INCREASING THE SENSITIVITY OF AMALGAM POLAROGRAPHY WITH ACCUMULATION ON A STATIONARY MERCURY DROP

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We have determined the optimum conditions for amalgam polarography with accumulation on a stationary mercury drop with a linearly changing potential. We have studied the effect of various electrolysis parameters (t/v and r) on the depth of the anode peak h.

In recent years a number of authors [1] have shown the possibility of determining certain elements in concentrations of $10^{-7}-10^{-8}$ M using amalgam polarography with accumulation on a stationary mercury drop. Under certain constant conditions some of the substance from solution is electrolytically concentrated in a mercury drop and then, with a potential changing linearly with time to the positive side, an anode peak is obtained when the amalgam dissolves. Other conditions being equal, the depth of the peak is proportional to the concentration of the substance in solution.

The aim of the present work was to find the optimum conditions and limits for the increase in sensitivity of this method.

The height of the cathode peak H and the electrolysis current i are proportional to the concentration of ions of the substance being determined C_1 and the surface of the drop S:

$$H = K_1SC_1; \; i = K_3SC_1. \tag{1}$$

If we assume that there is practically no reduction in the concentration of ions in the solution during preliminary electrolysis, then, assuming that after electrolysis the metal is almost uniformly distributed in the drop [2, 3], we can obtain [6] an expression for the depth of the anode peak* h:

$$h = K_2SC_2 = 3\frac{K_2K_3}{zF}\cdot\frac{t}{r}\cdot SC_1. \tag{2}$$

Here C_2 is the concentration of metal in the amalgam; r is the radius of the drop; t is the duration of electrolysis; z is the number of electrons taking part in the electrode reaction; F is the Faraday constant.

When working with lead solutions with a supporting electrolyte of 0.1 N KOH we obtained: $K_1 = 240$; $K_2 = 7.5$; and $K_3 = 10^4$ A·cm·mole^{-1}. In further calculations we will assume that the constants K_1, K_2 and K_3 are independent of the volume of the solution, the duration of electrolysis and the radius of the drop. We will also assume that electrolysis occurs with mixing of the solution, the hydrodynamic conditions in all experiments remaining constant. During electrolysis for 10 min on a drop with radius 0.040 cm the metal concentration in the drop increased by a factor of 2400 compared with the ion concentration in the solution, and the sensitivity h/H increased by a factor of 75, i.e., the sensitivity increased 33 times more slowly than the metal concentration in the drop, since the proportionality constant K_2 for the anode peak was 1/33 of that for the cathode peak.

The sensitivity of the method is determined by the signal-to-noise ratio [4]. If the height of the cathode peak is expressed by the Sevcik equation [5], then the ratio of the height of the cathode peak to the charge current [4] will have the form

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* Due to the special conditions of diffusion of metal from the mercury drop in the production of an anode peak the proportionality between its depth and the surface of the drop is not obvious. However, our experiments with mercury drops of varying size showed that relationship (2) corresponds fairly closely to the experimental data.

$$\frac{H}{i_c} = \frac{2.7 \cdot 10^5 \cdot z^{3/2} S D^{1/2} V^{1/2} C_1}{S C_{sp}^{2} V} = \frac{2.7 \cdot 10^5 \cdot z^{3/2} D^{1/2} C_1}{C_{sp}^{2} V^{1/2}}. \quad (3)$$

Here D is the diffusion coefficient, $cm^2 \cdot sec^{-1}$; C_{sp}^2 is the specific capacity of the electric double layer, $\mu F \cdot cm^{-2}$; V is the rate of change in potential, $V \cdot sec^{-1}$.

A signal-to-noise ratio of unity is assumed to be the sensitivity limit. Hence the lowest ion concentration in the solution with change in the cathode peak for values: $z = 2$; $D = 10^{-5}\ cm^2 \cdot sec^{-1}$; $C_{sp} = 20\ \mu F \cdot cm^{-2}$; $V = 0.01\ V \cdot sec^{-1}$; $H/i_c = 1$ is equal to

$$C_{1_{min}} = \frac{H}{i_c} \cdot \frac{C_{sp}\ V^{1/2}}{2.7\ \ 10^5 \cdot z^{3/2} D^{1/2}} \simeq 10^{-4} \text{ mmole/liter.} \quad (4)$$

Due to the presence of impurities in the solution (mainly residual oxygen) the actual limit of sensitivity is a concentration of 10^{-2}–10^{-3} millimole/liter. The sensitivity of amalgam polarography is much higher than that of ordinary polarography because of the greater depth of the peak (signal) with unchanged charge current (noise) due to the concentrating of metal in the mercury drop. The height of the cathode peak can also be increased by increasing the surface of the mercury cathode. However, the charge current increases to the same extent and the sensitivity is therefore unchanged. Higher rates of change in potential in oscillographic polarography give a higher cathode peak but the sensitivity then even deteriorates, as can be seen from formula (3).

