# ALTERNATING-CURRENT METHODS OF POLAROGRAPHY

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In alternating-current polarography the polarizing voltage used consists of a direct-current voltage, which varies linearly and relatively slowly with time, together with an alternating-current voltage of low amplitude, which may be sinusoidal, square-wave [1], triangular [2], sawtooth [3], or trapezoidal in form.

The current through the cell consists of the alternating components of the electrochemical reaction current $i_{el}$ and of the capacity of the double layer current $i_c$.

The electrochemical reaction component of the current is normally used for analytical purposes. The capacity component is the main source of interference. Combined determination of these components prevents the advantage of a gain in sensitivity by use of the method. Various means of separating the components can be used to increase the sensitivity. The principle methods of separation are by compensation, by phase, and by time.

## Compensative Selection of the Signal

Various methods have been described [4-7] for compensative selection of the signal when the cell is polarized by an alternating-current voltage. The polarographic cell may constitute one arm of a bridge, while another arm consists of a capacitance $C_k$ in series with a resistance $R_k$, to compensate for the capacity C of the double layer and the ohmic resistance R of the cell. The resistance R includes the resistances of the capillary, the solution, and the auxiliary electrode circuit. The two other arms of the bridge consist of resistances $R_1$ and $R_2$. The condition for compensation of the capacity of the double layer can be expressed by the equation:

$$C = C_k \frac{R_1}{R_2}. \qquad (1)$$

The sensitivity of determination by this method is not better than $10^{-5}$ to $5 \cdot 10^{-6}$ M [7, 8]. This is because, at low concentrations, the ratio of the double-layer capacity current to the electrochemical reaction current is quite high.

Suppose that the concentration of a divalent reducible depolarizer, to be determined, is $C_0 = 5 \cdot 10^{-6}$ M; the diffusion coefficient $D = 10^{-5}$ cm$^2 \cdot$t$^{-1}$; the duplex amplitude and frequency respectively of the alternating voltage are $E_m = 5$ mV and $f = 100$ Hz ($\omega = 628$ rad/sec); the diameter of the mercury drop = 1 mm so that its surface area $A \approx 0.03$ cm$^2$.

The alternating component of the electrochemical reaction current corresponding to the half-wave voltage is given by the equation [9]:

$$i_{el} = \frac{n^2F^2}{4RT} AD^{1/2}\omega^{1/2}E_m C_0. \qquad (2)$$

Substituting the above values in this, we obtain $i_{el} = 0.23$ μA.

The double-layer capacity current is given by the equation: $i = \omega AC_d(U)E_m$, where $C_d(U)$ is the differential capacity. Suppose that $AC_d(U) = 0.5$ μF, then $i_c = 1.58$ μA.

Hence, the ratio $i_c/i_{el} = 6.9$. It is true that this fact in itself is not decisive, since almost complete compensation for the capacity of the double layer can be achieved if condition (1) is fulfilled. However, under practical conditions, it is significant that the capacity of the double layer does not remain constant, even during the polarography of a single element. Thus, over a potential range −0.6 to −0.8 V, with N $Na_2SO_4$ as supporting electro-

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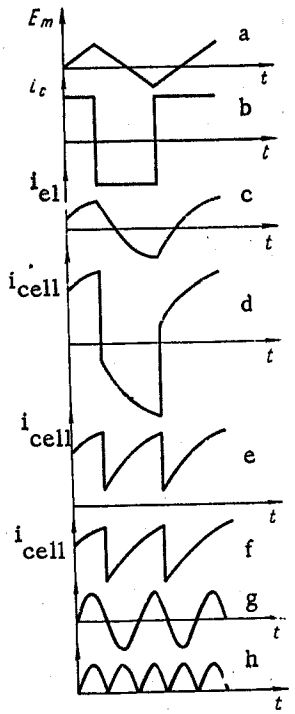


Fig. 1. Time diagrams of the currents through a polarographic cell when an alternating voltage of triangular form is applied: a) alternating voltage; b) alternating component of double-layer capacity current; c) alternating component of electrochemical reaction current; d) alternating component of cell current; e) cell current after rectification; f) cell current after filtration of constant component; g) second harmonic of cell current; h) cell current after secondary rectification.

