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CRITERIA FOR OPTIMUM CONDITIONS IN ALTERNATING CURRENT POLAROGRAPHY

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We have investigated and determined the conditions which the supporting electrode should satisfy, in order to obtain maximum sensitivity and the required resolving power, when working with alternating current polarographs.

The sensitivity and resolving power of a polarographic analysis are determined by the parameters of the polarograph and the quality of the supporting electrolyte. With modern alternating current polarographs it is possible to determine down to 10^{-7} mole/liter of material when using a dropping mercury electrode, and down to 10^{-9} mole/liter when using a stationary mercury drop for polarography after preelectrolysis. The corresponding resolving powers are 5000 : 1 and 30,000 : 1.

For successful practical operation it is necessary that the solution for polarography should be correctly prepared; otherwise the sensitivity and resolving power may be worse by a factor of ten or a hundred.

In our previous work on vector polarography we formulated criteria,* which should be satisfied by the supporting electrolyte, in order to obtain maximum sensitivity and a required resolving power. Let us call this supporting electrolyte the optimum. We will assume that, for any given solution, the electrode reaction is determined by the value of the polarization voltage; the supply of material to the electrode-solution boundary is achieved by diffusion and by the natural convection in the solution resulting from the growth and breaking away of the mercury drops; the cell is fed by a sinusoidal voltage of low amplitude ($\leq RT/nF$) from a source of low internal resistance.

Allowing for these initial conditions, we can formulate the following criteria for optimum working.

I. The electrode processes should be polarographically reversible:

$$K_G > 0.15\omega^{1/2}\ \mathrm{cm}\cdot\mathrm{sec}^{-1}.$$

II. The number of electrons participating in the electrode process should be the maximum possible.

III. The difference between the half-wave potentials of the components should satisfy the equation:

$$\frac{C_1^0}{C_2^0} = \frac{n_2^2 D_2^{1/2}}{n_1^2 D_1^{1/2}} f_{02}\,\mathrm{ch}^2\,[20n_1\,(E_{2\,1/2} - E_{1\,1/2})].$$

IV. Each component of the solution analyzed should correspond to only one wave on the polarogram.

V. The specific resistance of the supporting electrolyte, with polarography in a two-electrode cell, should not exceed 10 Ω·cm (the specific resistance of 1 M KCl).

The value of the velocity constant K_G determines the difference between polarographically reversible, irreversible, and partially reversible processes; ω is the frequency of the alternating voltage fed to the cell; τ is the life of a drop. The theory of alternating current polarography gives rigid equations for polarograms obtained with the above forms of electrode reaction, but these equations are complicated and cumbrous, so that they are difficult to use in practice.

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*These criteria for optimum conditions are applicable to all forms of alternating current polarograph.

Reversible Reactions

a) The vector polarogram is bell-shaped, with a well defined maximum (peak).

b) The height of the maximum is proportional to the initial concentration of the substance in the cell.

c) The vector polarogram is symmetrical about a vertical axis passing through its maximum.

d) The peak potential of the vector polarogram is the same as the reversible half-wave potential of a classical polarogram.

e) The half-wave width of the vector polarogram is determined by the number of electrons participating in the electrode reaction.

Partially Reversible Reactions

a) In most cases the vector polarogram is bell-shaped, with one well defined maximum.

b) The height of the maximum is proportional to the initial concentration of the substance.

c) When the velocity constant K_G is reduced, the height of the maximum decreases.

d) The peak potential of the vector polarogram is not the same as the reversible half-wave potential, but is shifted relative to the latter in the negative potential direction when the conversion coefficient $\alpha > 0.5$, or in the positive potential direction when $\alpha < 0.5$.

e) The half-wave width is somewhat increased by a reduction in the velocity constant.

f) When $\alpha < 0.5$, the vector polarogram has two peaks for a certain range of K_G values.