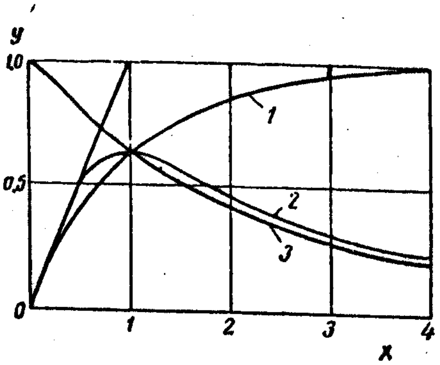

Fig. 1. Effect of the value of t/v and the radius of the drop r on the depth of the anode peak h. Curves plotted in the coordinates: 1) h/a, b; 2) $h/ab^{1/2}$; 3) h/ab, b.

When the ion concentration in the solution is practically constant during electrolysis the depth of the anode peak is proportional to the ion concentration, the time of electrolysis, and the radius of the mercury drop and is independent of the volume of solution [see formula (2)].

With a noticeable reduction in concentration of the solution during electrolysis the expressions for the depth of the anode peak [6] will have the form

$$h = af;\ f = 1 - e^{-b} \quad (5)$$

$$b = \frac{4\pi K_3}{zF} r^2 \frac{t}{v} = b' r^2 \frac{t}{v}; \quad (6)$$

$$a = 3K_2 (C_1^0 v) \frac{1}{r} = a' \frac{1}{r}. \quad (7)$$

The character of the dependence of the peak depth on the duration of electrolysis t, the volume of solution v and the radius of the drop r is determined [see formula (6)] by the values of the dimensionless parameter b. When $b < 0.1$ we obtain $f \approx b$ and $h = ab$, which coincides to an accuracy of 5% with formula (2) for a constant concentration of solution. When $b > 3$ we obtain $f \approx 1$ and $h = a$, which corresponds to practically complete transfer of the substance from the solution to the mercury drop during the electrolysis.

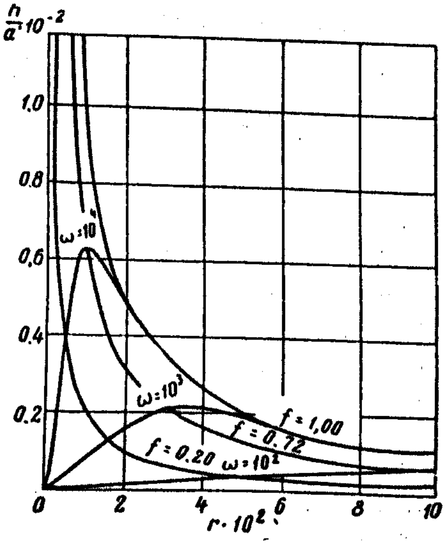

Fig. 2. Effect of the value of t/v and the radius of the drop r on the depth of the anode peak h.

For practical purposes it is particularly interesting to examine the dependence of the peak depth on the duration of electrolysis, the volume of solution and the radius of the drop when the same weight of high-purity metal is dissolved in various volumes of solution (supporting electrolyte). The value of the product $C_1^0 v$ in formula (7) then remains constant and, consequently, the quantity a only depends on the radius of the drop. It can be seen from formulas (5)–(7) that in this case the depth of the peak can be considered as a function of only two variables r and t/v. Figure 1 shows these relationships in a dimensionless form. From considerations arising from formulas (5)–(7), as the

(X, Y) coordinates we chose: for the dependence of h on t/v – the coordinates h/a, b (curve 1); for the dependence of h on r – the coordinates $h/ab^{1/2}$, $b^{1/2}$ (curve 2). It can be seen from the figure that with a noticeable reduction in the concentration of solution during electrolysis in the range $0.1 < b < 3$ with increase in the time of electrolysis or with reduction in the volume of solution the peak depth approaches the limiting constant value (curve 1), and with increase in the radius of the drop it passes* through a maximum (curve 2) when the parameter $b = 1.26$. From curve 1 in Fig. 1 we can conclude that the duration of electrolysis should be increased or the volume of solution decreased only to a certain value, corresponding to $b < 3$. Further increase in the time of electrolysis or reduction in the volume of solution will not lead to an increase in the depth of the peak, since practically all ions from the solution are discharged on the mercury drop.

To allow for the depletion of the solution by metal ions during electrolysis, formula (5) should be used in the form

$$\frac{h}{h_0} = \frac{h}{ab} = \frac{f}{b}. \tag{5a}$$

Here $h_0 = ab$ is the depth of the anode peak under the given conditions, but with no depletion of solution, for example, in a large volume of solution. Curve 3 (in coordinates h/ab) shows that when the parameter b rises from 0.1 to 1.0 due to a reduction by a factor 10 in volume or the same increase in time of electrolysis, the height of the peak only increases 6.3-fold, due to depletion of the solution.

