MAXIMUM SENSITIVITY OF AMALGAM POLAROGRAPHY WITH PRELIMINARY ACCUMULATION

(UDC 543)

V. A. Igolinskii and A. G. Stromberg

S. M. Kirov Polytechnic Institute, Tomsk

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The maximum sensitivity of amalgam polarization on a stationary electrode with preliminary accumulation is determined, and it is shown that the theoretical sensitivity is considerably higher than that attained in practice. A theoretical basis is also indicated for markedly increasing the sensitivity by changing the geometrical shape of the electrode. A silver amalgam electrode is proposed by which determinations can be made of 10^{-11}-10^{-12} g-mole of zinc.

In developing new analysis methods and improving those already known, it is important to know the theoretical limits of their sensitivity. The present work attempts to calculate, however roughly, the limits of sensitivity of amalgam polarography on a stationary electrode.

In the articles so far published on amalgam polarography with preliminary accumulation, the indicator electrode described is a stationary mercury drop. Suppose that the following electrochemical reaction takes place at the surface of the stationary amalgam electrode:

$$Me \rightleftarrows Me^{z+} + ze. \tag{1}$$

Let us determine the minimum quantity q of metal, dissolved in the mercury drop (after preliminary electrolysis), which can be measured by amalgam polarography with accumulation with an accuracy of 10%. We shall assume that the anode peak obtained in recording the anode polarogram (Fig. 1) is situated between the potentials φ_1 and φ_2, i.e., that the currents at potentials φ_1 and φ_2 are considerably less than the peak current being, say, 1% of its value. Let Δt be the time for the potential to change from φ_1 to φ_2, assuming that the potential changes linearly with time; then

$$\Delta t = \left|\frac{\varphi_2 - \varphi_1}{w}\right|,$$

where w, V/sec, is the rate of change of the potential.

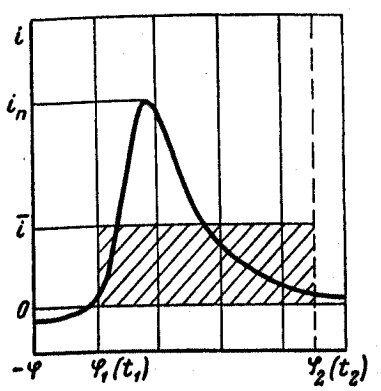

Fig. 1. Anode peak.

Let us also assume that during this time practically all the substance in the drop is oxidized. We shall not consider oscillographic polarography, in which, owing to the high rate of potential change during the anode cycle, only a small fraction of the metal leaves the mercury drop. Experiment shows that when the rate of potential change is 400-800 mV/min, 85-90% of the substance in the mercury drop is oxidized.

The mean oxidation current at time Δt is

$$\bar{i} = \frac{1}{\Delta t}\int_{t_1}^{t_2} i\,dt. \tag{2}$$

It is evident (see Fig. 1) that $\bar{i} < i_p$ (where i_p is the peak current).

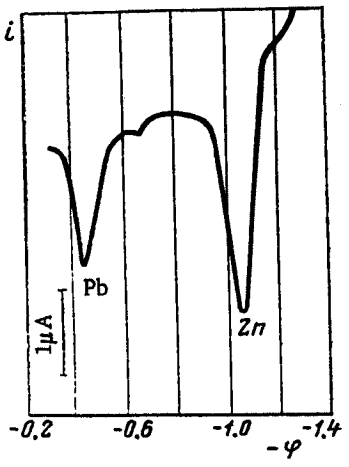

Fig. 2. Anode polarogram on amalgamated silver electrode. Zinc concentration $1.4 \cdot 10^{-10}$ M; volume of solution 10 ml; electrode area 0.5 cm^2; duration of preliminary electrolysis 5 min at −1.55 V; rate of change of potential 16 mV/sec.

Thus,

$$\bar{i} = \frac{qzF}{\Delta t} < i_p. \qquad (3)$$

Here $\bar{i}$ is the mean oxidation current in A; q is the quantity of substance oxidized during time Δt, in g; z is the number of electrons taking part in the electrode reaction; and F is Faraday's constant in C/mole.

To measure the peak current with a given accuracy, it must be at least m times greater than the noise. In the most favorable case, the latter will be the charging current [1,2]:

$$i_c = S \cdot C_y \cdot w. \qquad (4)$$

Here i_c is the charging current, S is the surface area, C_y is the differential capacity of the electrical double layer, and w is the rate of change of the potential.

