

# High-voltage accumulation of metals as a tool to decrease the detection limit of anodic stripping voltammetry

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**Abstract** High-voltage accumulation (HVA) of metals on electrodes is shown to increase the rate of metal deposition as well as allow a substantial decrease of the detection limit of anodic stripping voltammetry (ASV). Using silver accumulation as an example, it is shown that advantages go along with keeping the reproducibility of analytical signal, its concentration dependence and dependence on accumulation time as usual for stripping voltammetry.

**Keywords** Sensor · Stripping voltammetry · Silver · High-voltage accumulation

## Introduction

The problem of reducing the detection limit of anodic stripping voltammetry (ASV) has been discussed more than once [1–4]. It is known that this parameter is essentially dependent on the composition of the supporting solution, the material of the indicator electrode, the method of its preparation, the kind of polarizing voltage, etc.

One of the important factors determining the success in reducing the detection limit is the method used to prepare (renew) the surface of the solid indicator electrode. Satisfying reproducibility of the results obtained using solid electrodes can be provided only after a complicated procedure of surface regeneration, which includes the stages of mechanical,

chemical, electrochemical, laser or ultrasonic treatment. Generalized data on different methods used to renew solid electrodes are available from literature [5–9].

A sufficiently universal method of regenerating the working surface of the indicator electrode (metal or graphite) is by cutting off a thin (0.5  $\mu\text{m}$ ) layer, with the help of a Hexanite-R cutter, directly in the solution under analysis before each polarization cycle was developed at the Laboratory of Electrochemistry of the Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of Russian Academy of Sciences (Novosibirsk). After cutting the electrode layer, the electrode surface is practically unaffected yet by the solution. The properties of the surface are independent of the time during which the electrode stays in solution before renewal; not only the surface area but also the initial properties of the electrode are conserved, both with respect to the structure and chemical composition.

Another factor affecting the detection limit is the use of different methods to accelerate the delivery of the analyte to the electrode surface at the stage of electroaccumulation. Different ways are known to enhance the mass transfer with the help of some physical methods. It was established that the rate of mass transfer increases by about one order of magnitude by application of ultrasonic and magnetic fields. So far, no attempts were made to affect the mass transfer in ASV with the help of the electric field, i.e., by increasing the voltage of metal electroaccumulation. There is the dominant opinion that a high potential of electrolysis does not cause an increase of the mass of deposited metal.

It is known that in solutions containing no supporting electrolyte and in the absence of a special exaltation effect (see further down), the electric field of the cathode accelerates the mass transfer of cations only by a factor of 2–3 [10–12]. Such a degree of acceleration of mass transfer does not compensate for the substantial dependence of migration

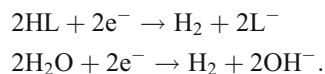
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The authors dedicate this paper to the 75th birthday of Dr. Nina Zakharchuk and wish her many years of health, luck and success.

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current on the presence of small amounts of nonelectroactive (supporting) ions, which causes substantial worsening of the reproducibility of results. For this reason, a conventional method to suppress migration in voltammetry is to add a large amount of indifferent supporting electrolyte. We demonstrated in Refs. [13–15] that exaltation phenomena can be efficiently used to intensify the mass transfer of cations. It was established that the use of exaltation effect caused by the joint evolution of hydrogen allows one to accelerate the electrodeposition of a number of metals by a factor of several hundred or thousand and to conserve the correctness and reproducibility of ASV results. Later, it was also confirmed in Ref. [16] that the intense evolution of hydrogen actually enhances migration processes, accelerated metal deposition and, at the same time, does not cause worsening of the analysis accuracy.