Irreversible Reactions

a) The vector polarogram has a symmetrical bell-shaped form with a well defined maximum.

b) The height of the maximum is proportional to the initial concentration, and the conversion coefficient does not depend on the value of the velocity constant.

c) The potential of the maximum of the vector polarogram is not the same as the reversible or irreversible half-wave potential of the classical polarogram. It is always shifted in the negative potential direction, and the shift increases with a decrease in the conversion coefficient and the velocity constant.

d) The half-wave width is inversely proportional to the product αn, and varies somewhat with the frequency.

A quantitative estimate of the effect of electrode reaction reversibility (the first criterion for optimum conditions) on sensitivity and resolving power was obtained by applying the simplified Matsuda equation [2] to two limiting cases: a reversible and an irreversible reaction.

If the Faradic impedance is treated as the polarization resistance in parallel with a pesudocapacity, then, for the maximum of the vector polarogram, the simplified Matsuda equation has the form:

$$(\overline{I}_{a\ \max})_{\text{rev}} = 0.183\overline{i}_d\,(\omega\tau)^{1/2}\,\frac{nF}{2RT}\,U_m \tag{1}$$

for a reversible reaction, and

$$(\overline{I}_{a\ \max})_{\text{irr}} = \frac{2}{\pi}\,\overline{i}_d\,\frac{\alpha nF}{RT}\,U_m\,[1 - 1.24\,(\omega\tau)^{-0.223}] \tag{2}$$

for an irreversible reaction.

Here, $\overline{I}_{a\ \max}$ is the maximum value of the active component of the current, averaged over the life of a mercury drop; $\overline{I}_d$ is the mean value of the limiting current from the Ilkovic equation; U_m is the mean value of the sinusoidal voltage.

We can now calculate the ratios of the currents for reversible and irreversible reactions for two common cases: $\alpha = 0.5$, $\tau = 4$ sec, $\omega = 314$, and $\alpha = 0.5$, $\tau = 4$ sec, and $\omega = 1256$.

From the above equations we have:

$$A = \frac{(\bar{I}_{a\,\max})_{\text{rev}}}{(\bar{I}_{a\,\max})_{\text{irr}}} = \frac{0.183\,(\omega\tau)^{1/2}}{\frac{2}{\pi}\alpha\,[1 - 1.24\,(\omega\tau)^{-0.223}]}\,. \tag{3}$$

Substituting the two sets of values for α, τ, and ω, we find that A is 14 and 25, respectively. Thus the current for a reversible reaction may be at least ten times the current for an irreversible reaction.

The capacity current is very little affected by the composition of the supporting electrolyte, so it follows that the error due to the capacity current will be much the same for reversible and irreversible reactions. In this case, the sensitivity will be determined by effective signal current: the greater this current the higher the sensitivity. Consequently, if, in the analysis of a given component, a supporting electrolyte is chosen which gives a reversible reaction, this will ensure the possibility of obtaining the maximum sensitivity. This confirms the correctness of the first criterion for optimum conditions.

It follows from the theory of alternating polarography that for reversible reactions:

$$K_G > 0.15\omega^{1/2}\ \text{cm} \cdot \text{sec}^{-1}, \tag{4}$$

and for irreversible reactions:

$$K_G < 3 \cdot 10^{-5}\tau^{-1/2}\ \text{cm} \cdot \text{sec}^{-1}. \tag{5}$$

Intermediate values of K_G corresponds to the occurrence of partially irreversible reactions.

It follows from (4) that, for a given value of K_G, the reaction may be reversible or partially irreversible, depending on the frequency fed to the cell. Reactions reversible at low frequency may become partially irreversible at higher frequency. Thus in classical polarography [3], a reaction is reversible if $K_G > 2 \times 10^{-2}$ cm · sec^{-1}, but in alternating-current polarography at 50 cps a reversible reaction corresponds to $K_G > 2.67$ cm · sec^{-1}. Thus, in the case of alternating-current polarography, the lower limit of the velocity constant to ensure reversibility of a reaction should be greater by two orders of magnitude than in the case of classical polarography. In other words, a reaction which is reversible in classical polarography may be partially irreversible in alternating-current polarography.

