NEW METHODS OF POLAROGRAPHY
(REVIEW)

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Translated from Zaovdskaya Laboratoriya, Vol. 28, No. 9,
pp. 1029-1036, September, 1962

The polarographic method, developed 40 years ago by J. Heyrovsky, rightly occupies an important place both in analytical chemistry and in physicochemical investigations – the study of composition, structure, and stability of complex particles in solutions, the structure of organic substances, the kinetics of chemical and electrochemical reactions, adsorption, and catalytic phenomena.

In the present article we review new methods of classical, alternating current, and oscillographic polarography for the solution of analytical problems.

Classical Polarography

The use of electrodes other than mercury, and the use of nonaqueous solutions, make it possible to extend the range of working potentials from +2.4 to −3.5 V, and hence to extend the range of materials which can be determined polarographically. For work in the range of anode potentials, an interesting technique is the replacement of noble metal electrodes by borocarbide, graphite, and other [1-4] electrodes; they are sufficiently stable electrochemically and they do not corrode to any great extent. The carbon-drop electrode [5] can be used to concentrate the products of electrolysis of organic substances with subsequent anodic oxidation.

The tendency to increase the accuracy in measuring $E_{\frac{1}{2}}$, especially when working with nonaqueous or mixed solvents, has led to the development of methods for the automatic compensation of the voltage drop in the cell circuit and the automatic correction of the polarograms [6-11]. A three-electrode system makes it possible to measure $E_{\frac{1}{2}}$ of clearly defined waves with errors not exceeding 1 mV.

Wolf [12, 13] recently suggested a new method – rapid polarography. The drop period is considerably reduced by the forced shaking of the drops, and the rate of change in the polarizing voltage is considerably increased, so that the whole polarogram is taken in one minute.

The forced reduction of the drop period proposed by Tereshchenko [14], Skobets and Kavetskii [15], has been successful [16]; unfortunately, it has not been applied extensively or developed further. Rapid polarography, apart from reducing the time for the operation, has a number of good features. The reduction in the drop period ($t \approx 0.2$ sec) leads to a considerable reduction in the oscillations which always introduce difficulties when processing the polarograms. The suppression of oscillations by damping distorts the polarogram and changes $E_{\frac{1}{2}}$. Wolf's data show that to obtain the usual polarogram of Pb^{2+} ions in 1 M KCl with small oscillations, strong damping is needed (the time constant $\tau = 4.8$ sec). In this case, the use of a rising and falling polarization voltage gives half-wave potentials of −0.490 and −0.458 V, respectively (i.e., $\Delta E_{\frac{1}{2}} = 32$ mV). Very slight damping is needed to obtain these oscillations in the rapid method ($\tau = 0.08$ sec); the noncoincidence of polarograms obtained with a rising and falling polarization voltage is much less in this case ($\Delta E_{\frac{1}{2}} = 8$ mV).

The reduction in oscillations also facilitates better separation of waves with similar half-wave potentials. In addition, the rapid falling of the drop (with the usual rates of mercury flow) provides more favorable hydrodynamic conditions near the mercury drop and the transfer of the concentration polarization from drop to drop (the depletion effect) becomes less likely.

In the latest types of electronic polarographs produced by Metrohm AG, Herisau (Switzerland), Polarecord E261 [17], there is a device for the forced shaking of the mercury drops (from 1 to 6 drops per sec) with control of the force of the impact and provision is made for increasing the rate of change in the polarization voltage for rapid operation.

The possibility of rapid recording of polarograms has also been described by Kalvoda and Smoler [18].

Elbel [19] has recently developed a method of pulse polarography. In this method the natural drop formation is not limited, the polarizing voltage is continually applied to the electrolytic cell; however, the recording of the current and the displacement of the voltage at the cell, proportional to the time, occur in a short interval just before the mercury drop breaks away. This method of recording the polarogram has definite advantages, although we still need more information on it. In pulse polarography it is not only that the recorded current is larger, but there is also a considerable reduction in the capacity current caused by an increase in the surface of the drop with time. The signal-to-noise ratio will be better if the current is measured nearer to the end of the drop period in a short interval of time. The reduction in the oscillations and capacity component of the current makes it possible to increase the resolving capacity and sensitivity of the method (for example, to observe two waves on the polarogram of a solution $2 \cdot 10^{-4}$ M Tl^{+} + 10^{-5} M Cd^{2+} in 1 M KCl), and also to increase the maximum permissible concentration of the more electropositive component.

