for a well-defined SW-peak of W(VI) can be defined: initial potential of  $-0.550 \text{ V}$ , final potential of  $-0.850 \text{ V}$ , frequency of 100 Hz, square-wave amplitude of 0.04 V and potential increment of 2 mV.

#### Calibration curve

The dependence between the peak current and the concentration of W(VI) were examined under the best conditions, mentioned above. The results of these examinations show a linear dependence on the concentration of W(VI) in the range of  $1.96 \cdot 10^{-6} \text{ mol dm}^{-3}$  to  $8.30 \cdot 10^{-6} \text{ mol dm}^{-3}$ . The regression analyses of the calibration curve, gives a correlation coefficient of 0.9918. The equation that depicts the calibration curve is:

$$I_p / \text{nA} = 63.1 c(\text{W(VI)}) / \mu\text{mol dm}^{-3} + 17.0$$

Also, an observation of the linear dependence between peak height and tungsten concentration in the higher concentration range  $1.00 \cdot 10^{-5} \text{ mol dm}^{-3}$  to  $8.30 \cdot 10^{-5} \text{ mol dm}^{-3}$  is made. Correlation coeffi-

cient is 0.9986 and the equation for the calibration curve is:

$$I_p / \text{nA} = 64.4 c(\text{W(VI)}) / \mu\text{mol dm}^{-3} - 2.1$$

The detection limit is  $2 \mu\text{mol dm}^{-3}$ , and the relative standard deviation of W(VI) ( $c(\text{W(VI)}) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ ) is 0.9 %.

### Interferences

The influence of Pb, Cd, Cu, Zn, Ni, Co and Fe on the current and the potential of the peak during the square-wave determination of W(VI) are investigated. In all these experiments, the concentration of W(VI) was constant ( $c(\text{W(VI)}) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ ) and the experiments were performed in the presence of  $6.0 \text{ mol dm}^{-3}$  HCl, as a supporting electrolyte. The voltammograms were recorded in a potential range wider than the one previously determined, because the influence of the metallic ions has been investigated on the current and the poten-

tial of the peak. The concentrations of the investigated ions were smaller, equal or greater than the concentration of the W(VI) in the voltammetric cell.

The results achieved in these experiments indicated that of all the ions examined, the strongest interferences occur in the presence of Cd(II) and Pb(II) ions. Actually, in the presence of Cd(II) ions, two peaks occur at the same position. When Pb(II) ions are present in the solution, the peak current decreases and another peak occurs at a potential of  $-0.580 \text{ V}$ , due to the reduction of the Pb(II) ions in HCl media. W(VI) and Cu(II) can be determined simultaneously, since in that case two well shaped peaks, well separated from each other and with high currents, are observed. In the presence of Fe(III) ions, a slight decrease of the current of the W(VI) peak is noticed. Zn(II), Co(II) and Ni(II) do not interfere in the voltammetric determination of W(VI).

### CONCLUSION

A rapid square-wave voltammetric method for microdetermination of W(VI) is based upon a quasi-reversible reaction of reduction of W(V) to W(III) in hydrochloric media ( $c(\text{HCl}) = 6 \text{ mol dm}^{-3}$ ), which was chosen by our measurements as the best supporting electrolyte. The best conditions for square-wave determination of W(VI) includes: initial potential of  $-0.550 \text{ V}$ , final potential of  $-0.850 \text{ V}$ , frequency of  $100 \text{ Hz}$ , square-wave amplitude of  $0.04 \text{ V}$  and potential increment of  $2 \text{ mV}$ . The peak current is proportional to the concentration of tung-

sten(VI) over the range  $2.00 \cdot 10^{-6} \text{ mol dm}^{-3}$ – $8.30 \cdot 10^{-6} \text{ mol dm}^{-3}$ . Also, a linear dependence between peak height and tungsten concentration exists in the higher concentration range:  $1.00 \cdot 10^{-5} \text{ mol dm}^{-3}$ – $8.30 \cdot 10^{-5} \text{ mol dm}^{-3}$ . The detection limit is  $2 \mu\text{mol dm}^{-3}$  under these conditions. The influence of several potentially interfering ions (Pb, Cd, Ni, Co, Cu, Zn and Fe) is investigated. Pb(II) and Cd(II) interfere when they are present at higher or equal concentrations than W(VI).

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## Резиме

**ЕЛЕКТРОАНАЛИТИЧКО ИСПИТУВАЊЕ НА ВОЛФРАМ ВО ХЛОРОВОДОРОДНА КИСЕЛИНА СО КВАДРАТНО-БРАНОВА ВОЛТАМЕТРИЈА****Верица Јакимовиќ, Симка Петровска-Јовановиќ и Корнелија Стојанова***Институт за хемија, Природно-математички факултет, Универзитет "Св. Кирил и Методиј",  
91 000 Скопје, Република Македонија***Клучни зборови:** волфрам; квадратно-бранова волтаметрија; електроаналитичко испитување

Развиен е нов електроаналитички метод за определување на волфрам со примена на SWV. Методот е базиран на следење на пик на потенцијал од  $-0,700\text{ V}$ , кој се должи на одвивање на квазиреверзибилна електродна реакција на редуција во хлороводородна киселина како основен електролит. Испитувањата покажуваат дека најдобри резултати се добиваат ако мерењата се вршат при следниве услови: почетен потенцијал:  $-0,550\text{ V}$ , краен потенцијал:  $-0,850\text{ V}$ , фреквенција:  $100$

Hz, амплитуда:  $0,04\text{ V}$  и потенцијален инкремент:  $2\text{ mV}$ . За основен електролит е одбрана хлороводородна киселина со  $c = 6,0\text{ mol dm}^{-3}$ . При овие услови линеарна зависност е забележана во граници од  $1,96 \cdot 10^{-6}\text{ mol dm}^{-3}$  до  $8,30 \cdot 10^{-6}\text{ mol dm}^{-3}$ . За да се примени методот за одредување на волфрам во примероци, неопходно е претходно да се отстрани влијанието на Pb(II) и Cd(II), кога тие се присутни во поголеми количества.