

INFLUENCE OF SOME METAL IONS ON THE SQUARE-WAVE PEAK OF TUNGSTEN IN HYDROCHLORIC ACID

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Abstract

Square-wave voltammetry (SWV) is used as a new method for quantitative determination of tungsten in drinking water and in some samples. Since only traces of some cations are present and a number of them exist simultaneously, their determination is not easy, and the possibility of interference exists. Therefore, special attention is given to the influence of some metal ions (Pb, Cu, Cd, Zn, Ni, Co and Fe) on the peak potential and the peak current of W(VI) ($c=5 \cdot 10^{-5}$ mol dm⁻³) in hydrochloric acid ($c=6$ mol dm⁻³), used as a best supporting electrolyte. The voltammograms are recorded under the follow conditions: initial potential -0.550 V; final potential -0.850 V; frequency 100 Hz; SW-amplitude 0.04 V; potential increment 2 mV. In the presence of Cd(II) ions, two peaks appear at the same potential. W(VI) and Cu(II) ions can be determinate simultaneously because two peaks (due to the presence of two metals) with nice shapes, high currents and good separation appear. In the presence of Pb(II) ion the peak high of W(VI) decreases and another peak appears at the potential of -0.58 V (v.s. Ag/AgCl ref. electrode). The presence of Fe(III) ions has the influence on the peak current of W(VI). Zn(II), Ni(II) and Co(II) ions do not interfere on the determination of W(VI).

Introduction

According to the literature information, tungsten is presence in drinking waters and it influence on some toxic metals, what is very importance looking from our aspect. It's presence is determined in dental metal products, too [1,2].

The electrochemical behavior of W(VI) had been investigated by many authors [3-7] using different polarographic methods. The influence of some ions on the polarographic signal of tungsten(VI) is examined, and it is very importance in our work.

For example, the polarographic behavior of tungsten(VI) at a dropping mercury electrode in mixtures of sulphuric acid and dimethyl sulphoxide has been examined [3].

A polarographic method has been developed for determining tungsten in ferrous materials in presence of Ti, V, Cr, Mo, Co, Ni and the other elements.

A polarographic method for determining W(VI) by the catalytic reduction with IO_3^- at a dropping Hg electrode in acetate buffer (pH=5) was studied [4]. The effects of various cations (Zn, Fe, Mn, Cu, Cd, V, U) and different anions were investigated.

Catalytic polarographic currents of chlorate and hydrogen ions have been studied in the presence of tungsten(VI)-catechol complexes [5]. Some metal ions (Mn, Sn, As, Cr and Pt) do not interfere, but Cu, V, Fe, Ni, Sb and Ti increase the intensity of the catalytic wave. A method is suggested from the authors for selective determination of trace amounts of W(VI) by using the wave for ClO_3^- reduction.

In presence of Pb(II) ions, the peak height of tungsten decreases and another peak is observed on the potential of -0.58 V, which is due to Pb(II) reduction (Fig.2). So that means, that Pb(II) ions had to be eliminated during the square-wave voltammetric investigation.

The peak potential of the signal of reduction of Cu(II) ions in hydrochloric acid is about -0.35 V. As can be seen, the peak potential of the two ions are different, so Cu(II) and W(VI) can be determined simultaneously. Also, the peaks of Cu(II) and W(VI) are with nice shapes and high currents (Fig.3)

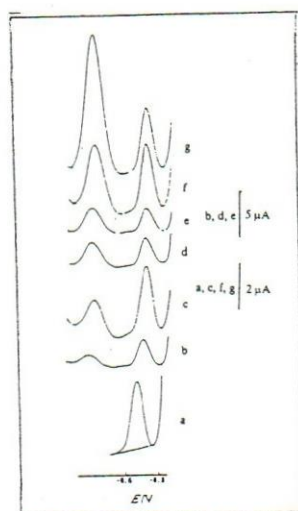


Fig.3. . The voltammograms of W(VI) in the presence of Cu(II) ions

- a) $c(W(VI)) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$
- b) $c(W(VI)) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ and $c(Cu(II)) = 2.00 \cdot 10^{-5} \text{ mol dm}^{-3}$
- c) $c(W(VI)) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ and $c(Cu(II)) = 3.98 \cdot 10^{-5} \text{ mol dm}^{-3}$
- d) $c(W(VI)) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ and $c(Cu(II)) = 5.96 \cdot 10^{-5} \text{ mol dm}^{-3}$
- e) $c(W(VI)) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ and $c(Cu(II)) = 7.93 \cdot 10^{-5} \text{ mol dm}^{-3}$
- f) $c(W(VI)) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ and $c(Cu(II)) = 9.90 \cdot 10^{-5} \text{ mol dm}^{-3}$
- g) $c(W(VI)) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ and $c(Cu(II)) = 1.96 \cdot 10^{-4} \text{ mol dm}^{-3}$

The results obtained by square-wave voltammetric analysis of tungsten(VI) in the presence of different concentration of Fe(III), are given in Table 1. It is evident that in the presence of Fe(III) ions, peak current of W(VI) decreases, without change of peak's form.

The aim of this work is to investigate the influence of some metal ions (Cu, Pb, Cd, Zn, Ni, Co and Fe) on the square-wave peak of tungsten in hydrochloric acid, as a best supporting electrolyte.

Experimental

Instrumentation - Voltammograms were recorded with a PAR Model 384 B Polarographic Analyzer coupled with a PAR 303 A Static Mercury Drop Electrode and DMP 40 Digital Plotter. The potentials were referred to the Ag/AgCl saturated reference electrode and platinum wire was used as a counter electrode. The electrolyte cell had a volume of 10 cm³. An inert atmosphere was maintained by passing for 4 min purified nitrogen through the solution and above it during the measurement. All experiments were performed at a room temperature.