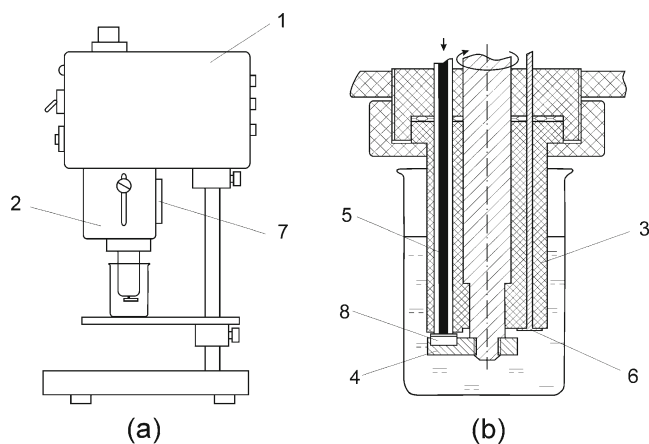
The exaltation effect was studied theoretically for the first time by Heyrovsky [12] and considered in detail by Kharkats [17, 18]. It was shown that the effect is connected with cation transfer under the action of the field created by the parallel discharge of neutral molecules at the cathode, if anions  $L^-$  are formed in this process. To neutralize their charge, the ingress of cations is necessary. Weak acids (HL) or water may serve as the neutral compound.



Because the current of reduction of the neutral compound (and hence the rate of generation of anions  $L^-$ ) can be very large, correspondingly high may be the acceleration of mass transfer of the cations that neutralize the created anions  $L^-$  including the discharging action of the metal under analysis. Evidently, in order to accelerate their deposition, it is important that the neutralization of the negative charge is mainly achieved by the cations under analysis. In this case, the acceleration of their delivery will be maximal. For this purpose, it is necessary to minimize the concentration of indifferent salts in the supporting electrolyte. The intensification of metal electrodeposition involving high voltage can be expected to allow not only obtaining an analytical signal enhanced by several times but also to achieve a substantial reduction of the detection limit. In the present work, we studied the possibility of decreasing the detection limit of silver with the help of the high-voltage mode of metal electroaccumulation on a graphite electrode renewed by in situ cutting off a thin surface layer.

## Methods and equipment

The general view of the sensor is presented in Fig. 1a. Casing 1 contains an electric motor connected kinematically with the device (casing 2) for feeding and renewing the



**Fig. 1** General view of the sensor (a) and its part submersible in solution (b). 1 casing, 2 device for feeding and renewing the indicator electrode, 3 cylinder made of nonconductive material, 4 knife (cutter), 5 indicator electrode, 6 auxiliary electrode, 7 reference electrode, 8 hexanite insert

indicator electrode. The submersible part of the sensor (Fig. 1b) is a cylinder 3 made of nonconductive material with hydrophobic properties. The drive axis of knife 4 passes through its central orifice. The casing of cylinder 3 contains indicator electrode 5, auxiliary electrode 6 and a flexible salt bridge of reference electrode 7. The indicator electrode is a rod made of hardened epoxy resin with a metallic wire or graphite–epoxy composite embedded in it. The working surface is the edge of the wire or a cylinder made of graphitized carbon which is renewed in the solution under analysis by cutting off a surface layer. The auxiliary electrode is a plate made of platinum-coated titanium, and the reference electrode is the calomel electrode.

The knife is a titanium arbor on which a cutting insert 8 made of hexanite or another rather hard material and a conductive tester simplifying the initial installation of the indicator electrode are fixed. For operation in the inversion mode, the sensor is equipped with a system of mixing with air or inert gas [19].

The scheme of the high-voltage accumulation (HVA) experimental set-up differs from the usual polarographic system only by an additional high-voltage unit that allows one to impose the potential difference up to 1,000 V at the indicator electrode and the auxiliary one. Stabilized high voltage is one of the basic conditions for the high-rate accumulation of metal deposit. After the electrodeposition process is ceased, the solution is replaced by the electrolyte suitable for the dissolution of the deposit (most frequently mineral acids), the electrode system is switched to the polarograph, and the inversion anode peak of metal dissolution is recorded using the 3-electrode circuit [19].