For the usual values of these quantities (S = 0.01 cm^2, C_y = 20 $\mu f/cm^2$, w = 0.01 V/sec), $i_c = 2 \cdot 10^{-9}$ A. Let us assume that, for measurements with an accuracy of at least 10%, the peak current must be not less than $10i_c$, i.e., $2 \cdot 10^{-8}$ A. Substituting this value in (3), and putting z = 2 and Δt = 10 sec, we get $q > 10^{-2}$ mole.

Consequently, amalgam polarography with preliminary accumulation can determine quantities of substance of the order of 10^{-12} mole with an accuracy of 10%, or, assuming the cell volume is 10 ml, analyze concentrations of the order of 10^{-10} mole/liter. However, as it is impossible to separate an appreciable amount of substance from solution on to a hanging mercury drop in practically realizable electrolysis times, this sensitivity is normally unattainable [3].

One way of increasing the sensitivity of amalgam polarography is to change the geometrical shape of the electrode. By studying the effect of depletion of the solution during preliminary electrolysis on the anode peak height, [4] derives an equation for the peak current, which may be expressed in the form

$$i_p = K_2 \cdot S \cdot \frac{Q}{V_2}\left(1 - e^{-\frac{K_1 \cdot S \cdot t}{z \cdot F \cdot V_1}}\right). \qquad (5)$$

Here, K_1 and K_2 are constants [4], S is the surface area occupied over which electrolysis takes place, V_2 is the volume of mercury over which is distributed the metal taking part in the electrode reaction, Q is the amount of metal in solution, t is the duration of preliminary electrolysis, V_1 is the volume of the solution, and F is Faraday's constant; the factor $\left(1 - e^{-\frac{K_1 \cdot S \cdot t}{z \cdot F \cdot V_1}}\right)$ is equal to the fraction of the metal initially in the solution which is separated by electrolysis during time t.

From (5) it is seen that, other conditions being the same, the peak current increases with increase of electrolysis time, approaching a limit corresponding to complete separation of the metal from solution at the electrode. When the metal is almost fully separated from solution, (5) takes the form

$$i_p = K_2 \frac{S}{V_2} Q. \qquad (6)$$

Thus the peak current for a given quantity Q of metal in solution depends on S/V_2,* i.e., the ratio of the surface over which the electrode reaction takes place to the volume in which the metal taking part in the electrode reaction is distributed. To a certain extent, S/V_2 characterizes the geometrical shape of the electrode. The electrode most commonly used at present for amalgam polarography is a hanging mercury drop [3,5]. The drop is a sphere and has minimum S/V_2 for any given volume. This electrode thus has the most disadvantageous shape possible as regards sensitivity. It is clear that the sensitivity can be increased by changing the electrode to one with greater S/V_2.

*The peak current may not be directly proportional to S/V_2, as K_2 may depend on the shape of the electrode.

For this purpose we suggest a mercury film electrode, taking the form of a thin film of mercury (1-3 μ) applied to the surface of a solid supporting layer, for which we would choose silver. This metal is easily amalgamated, only slightly soluble in mercury (~0.05%), and does not form additional intermetallic compounds with the metals under investigation [6,7]. In contrast to earlier work on the use of amalgamated silver electrodes [8-12], the present authors' aim is to secure maximum sensitivity improvement and thus use amalgam polarography with accumulation for determining small quantities of substance of order 10^{-10} mole/liter.

The electrode is a silver wire of length 1-2 cm and diameter 1 mm, glued into a glass tube with epoxy resin. The wire is electrolytically coated with a mercury film of 2 μ thickness from a saturated solution of $Hg_2(NO_3)_2$ in the electrolyzer (current strength 5.5 mA for 2 min to cover 0.5 cm^2). After rubbing with tracing paper to spread the mercury evenly, the electrode is carefully washed. Each wire can be used for many repeated determinations (20 or more) without noticeably changing its properties. After 6-8 h working, the electrode is regenerated, removing the mercury film from the surface by dissolving it electrolytically in saturated mercury nitrate solution in the same electrolyzer and under the same conditions; the dull silver surface is then polished to brightness with a piece of silver wire and reamalgamated.

As our investigations showed, this electrode has a considerably greater sensitivity than the drop type. Its resolving power is high, as the polarograms take the form of sharp peaks (half-width of the order of 50-80 mV for Pb, Tl, and Cd) owing to the rapid passage of metal from the thin film of amalgam. Furthermore, the duration of the preliminary electrolysis is considerably reduced.

As an example, Fig. 2 shows anode polarograms for zinc, obtained with the film electrode. The background was 0.1 M high-purity NH_4Cl solution made with water distilled three times in quartz apparatus. As shown by the experiment, extra-pure ammonium chloride contains only small amounts of lead, which can be taken into account and do not interfere with work with the film electrode. The calibration move is a straight line through the origin of coordinates.

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