Curve 2 shows that for each value of the parameter t/v there is a certain optimum radius of the drop r ($b = 1.26$) at which the depth of the peak is a maximum. From the condition $b = 1.26$ and formulas (5)-(7) we obtain

$$r_m = \left(\frac{1.26v}{b't}\right)^{1/2}, \tag{8}$$

$$h_m = \frac{a'}{r_m}(1 - e^{-1}) = 0.72\,\frac{a'}{r_m}, \tag{9}$$

where

$$a' = 3K_2\,(C_1^0 v) = \text{const}. \tag{10}$$

A study of the graphs in coordinates h/a' and r (Fig. 2) gives a clearer idea of the optimum value of the parameters t/v and r for an increase in sensitivity of the method for a given weight of material and the acceptable values of the variables t, v, and r. Rewriting formula (5) in the form

$$\frac{h}{a'} = f\frac{1}{r}, \tag{11}$$

we see that for each constant value f (or b) in coordinates h/a' and r there is a hyperbola. The possible values of the depths of the peaks h/a' will then be arranged on the area of the graph (see Fig. 1), bounded by the hyperbola for $f = 1$ and the axes of the coordinates; this is because f, according to formula (5), cannot be greater than unity. We will designate $\omega = b'(t/v)$. The maxima of the curves on this graph for constant values of the parameter ω will then lie on the hyperbola $f = 0.72$, and for higher values of r will merge with the hyperbola $f = 1$. To obtain larger anode peaks we must therefore reduce the volume of solution, increase the time of electrolysis and, for selected values of ω, change the radius of the drop to the optimum value.

Theoretically, for very high values of ω and fairly small optimum values of r_m, equal to $(1.26/\omega)^{1/2}$, in accordance with formula (8) we can obtain anode peaks for the dissolving of metal from the amalgam which are as large as required. The limit will be set by the practically acceptable values of t, v, and r. The table gives calculations of the peak height for three values of the parameter ω. For the calculation of the constants b' and a' from the formulas (6) and (7) we took the values: $K_3 = 10^4$; $K_2 = 7.5$; $C_1^0 v = 2 \cdot 10^4$ millimole/liter · ml. Using these data, we obtain: $b' = 0.655$, $a' = 4.5 \cdot 10^{-3}$. We take the value of one millimeter of the scale for maximum sensitivity of the galvanometer as $2 \cdot 10^{-2}\ \mu A \cdot mm^{-1}$. It can be seen that with a 100-fold increase in the parameter ω (e.g., with a reduction by a factor 10 in volume of the solution and simultaneous tenfold increase in the time of electrolysis) and a corresponding reduction by a factor 10 in optimum radius of the drop there is a tenfold increase in the op-

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* An investigation of formula (5) at the maximum with the condition $C_1^0 v = \text{const}$ leads to the formula: $1 + 2b = e^{-b}$. By the method of selection we find that this relationship is satisfied when $b = 1.26$.

timum depth of the peak. If the radius of the drop is unchanged, then the height of the peak is only doubled (see Fig. 2).

Calculation of Peak Depth

ω, cm^{-2}	t, sec	v, ml	$\frac{t}{v} = \frac{\omega}{b'}$, sec · ml^{-1}	$r_m \cdot 10^2 = \left(\frac{1.26}{\omega}\right)^{1/2} \cdot 10^2$ cm	$\frac{h_m}{a'} = \frac{0.72}{r_m}$	$h_m \cdot 10^2$ μA	h_m, mm
100	1530	10.0	153	11.2	6.43	2.89	14.5
1000	3060	2.0	1530	3.55	20.3	9.13	46
10000	15300	1.0	15300	1.12	64.3	28.9	145

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THE DETERMINATION OF TUNGSTEN IN AMMONIUM PERRHENATE BY SQUARE-WAVE POLAROGRAPHY

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Tungsten in perrhenate is determined by square-wave polarography with a supporting electrolyte of 6 N HCl. We have studied the interference of accompanying elements. The sensitivity of the method is $1 \cdot 10^{-4}$% for a 0.2 g sample. The mean square deviation is 26%.

The sensitivity of colorimetric methods for the determination of tungsten in rhenium products is too low. Square-wave polarography has therefore been used.

Tungsten is reversibly reduced only from strongly acid chloride solutions and from solutions of some complex formers, for example oxalates.* Tungsten has not yet been determined with a square-wave polarograph.

Preliminary experiments established that in chloride solutions with acid concentration up to 6-5 N tungsten gives peaks of two-electron reduction at about −0.6 V. The height of these peaks depends on the acid concentration; in solutions with acid concentration above 6 N the determination of tungsten is affected by hydrogen. The negative slope of the tungsten peak** prevents the determination being carried out if the W concentration is less than 0.1-0.2 μg/ml. The tungsten peak disappears for hydrochloric acid concentrations below 3 N. A 6 N solution is therefore the most convenient supporting electrolyte for the determination of tungsten. An additional advantage of this solution is its azeotropic character.

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