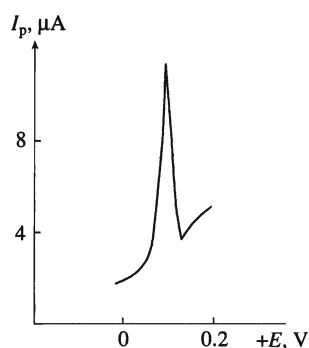
To achieve the highest efficiency of electromigration mass transfer, metal electrodeposition is to be carried out from the solutions of weak acids (boric and acetic) or from

extremely diluted solutions (0.001–0.01 M) of sulfuric, hydrochloric acids, ammonium chloride or alkali, when mainly water serves as the donor of protons. The electroconductivity of these solutions is low, so voltage ( $V_{\text{acc}}$ ) may be increased to 1,000 V. The upper limit of voltage is restricted by arcing at the working electrode. Analytical signals were not obtained under the conditions of arcing. For diluted solutions of strong acids (0.01 M  $\text{H}_2\text{SO}_4$ ), the upper limit of  $V_{\text{acc}}$  is 50 V, while in the solutions of weak acids, for example, in 1 M  $\text{H}_3\text{BO}_3$ , voltage can be increased to 1,000 V.

## Results and discussion

Ways allowing one to reduce detection limit with the help of the HVA mode were studied for silver as an example. The major factors determining the value of the analytical signal are the nature of supporting solutions for electroaccumulation in the HVA mode and anode dissolution of the deposit, voltage, accumulation time and the rate of potential sweep. For silver electrodeposition, we tested the following supporting solutions: 0.003 M  $\text{CH}_3\text{COOH}$ , 0.03 M  $\text{H}_3\text{BO}_3$  and a mixture of the latter solution with 0.001 M  $\text{CH}_3\text{COOH}$  in twice distilled water. The best results were achieved with silver deposition from a mixture of boric and acetic acids.

The appearance and parameters of the peaks of anodic dissolution of silver deposit are dependent on the composition of the solution intended for the anodic dissolution of the deposit. After the stage of silver electroaccumulation, the supporting solution was acidified by adding 0.1 cm<sup>3</sup> concentrated mineral acid ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{HClO}_4$ ), and anodic polarization of the electrode was performed. The best acceptable shape and parameters are those of the peak of the current of silver deposit dissolution in 0.05 M  $\text{HCl}$  solution (Fig. 2). An increase of the concentration of hydrochloric acid in the background solution has no noticeable effect on the analytical signal.

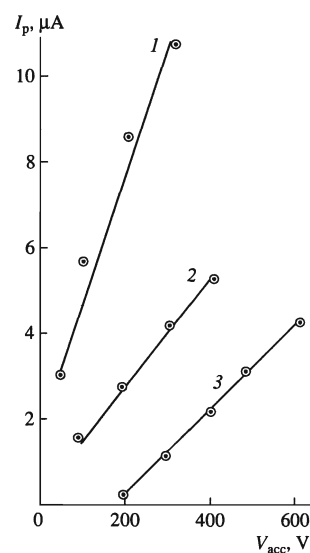


**Fig. 2** Voltammogram of anodic stripping of  $1 \times 10^{-9}$  M  $\text{Ag}^+$  in supporting electrolyte containing 0.04 M  $\text{HCl}$  ( $V_{\text{acc}}=400$  V,  $\tau_{\text{acc}}=1$  min)