The frequency is a parameter of the polarograph and does not depend on the composition of the solution, so that individual methods of preparing a solution should be required for use with polarographs of different frequencies. This is unnecessary in practice because high frequencies cannot be used with high sensitivity alternating-current polarographs, even in the case of reversible reactions, because they lead to unfavorable signal to noise ratios. The effective signal, which is the electric current, is proportional to $\omega^{1/2}$ in accordance with Eq. (1). The main source of error is the capacity current, dependent on the capacity of the double layer; this is proportional to ω. For this reason, relatively low frequencies of 50-300 cps are always used in polarography.

Suppose that we have selected a low frequency and have prepared a solution with a value of K_G such that Eq. (4) is obeyed, i.e., the conditions for reversibility are fulfilled. Then the polarographic reaction should become partially irreversible when the frequency is increased. The effect of irreversibility should be to reduce the polarographic maximum, whereas the effect of frequency alone should be to increase it. It is clear that the resulting effect will depend on the actual values of these factors.

The table, taken from Matsuda's paper, shows that, near the limits of reversibility, a decrease in K_G by an order of magnitude reduces the current only by a few per cent. At the same time, an increase in frequency of two orders of magnitude should increase the current by approximately one order of magnitude. Thus a change in the operating frequency by one or two orders should have little practical effect on the reversibility conditions. Consequently, if the reversibility conditions are satisfied for any given type of polarograph, this should in practice apply to all alternating-current polarographs, regardless of concrete differences.

The second criterion for optimum conditions requires that the electrode process should occur with participation of the maximum number of electrons. The desirability of this requirement is obvious from the equation for maximum polarographic current (1). Indeed, $\underline{n}$ occurs here in two factors, once directly and once in the mean value of

The Effect of K_G on the Ratio of the Currents for Partially Irreversible and Reversible Reactions (frequency 50 cps; τ = 4 sec; α = 0.5)

K_G cm · sec^{-1}	∞	10^{-1}	$3 \cdot 10^{-2}$	10^{-2}	$5 \cdot 10^{-3}$	10^{-3}	10^{-4}
Current ratio	1	0.94	0.73	0.39	0.23	0.09	0.08

$\bar{I}_d$ from the Ilkovic equation. Thus $\bar{I}_{a\,\max}$ is proportional to n^2. Interference by the capacity current does not depend on *n*, so that the sensitivity is also proportional to n^2. For example, if *n* can be 3 for a given substance, but a solution is chosen such that n = 1, then the sensitivity is reduced to a ninth. If the reaction is irreversible, and the frequency is 50 cps, then the current is further reduced by a factor of 1/14. The combined effect is that the sensitivity is reduced by a factor of 1/126. It is readily intelligible that it is impossible and undesirable to compensate for this loss in sensitivity by improving the polarograph itself. A good polarograph can only be used with advantage when suitably prepared solutions are used.

Up till now we have considered the criteria for optimum conditions as applied to obtaining the highest sensitivity. We will now consider the conditions for obtaining a required resolving power. This is taken to mean the ratio of the concentration of a second component to the concentration of the component to be determined, at which it is possible to measure the concentration of the component to be determined with a given precision.

In polarographic analysis it is difficult to ensure that a high resolving power will be achieved, because the potential range for the polarography of some substances is quite small, and is always restricted to about 3 V. At the same time the potential range occupied by one substance is quite appreciable and is greater the higher the concentration of the substance. Consequently, if there are several substances present in the solution, they interfere with each other. In order to reduce this interference to a minimum, it is necessary to prepare the solution for polarography in a special way. The separation of two components is easier the greater the difference in potential between the peaks of the two components on the polarogram, and the smaller the range of potential occupied by each.

In order to characterize the potential range occupied on the polarogram, without reference to the concentration, we use the conception of "half-wave width" σ, which is defined as the difference in potential between the two points on the polarogram at half the maximum peak height. The greater σ the greater is the potential range occupied on the polarogram.

