

THE PHASE METHOD OF POLAROGRAPHY *

G. V. Tuev and L. S. Zaretskii

The North Kazakh Branch of the Design Office of "Tsvetmetavtomatika"
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Measurement of the phase angle between the total current through the cell and the capacity current is suggested as a means of suppressing the effect of instability of the electrode surface in a polarographic concentration meter. The method can be used for automatic control of the cadmium content of zinc electrolytes.

In recent years polarographic methods have provided a basis for instruments for the automatic control of the composition of industrial solutions. The prospects in this direction are for alternating current polarography [1].

In alternating-current polarography, a direct current polarizing potential, equal to the half-wave potential of the component to be analyzed, is applied to the cell electrodes and is accompanied by a sinusoidal voltage of low amplitude. In addition to a constant current and a current with the period of drop formation, there passes through the cell an alternating current with a frequency the same as that of the alternating potential [2]. This alternating current is made up of two components:

$$i_e = I_e \sin\left(\omega t + \frac{\pi}{4}\right)$$

and

$$i_c = I_c \sin\left(\omega t + \frac{\pi}{2}\right).$$

The component i_e is determined by the electrochemical reactions occurring at the cell electrodes, and the component i_c is determined by the capacity of the double layer. We can isolate the active electrolytic current i_a by eliminating the capacity current i_c , which contains no useful information [3].

The amplitude of the active component of the electrolytic current, after amplification, is given by the equation:

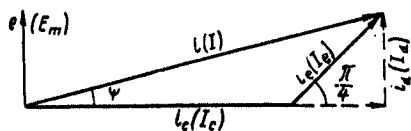
$$I_a = KAD^{1/2}\omega^{1/2}E_mC^0.$$

Here, A is the surface of the polarized electrode of the cell; D is the diffusion coefficient; ω is the frequency of the applied voltage; E_m is the amplitude of the applied voltage; C^0 is the concentration of the component to be analyzed; K is a constant, including universal constants and the amplification coefficient of the amplifier used in measuring I_a .

The electrode surface A , the amplitude of the applied alternating voltage E_m , and the amplification coefficient of the amplifier may all vary with time, so that it is necessary to calibrate the instrument before each measurement. Under laboratory conditions, the calibration can easily be adjusted by altering the amplification coefficient.

When using the same instrument as an automatic concentration meter there is inevitably trouble with calibration instability, which markedly reduces the field of application of the instrument. In fact, the electrode surface can change over wide limits as the result of blockage by salts of the orifice from which the mercury emerges, and because of changes in the concentrations of surface active materials which can alter the surface tension of mercury. The frequency and amplitude of the applied voltage may also alter with time. Ageing of tubes and components can give rise to changes in the amplification coefficient of the amplifier. All these factors produce changes in the

* Author's Certificate No. 775877/24-3, *Byulleten' izobretenii i tovarnykh znakov*, 4 (1962).



Vector diagram of currents through polarographic cell.

Consider a vector diagram of the current through the cell (see figure). The capacity current i_c leads the applied voltage \underline{e} by $\pi/2$, and the electrolytic current i_e leads the applied voltage by $\pi/4$ (for reversible reactions). The angle ψ between the full alternating current \underline{i} through the cell and its capacitive component i_c is given by:

$$\tan \psi = \frac{I_e \cos \frac{\pi}{4}}{I_c + I_e \cos \frac{\pi}{4}}$$

where the capital letters denote the amplitudes of the corresponding currents.

Then

$$I_e = \frac{n^2 F^2}{4RT} AD^{1/2} \omega^{1/2} E_m C^0,$$

so that

$$\operatorname{tg} \psi = \frac{\frac{n^2 F^2}{4RT} AD^{1/2} \omega^{1/2} E_m C^0 \cdot \cos \frac{\pi}{4}}{\omega A C_D(u) E_m + \frac{n^2 F^2}{4RT} AD^{1/2} \omega^{1/2} E_m C^0 \cos \frac{\pi}{4}}$$

Putting in the values of the universal constants and rearranging, we have:

$$\operatorname{tg} \psi = \frac{1}{\frac{\omega^{1/2} C_D(u)}{685 \cdot 10^6 n^2 D^{1/2} C^0} + 1}$$

Let

$$\frac{\omega^{1/2} C_D(u)}{685 \cdot 10^6 n^2 D^{1/2}} = S. \quad (1)$$

Then

$$\operatorname{tg} \psi = \frac{1}{\frac{S}{C^0} + 1}$$

We may introduce the approximation that, at low enough concentrations, $S/C^0 \gg 1$ and $\tan \psi \approx \psi$.

Then

$$\psi = C^0/S. \quad (2)$$

It follows from Eqs. (1) and (2) that the phase difference between the overall current through the cell and its capacitive component varies linearly with the concentration at low concentrations; it is independent of the electrode surface and the applied alternating voltage. The method of measuring phase difference also eliminates the influence of instability of the amplifier.

An automatic cadmium concentration meter (the APK-475), based on the above phase method of polarographic analysis, has been developed by the North Kazakh Branch of the Design Office of TsMA. Two of these instruments

have been introduced at the "Élektrotsink" and "Ukrtsink" plants and used successfully for automatic control of the cadmium content of zinc electrolytes, after purification from copper and cadmium.

LITERATURE CITED

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2. S. B. Tsfasman, *Zavodskaya Laboratoriya*, 26, 9 (1960).
3. S. B. Tsfasman, *Electronic Polarography* [in Russian] (Metallurgizdat, 1960), p. 29.
4. P. Delahaye, *New Instruments and Methods in Electrochemistry* [Russian translation] (IL, 1957), p. 192.

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.*