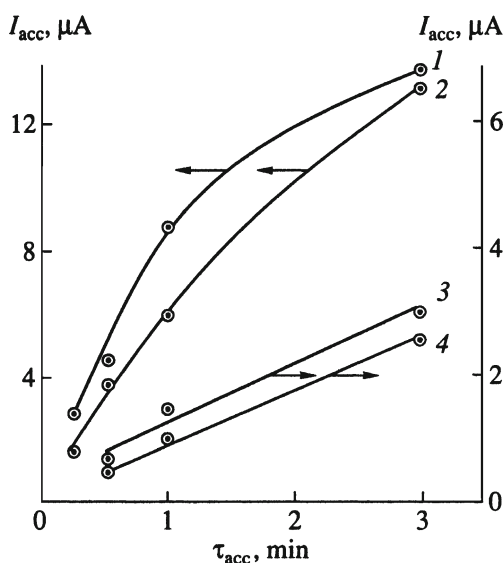
Figure 3 shows the dependence of the peak current of silver dissolution on voltage for silver concentrations  $1 \times 10^{-8}$ ,  $1 \times 10^{-9}$  and  $1 \times 10^{-10}$  M. In all cases, the dependencies are linear and within the studied voltage range; they do not have any plateaus typical for usual SVA modes. Similar dependencies for other metal cations were obtained in Ref. [20].

When operating in the HVA mode, the time necessary for metal accumulation decreases substantially in comparison with the usual SVA modes. As an example, Fig. 4 shows the dependencies of peak current on accumulation time for silver concentrations in solution  $1 \times 10^{-8}$ ,  $1 \times 10^{-9}$  M. One can see that for silver concentration  $1 \times 10^{-8}$  M and accumulation voltage of 100–200 V, the dependence of current peak on accumulation time has a plateau and, thus, the time should not exceed 3 min. At lower concentrations, the optimal accumulation time is to be increased. However, in our experiments, even for concentrations  $1 \times 10^{-11}$ – $1 \times 10^{-12}$  M it did not exceed 5 min. It should be stressed that for low silver content (straight lines 3 and 4) the condition for the appearance of the analytical signal is accumulation voltage above 200 V.

With an increase in the sensitivity of the instrument to recording the signals of silver in the solution with the concentration of silver ions below  $1 \times 10^{-10}$  M, copper and mercury signals started to appear in the background voltammograms; these signals interfere with silver determination. The source of copper ions may be the reagents contaminated with it, while the source of mercury is the calomel reference electrode. The effect of mercury ions was eliminated by replacing the stationary reference electrode with a trailing (remote) one. One of the methods to remove the interfering



**Fig. 3** Current of a silver peak as a function of accumulation voltage at a concentration of silver ions ( $c_{\text{Ag}}$ ) of  $1 \times 10^{-8}$  M,  $2 \times 10^{-9}$  M and  $1 \times 10^{-10}$  M and at  $\tau_{\text{acc}}$  of 15 s, 2 min and 3 min



**Fig. 4** Current of a silver peak as a function of accumulation time at a concentration of silver ions ( $c_{Ag}$ ) of 1, 2, (left scale)  $1 \times 10^{-8}$  M and 3, 4 (right scale)  $1 \times 10^{-9}$  M and at a  $V_{acc}$  of 1, 4 200, 2 100 and 3 300 V

action of copper signals is to bind it into a complex compound with Trilon B. This method caused not only a decrease of copper peak but also a decrease of the signal of silver, which is undesirable when working with ultra-low concentrations of the ions of this metal. A complete absence of the signals of copper in the background voltammogram was achieved after preliminary (before introducing silver) treatment of the supporting solution with the cation-exchange resin.