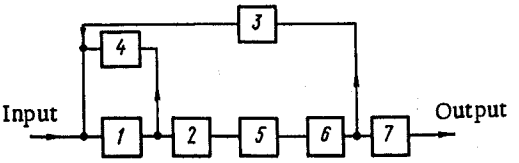


Fig. 2. Block diagram of amplifying transformer equipment as used in Barker's square-wave polarograph.

lyte, the differential capacity alters from 20 to 15 $\mu F/cm^2$ [10]. With the above parameters for the mercury drop, the capacity of the double layer varies in the range 0.626 to 0.47 $\mu F$. With N KCl as supporting electrolyte, and with the above range of potential, $C_d$ (U) varies from 19 to 17.5 $\mu F/cm^2$, i.e., C = 0.57 to 0.525 $\mu F$.

Thus, in the first case the change in the double-layer capacity current, for the given range of potential, amounts to 0.5 $\mu A$, while in the second case it is 0.14 $\mu A$. In the first case the change in the double-layer capacity current is more than twice the useful signal. Thus, the method proposed for compensating for the capacity of the double layer applies to one point only, and does not give much gain in sensitivity, as compared with classical polarography.

## Phase Selection of the Signal (Vector Polarography)

When a sinusoidal alternating-current voltage is used, the active component of the reaction current $i_a$ differs in phase by 90° from the total capacity component $i_c$, including the current associated with the capacity of the double-layer and with pseudocapacities. This can be used for separate measurements of the active and reactive components of the cell current by means of a phase-sensitive device, and provides a basis for increasing the sensitivity.

However, the conditions for separating these components are complicated considerably by the presence of large ohmic resistances in the cell circuit.

Consider the effect of an ohmic resistance R on the conditions for measuring the useful signal. In the case when there is no depolarizer present, the conductivity of the cell V is determined by the equation:

$$Y = \frac{R}{R^2 + 1/\omega^2 C^2} + j\,\frac{1}{(R^2 + 1/\omega^2 C^2)\,\omega C}. \qquad (3)$$

It is clear, from Eq. (3), that the cell current will contain active $i'_a$ and reactive $i'_c$ components:

$$i'_a = E_m \frac{R}{R^2 + 1/\omega^2 C^2}; \qquad i'_c = E_m \frac{1}{(R^2 + 1/\omega^2 C^2)\,\omega C}. \qquad (4)$$

On substituting, in accordance with the assumed conditions, we have:

$$i'_a = 5\cdot 10^{-3}\ \frac{100}{100^2 + (2\cdot 3.14\cdot 100\cdot 0.5\cdot 10^{-6})^{-2}} = 0.05\ \mu A. \qquad (5)$$

According to Eq. (2), at a depolarizer concentration of $10^{-7}$ M, the electrochemical reaction current amounts to 0.0046 $\mu A$. Comparison of this value with the current derived from Eq. (5) shows that the active component of the current, dependent on the ohmic resistance of the cell and the capacity of the double layer, is almost 11 times

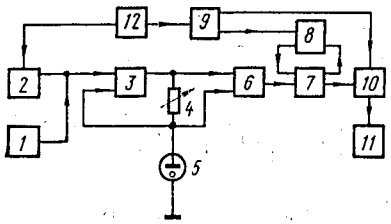


Fig. 3. Block diagram of alternating-current polarograph with trapezoidal form of alternating voltage.

the useful signal. Considering that the capacity of the double layer alters with a change in potential, we must expect distortion of the form of the polarogram, depending on how much the capacity of the double layer changes. This distortion will appear in the form of a slant to the background line, the steepness of which will depend on the ohmic resistance of the cell and the change in capacity of the double layer. Thus the slant in the background line, over the potential range −0.6 to −0.8 V, will be 0.034 μA in N $Na_2SO_4$ and 0.01 μA in N KCl.

With a vector polarograph, accordingly, depolarizers can be determined at concentrations of $10^{-7}$ and less when the cell has a low ohmic resistance.

## Polarography with Triangular and Sawtooth Forms of Alternating Voltage

Using the method of alternating-current polarography with a triangular form to the alternating voltage, we can also create conditions for the required elimination of the capacity current [2, 11]. When a triangular voltage is fed into the cell (Fig. 1a), the cell current shows an alternating component of the capacity current in the form of a series of pulses of opposite polarity (Fig. 1b), and an alternating component of the electrochemical reaction current in the form of distorted triangles (Fig. 1c).