Reagents - The solution of H₂WO₄ ($c = 0.01 \text{ mol dm}^{-3}$) was prepared by dissolving the appropriate amount in NaOH ($c = 0.2 \text{ mol dm}^{-3}$) and then standardized against EDTA [8]. A working W(VI) solution was obtained by suitable dilution. The solution of hydrochloric acid ($c = 10 \text{ mol dm}^{-3}$) and NaOH ($c = 2 \text{ mol dm}^{-3}$) were prepared. All reagents were of analytical grade. The metal solutions were prepared from analytical grade chloride and nitrate salts (Merck). They were standardized by known methods and freshly diluted further as required. Double distilled deionized water was used for preparation the solutions and for rinsing.

Results and discussions

The effects of various parameters (concentrations of supporting electrolyte, frequency, amplitude and potential increment) on the square-wave voltammetric response, but also the calibration curve, v.s. $c(W(VI))$, detection limit and relative standard deviation are established in our previous work[9] (in press).

In this work special attention was given to the influence of some metal ions (Cu, Cd, Pb, Ni, Co, Zn and Fe) on the peak potential (E_p) and peak current (i_p) of W(VI). A systematic study was made to the possible interference in presence of some metal ions because they could form complexes with tungsten and they are present in waters and food samples.

The experiments were conducted at constant concentration of tungsten in cell ($c(W(VI)) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$) in hydrochloric acid ($c = 6 \text{ mol dm}^{-3}$) under previously defined terms: initial potential -0.550 V; final potential -0.850 V; frequency 100 Hz; potential increment 2 mV; amplitude 0.04 V; deposition time 0 s and equilibrium time 0 s. The voltammograms were recorded in the larger potential range than previously, because the influence of the metal ions is investigated in this work.

Co(III), Ni(II) and Zn(II) had no influence on the position and height of the tungsten's peak.

In presence of Cd(II) two peaks appear, and the peak potential of the peak of tungsten is changed (Fig.1).

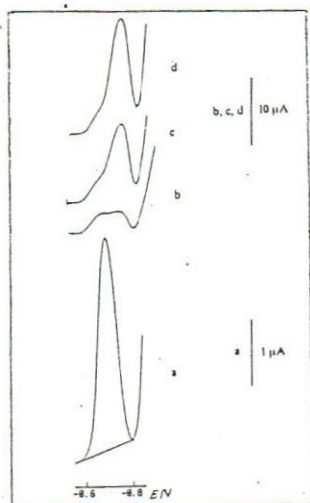


Fig.1. The voltammograms of W(VI) in the presence of Cd(II) ions

- a) $c(\text{W(VI)}) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$
- b) $c(\text{W(VI)}) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ and $c(\text{Cd(II)}) = 3.70 \cdot 10^{-5} \text{ mol dm}^{-3}$
- c) $c(\text{W(VI)}) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ and $c(\text{Cd(II)}) = 1.06 \cdot 10^{-4} \text{ mol dm}^{-3}$
- d) $c(\text{W(VI)}) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ and $c(\text{Cd(II)}) = 1.70 \cdot 10^{-4} \text{ mol dm}^{-3}$

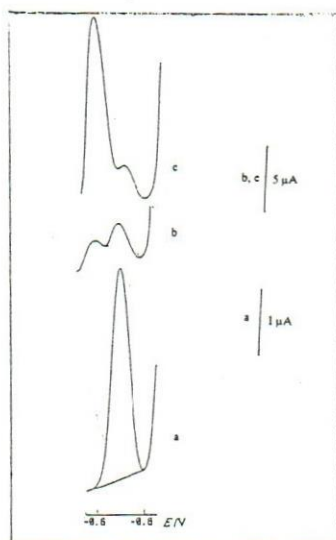


Fig.2. The voltammograms of W(VI) in the presence of Pb(II) ions

- a) $c(\text{W(VI)}) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$
- b) $c(\text{W(VI)}) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ and $c(\text{Pb(II)}) = 2.16 \cdot 10^{-5} \text{ mol dm}^{-3}$
- c) $c(\text{W(VI)}) = 4.97 \cdot 10^{-5} \text{ mol dm}^{-3}$ and $c(\text{Pb(II)}) = 2.16 \cdot 10^{-4} \text{ mol dm}^{-3}$

Table 1. The value of the E_p and i_p of W(VI) in the presence of Fe(III) ions

Ions	W(VI)	W(VI), Fe(III)				
$c/\text{mol dm}^{-3}$	$4.97 \cdot 10^{-5}$	$3.662 \cdot 10^{-7}$	$1.273 \cdot 10^{-6}$	$9.88 \cdot 10^{-6}$	$9.600 \cdot 10^{-5}$	$1.000 \cdot 10^{-3}$
E_p/V	-0.698	-0.692	-0.692	-0.690	-0.690	-0.694
i_p/nA	3211	3206	3205	2997	3046	2838

Conclusion

The influence of various foreign ions on the square-wave voltammetric determination of W(VI) was studied. Powerful interference effects, which are manifested through deformation of the peak, change of peak current and appearance of another peak were noticed in the presence of Cd(II) ions.

W(VI) and Cu(II) ions can be determined simultaneously because two peaks with nice shapes, high currents and well separated appear, in the voltamogram when hydrochloric acid is used as a supporting electrolyte.

Pb(II) ions interfered with determination of W(VI). They influence the form of the peak and decrease its height. Fe(III) ions cause decrease of the peak height of the peak of W(VI) without its deforming. Zn(II), Ni(II) and Co(II) did not show any interference effects.

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