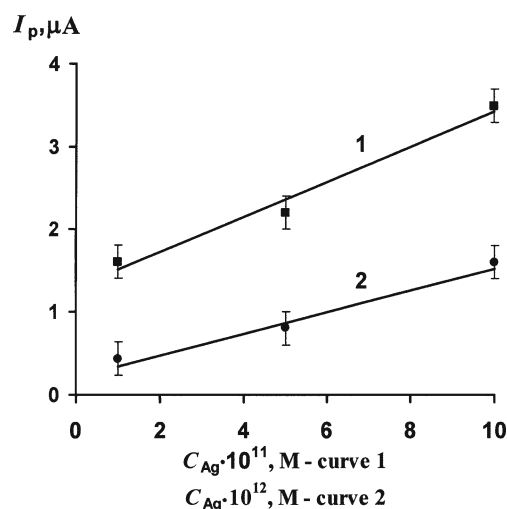
At silver ion concentration below  $1 \times 10^{-11}$  M, the most important interference is due to the adsorption of silver ions on the surface of the glass of chemical vessels. According to Ref. [21], at  $1 \text{ cm}^2$ , the surface adsorbs  $1 \times 10^{-11}$ – $1 \times 10^{-12}$  mol of metal ions. To eliminate the effect of silver adsorption, the working solutions with silver ion content  $1 \times 10^{-11}$  M and below were prepared in a Teflon electrolytic cell immediately before electrodeposition. In this case, the relative standard deviation of the determined peak current value  $I_p = (1.6 \pm 0.3) \mu\text{A}$  for silver deposition from the solution with silver ion content  $1 \times 10^{-11}$  M ( $V_{acc} = 400$  V, accumulation time  $\tau_{acc} = 5$  min) was  $s_r = 0.25$  ( $n = 10$ ,  $P = 0.95$ ).

A decrease in silver ion content by an order of magnitude required an increase in the volume of the solution under analysis. This is explained by the fact that the solution under analysis should contain the amount of silver ions sufficient for the deposition of at least one-tenth of the monolayer. On the surface of the microelectrode with an area of  $2.5 \times 10^{-3} \text{ cm}^2$ , silver monolayer is more than  $2 \times 10^{-12}$  mol. Meanwhile, the electrolytic cell  $30 \text{ cm}^3$  in volume with silver concentration of  $1 \times 10^{-12}$  M contains only  $3 \times 10^{-14}$  mol of  $\text{Ag}^+$ . Because of this, for the stable appearance of the anode peak at the silver concentration of  $1 \times 10^{-12}$  M, it is necessary to use a large volume of the solution (in our

case  $400 \text{ cm}^3$ ), and circulation of this solution between the vessel containing it and the cell is required. During silver electroaccumulation at  $V_{acc} = 400$  V, the solution circulated for 5 min between this vessel and the cell. The reproducibility of silver peak current  $I_p = (0.43 \pm 0.19) \mu\text{A}$  obtained under the chosen experimental conditions in a series of experiments ( $n = 11$ ,  $P = 0.95$ ) was  $s_r = 0.66$ . This detection limit for silver is comparable with that achieved by means of adsorption voltammetry [22] and is 2–3 orders of magnitude below the concentrations determined with silver accumulation at usual potential values [23]. Calibration dependencies  $I_p = f(c_{Ag})$  for silver ion concentration ranges  $10^{-11}$ – $10^{-10}$  and  $10^{-12}$ – $10^{-11}$  M are shown in Fig. 5. One can see that these dependencies have the appearance close to the linear one. Relatively low slope of these dependencies is likely to be connected with the fact that in the case of so low concentrations at the electrode, silver gets accumulated in the form of microphase (atom-sized layers). It is known [23, 24] that the angular coefficient of the dependencies of currents of the peaks of dissolution for these deposits on the concentrations of the metal in solution is much lower than that for the case of the dissolution of thicker deposits (macrophase).

## Conclusion

The presented data prove that the utilization of the so-called exaltation effect allows not only to enhance the rate of metal cation deposition but also to achieve a substantial decrease in the detection limit. It is demonstrated that ASV with high-voltage electrodeposition of metals can be used to analyze ultra-small amounts of metal ions because the dependence of the anodic dissolution peak of metal on time of accumulation and on concentration is qualitatively conserved.



**Fig. 5** Calibration graphs of  $I_p$  versus silver concentration obtained with the graphite electrode at  $V_{acc} = 400$  V and  $\tau_{acc} = 5$  min for 1  $10^{-11}$ – $10^{-10}$  and 2  $10^{-12}$ – $10^{-11}$  M  $\text{Ag}^+$  solutions

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