The effect of the capacity current can be considerably reduced as the result of a series of operations: filtration of the constant component of the cell current, full-wave rectification of the signal, subsequent separation of the constant component of the current, separation of the second harmonic component of the signal, and secondary rectification. The signal may be amplified at the separate stages. As the result of these operations the alternating component of the capacity current can be largely eliminated, and realistic conditions can be created for isolation of the electrochemical reaction current (Fig. 1d to h) at a frequency of $2f_0$.

An apparatus of this type gave a sensitivity of $5 \cdot 10^{-6}$ M for cadmium in N KCl [2]. In the description of the block diagram of the apparatus [2], the authors omitted the operations of filtration of the constant component of the signal before the first rectification, and of the secondary rectification after amplification of the signal with a tuned amplifier. This gives an incorrect picture of the operation of the apparatus.

The sensitivity of the method could obviously be improved to that of modern alternating-current polarographs [11]. To avoid nonlinear distortions of the signal in the detection of the alternating component of the cell current, both primary and secondary rectifications should be achieved with synchronous detectors, and, after the primary rectification, a time cut-off and signal storage should be introduced. The cut-off prevents the passage of the cell current through the subsequent elements of the circuit from the instants corresponding to the extreme points of the triangular voltage. At these instants the capacity current gives large over-shoots, which lead to overloading of the electronic circuit of the instrument, and hence also to worse filtration.

There have also been proposals to use a sawtooth voltage as an alternating polarizing voltage [3]. However, owing to the large overshoots of the capacity current at the instants when the sawtooth voltage drops away, the parameters of the polarograph will be much less satisfactory than with the use of a triangular voltage.

With the above described operations the signal is isolated as follows: in the depolarizer concentration range for which $i_c \ll i_{el}$, the proportionality coefficient for the graph relating initial signal and depolarizer concentration differs from the proportionality coefficient for the concentration range where $i_c \gg i_{el}$. With $i_c < i_{el}$ there will be a nonlinear part to the graph. Accordingly, to ensure proportionality of the graph over the whole concentration range, it is necessary to select a frequency for the alternating voltage that satisfies the condition $i_c \geq i_{el}$.

## Polarography with a Square Wave or Trapezoidal-Shaped Alternating Voltage

The most sensitive methods employ square wave and trapezoidal voltages, combined with time selection of the signal. To avoid the capacity current, the alternating component is measured over a short time interval corresponding to the ends of the horizontal parts of the positive and negative half-waves. Here the capacity current dies away to a negligibly small value, while the reaction current has its final value. The sensitivity of a square-

wave polarograph ranges from $10^{-7}$ to $5 \cdot 10^{-8}$ M [12, 13]. The great sensitivity is largely associated with the use of amplifying transformer equipment. In all forms of alternating-current polarography, with amplification of the useful signal, it is necessary to suppress to a considerable extent (by a factor of a hundredth) both the constant component of the cell current and the component with the drop formation frequency. At first glance it would appear that this problem can easily be solved if, in order to amplify a voltage proportional to the total cell current, we use an alternating-current amplifier with frequency characteristics such that the cell current component with a frequency of 0 to 0.5 Hz is attenuated by a factor of 1/100 to 1/200, as compared with the current component at the working frequency, i.e., the frequency of the square-wave voltage. However, at the working frequency and its harmonics, an amplifier of this type shows such phase distortion, that it is only possible to isolate the useful signal at a concentration of $10^{-5}$M. Barker, in his square-wave polarograph, used the amplifying transformer equipment, shown in Fig. 2, to amplify the useful signal. Here a voltage, proportional to the total cell current, is amplified without phase distortion by the direct-current amplifier 1.

The pulses of double-layer capacity current, after preliminary amplification by the direct-current amplifier, are blocked by the control diode 2. Attenuation of the constant component and of the component at the drop-formation frequency is achieved by means of an integrating amplifier 3, included in the negative feed-back circuit of the equipment.