It is known that for reversible processes:

$$\sigma = 3.52 \frac{RT}{nF} = \frac{88}{n} \text{ mV}, \tag{6}$$

and for irreversible processes:

$$\sigma = 2.72 \frac{RT}{\alpha nF} (\omega\tau)^{0.068} = \frac{68}{\alpha n} (\omega\tau)^{0.068} \text{ mV}. \tag{7}$$

Thus σ is inversely proportional to *n*. It was shown above that the peak height is proportional to n^2. In other words, the polarographic peak grows taller and narrower with increasing *n*, and becomes shorter and broader with decreasing *n*.

It follows that fulfillment of the second condition for optimum conditions favors high sensitivity and high resolving power.

The half-wave width is greater for irreversible processes because α is always less than one. Thus, if n = 2, ω = 314, τ = 4 sec, and α = 0.5, then σ = 110 mV, whereas, for a reversible process with n = 2, we have σ = 44 mV.

If the reactions of both the secondary and the analytical components are reversible, then the necessary conditions for resolution is given by the equation [5]:

$$\frac{C_1^0}{C_2^0} = \frac{n_2^2 D_2^{1/2}}{n_1^2 D_1^{1/2}} f_{02} \operatorname{ch}^2 [20 n_1 (E_{2\,1/2} - E_{1\,1/2})]. \tag{8}$$

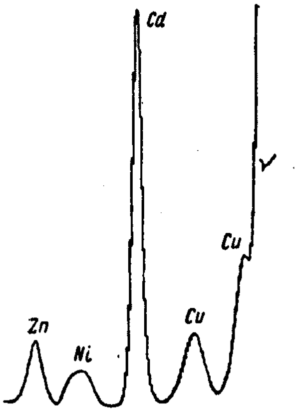

Fig. 1. Vector polarogram of Cu, Cd, Ni, and Zn in an ammoniacal supporting electrolyte. Concentrations 5 × 10^{-4} M; τ = 3.2 sec; t_{set} = 2.6 sec; v = 4 ml; sensitivity 7.

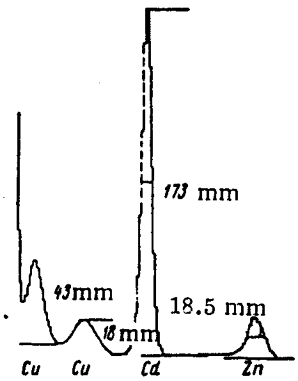

Fig. 2. Polarogram of Cu, Cd, and Zn, in a supporting electrolyte 1 M in NH_4OH and 1 M in $(NH_4)_2SO_4$, recorded with a square wave polarograph. Concentrations 10^{-4} M.

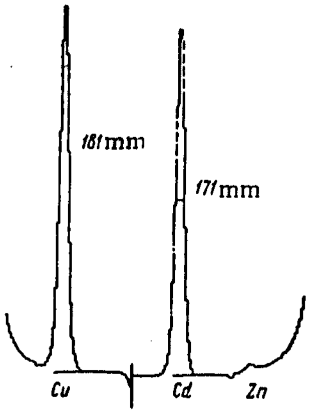

Fig. 3. Polarogram of Cu, Cd, and Zn, in a supporting electrolyte 2 M in $(NH_4)_2SO_4$ and 1 M in H_3PO_4, recorded with a square wave polarograph. Concentrations 10^{-4} M.

Here the indices 1 and 2 refer to the secondary and analytical components respectively; f_0 is the relative error; $E_{1/2}$ is the reversible half-wave potential.

It is evident from the equation that, in order to have a high resolving power, it is necessary to have a large difference in half-wave potential. This confirms the correctness of criterion III.

Supporting electrolytes, in which the component to be analyzed gives two waves, may be encountered in polarographic practice. For analytical purposes it is quite enough to have only one wave, either for determining the nature of a component or its concentration. The second wave can give no additional information and, by occupying a definite potential range, interferes with the determination of other components. In addition, both waves are reduced in height because of the low value of $\underline{n}$. For these reasons criterion IV requires that each component should give only one wave on the polarogram.