The amplifying transformer equipment of the Barker square-wave polarograph also contains a diode stripper 4 for duplex clipping of the capacity current pulses, a storage unit 5, an additional direct-current amplifier 6, and a final alternating-current amplifier 7. The phase distortion, introduced by the final amplifier, does not affect the operation of the equipment nor of the polarograph as a whole, since the signal reaching this amplifier is free from capacity current pulses. The equipment suppresses those components of the cell current with frequencies between zero and that of drop formation by a factor of better than 1/100, but amplifies the alternating component of the useful signal at the operating frequency without phase distortion, thus giving an effective separation of the electrochemical reaction current from the double-layer capacity current.

Also of interest is the polarographic method of analysis with use of a trapezoidal alternating voltage. This provides the same analytical possibilities as the square wave [14], but the instrument is simpler, since the ratio of the amplitudes of the capacity current pulses and of the alternating components of the electrochemical reaction current is considerably less than with a square-wave polarograph. This makes it possible to use a simpler amplifier, with control of the amplification coefficient, to amplify the useful signal.

In the square-wave polarograph the amplitude of the capacity current pulses $I_{c_1}$ is given by

$$I_{c_1} = E_m/R; \tag{6}$$

while with a trapezoidal voltage it is

$$I_{c_2} = Cv, \tag{7}$$

where v is the rate of change of the trapezoidal voltage.

The rate of change of the trapezoidal voltage is equal to the ratio of the duplex amplitude of this voltage to the time of build up or decay of this voltage. The time of buildup (or decay) of the trapezoidal voltage is conveniently adjusted to be 1/4 of the frequency period of the voltage. We can therefore write

$$v = E_m/(T/4) = 4E_m f, \tag{8}$$

where T is the frequency period of the trapezoidal voltage.

Substituting (8) in (7), we obtain

$$I_{c_2} = 4CE_m f. \tag{9}$$

Dividing (6) by (9) we obtain the ratio of the amplitudes of the capacity current pulses in square-wave and trapezoidal polarography:

$$I_{c_1}/I_{c_2} = 1/4RCf. \tag{10}$$

Putting in the appropriate data, we obtain $I_{C_1}/I_{C_2} = 50$.

Thus, using appropriate data for R, C, and $f$, the amplitude of the capacity current pulses with a trapezoidal voltage is only 1/50 of that with a square-wave voltage. This means that the apparatus can be simplified.

Instead of using a pure trapezoidal voltage as the alternating-current component of the polarizing voltage, we may use one which is similar in form, obtained by duplex clipping of sinusoidal or exponential pulses.

The form of the capacity current pulses is then different from what it is in the case of pure trapezoidal pulses. However, there is no significant change in the form of the electrochemical reaction current pulses.

Our method has been put into practice in the PPT-1 alternating-current polarograph, developed by the All-Union Scientific-Research Institute for the Automation of Ferrous Metallurgy, and produced by the Gomel'sk Plant for Measuring Instruments. Figure 3 shows a block diagram of this alternating-current polarograph, with a trapezoidal form of applied alternating voltage.

The total polarizing voltage consists of a slowly alternating voltage, provided by the voltage source 1, and of an alternating voltage trapezoidal in form from the source of trapezoidal voltage 2. This acts through the direct-current amplifier 3, which fulfills the role of a potentiostat and the measuring resistance 4 to the cell 5.

Passage of the alternating component of the cell current through the measuring resistance 5 creates in the latter a fall in voltage. The voltage is then increased, starting with the alternating-current preamplifier 6 with phase correction, and then by the control amplifier 7.

The amplifier is provided with negative feed back through the control valve 8. In the absence of a control pulse the valve is open, and the feed-back circuit of the amplifier 9 is closed; the transmission coefficient of this amplifier is close to unity. Under the influence of a control pulse, when the capacity current becomes a minimum, the valve closes, the feed-back circuit opens, and the transmission coefficient of the amplifier becomes close to 50. In this way the capacity current pulses pass through the amplification channel with the transmission coefficient of the control amplifier equal to unity, but the pulses of electrochemical reaction current pass with a transmission coefficient equal to 50. The signal then passes to the phase detector 10 and the recorder 11. Control pulses are fed in for normal operation of the phase detector with the pulse shaper 9.

The master oscillator 12 generates a sinusoidal voltage at the working frequency, which is fed into the source of trapezoidal voltage to shape the trapezoidal voltage, and into the pulse shaper to form control pulses.

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