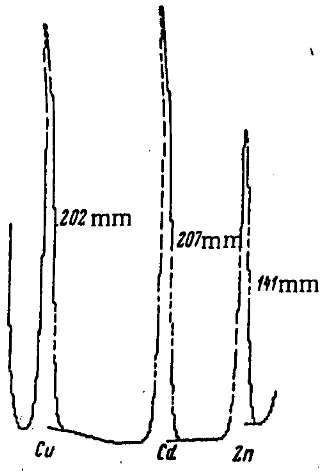

Fig. 4. Polarogram of Cu, Cd, and Zn, in a supporting electrolyte of 1 M H_3PO_4, recorded with a square wave polarograph. Concentrations 10^{-4} M.

With highly sensitive alternating-current polarographs there are special devices for eliminating the interfering effect of the capacity current arising from the capacity of the double layer. The effectiveness of these devices depends on the ohmic resistance of the supporting electrolyte; the smaller this resistance the easier it is to eliminate the effect of the capacity current. In the case of a vector polarograph, a high resistance of the supporting electrolyte creates an uncompensated internal phase shift, which is particularly affected by the change in capacity of the double layer resulting from the change in polarization voltage. In square wave polarography, an increase in the resistance of the supporting electrolyte leads to an increase in the time constant of the cell, and this means that the capacity current cannot drop to zero during a half-period of the alternating voltage. It is for this reason that criterion V restricts the value of the specific resistance of the supporting electrolyte.

Recently endeavors have been made to reduce the effect of the ohmic resistance of the supporting electrolyte by introducing a third electrode into the cell. Depending on the quality and design of the circuit associated with the third electrode, the requirement as to resistance can be relaxed when a three-electrode cell is used.

A few practical examples may be given to illustrate the above considerations.*

An ammoniacal supporting electrolyte is often used in classical polarography for the determination of copper, cadmium, nickel, and zinc. The wave heights are approximately the same for Cd, Ni, and Zn for the same molar concentrations. Figure 1 shows a vector polarogram of these components (frequency 50 cps), and Figs. 2, 3, and 4 show polarograms obtained with a Barker polarograph (frequency 225 cps).

It is clear from Figs. 1 and 2 that, in an ammoniacal supporting electrolyte, the wave height of cadmium was greater by an order of magnitude than the wave heights of nickel and zinc. This was due to the partial irreversible reduction of these two elements. Copper had two waves corresponding to $Cu^{2+} \rightarrow Cu^{+}$ and $Cu^{+} \rightarrow Cu^{0}$. Thus an ammoniacal supporting electrolyte was far from being the best, and in this case was only suitable for the polarography of cadmium.

Figure 3 shows a polarogram for Cu, Cd, and Zn, in a supporting electrolyte 2 M in $(NH_4)_2SO_4$ and 1 M in H_3PO_4. Here the copper had only one wave, corresponding to a two electron process. The Cu and Cd waves were of similar height, and were well separated from each other. Zn hardly showed up with this supporting electrolyte.

The polarogram of Cu, Cd, and Zn, recorded with phosphoric acid as supporting electrolyte (Fig. 4), had well defined waves of all the components, which were reduced reversibly with two electrons involved. The separations between the peak potentials were sufficient for very high resolving powers. This supporting electrolyte satisfied all the criteria for optimum conditions.

LITERATURE CITED

1. S. B. Tsfasman, Electronic Polarography [in Russian] (Metallurgizdat, 1960); Zavodskaya Laboratoriya, 26(7), 888 (1960).
2. H. Matsuda, Z. Electrochem., 2, 9, 997 (1958).
3. P. Delahaye, New Instruments and Methods in Electrochemistry [Russian translation] (IL, 1957).
4. S. B. Tsfasman, Electronic Polarographs [in Russian] (Metallurgizdat, 1960).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. ***Some or all of this periodical literature may well be available in English translation.*** **A complete list of the cover-to-cover English translations appears at the back of this issue.**

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*The data are taken from experimental work by R. G. Pats and R. M. Salikhdzhanova.