There is a method for recording polarograms in an excess of the more easily reduced components [20]. The current is measured alternately at potentials up to the formation of a wave and after – synchronously, at certain moments of life of the mercury drops. The recorded difference in currents will be proportional to the concentration of the depolarizer which is being determined, regardless of the presence of more easily reduced substances.

Alternating Current Polarography*

The principal and analytical possibilities of alternating current polarography are covered in some detail in the literature [21-23]. We would like to discuss certain recent work aimed at increasing the sensitivity of the alternating current methods.

It is a well-known fact that alternating current polarography is only superior to classical polarography in the resolving capacity – independent determinations can be made of substances with $\Delta E_{\frac{1}{2}} \geq 40$ mV with a concentration ratio of 1 : 1000. The interference caused by the passage of a capacitance current prevents the sensitivity being increased. The large value of the capacitance component of the current in the cell circuit, and its dependence on the presence of surface-active substances, is used in the tensometric method for determining electrolytically inactive substances which have surface-active properties [24, 25].

Barker [27] developed a method using a square voltage; his instrument, called the square-wave polarograph, had superior analytical qualities [28]. However, the difficulties introduced by the equipment in the case of a square voltage have made it necessary to seek other possibilities to avoid the interfering influence of a capacitance current.

A method has been described [29] for compensating the capacitance current by using a special attachment to the Breyer alternating current polarograph. The attachment includes capacitances and resistances, and it can compensate the capacitance current. This method was used to determine traces of cadmium and lead (10^{-3}%) in indium, which had been subjected to zone purification; according to the authors, this method was able to give complete compensation of the capacitance current [30]. A phase method [21, 26, 31-33] has been suggested for separating the capacitance current from the Faraday current, using the phase shift of the Faraday current with respect to the supply voltage by an angle from 0 to 45° and the phase of the capacitance current by an angle of 90° (with zero resistance of the cell circuit).

The Tsfasman vector-polarograph [31] is based on the phase method of separating the capacitance current; it records the dependence of a vector of the active component of the cell current on the polarizing voltage. The determination of Cd^{2+} ions in pure solutions and in the presence of a 1500-fold excess of Cu^{2+} ions gave good results (as low as 10^{-7} M) with fairly simple apparatus.

Smith and Reinmuth [33] used a stationary mercury electrode in the alternating current method with phase separation of the capacitance current; they obtained a well-defined polarogram of a 0.1 M HCl solution containing 10^{-8} mole/liter of Cd^{2+} ions. The reproducibility was 1%. The authors feel that the sensitivity of the method can be increased.

The two-frequency method of separating the capacitance current [26] was more complex, but it permitted higher resistances in the cell circuit without a serious deterioration in the quality of the separation. The use of

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*This type of polarography is discussed in greater detail in this issue of the journal by V. I. Bodyu, I. V. Kozlova, and Yu. S. Lyalikov.

a compensator [31, 34] to eliminate the effect of the voltage drop in the cell circuit on the peak value of the current and on the phase shift makes it possible to study solutions with a high resistance.

Bauer [35] described a method using the higher harmonics to increase the sensitivity and resolving capacity (at an amplitude of 15 mV and a frequency of 130 Hz). This avoids interference caused by the presence of a double electrical layer.

The square-wave polarograph has certain limitations (low sensitivity when determining irreversibly reducible depolarizers, the sensitivity cannot be increased further because of capillary interference, and the necessity for using comparatively concentrated supporting electrolytes [28]); Barker [36, 37] therefore developed a method of pulse polarography. At a certain moment in the life of the drop the polarizing pulse changes the potential of the mercury drop electrode in 40 msec to a value which becomes more and more negative.

The resulting pulse polarogram is similar in form to the usual type. The differential method is more sensitive and has a greater resolving capacity; in this method the polarograms have a maximum.

By prolonging the interval of polarization time it is possible to eliminate the influence of capillary interference; this interference decays rapidly with time, and solutions with a higher resistance can be used. In favorable cases, reversibly reducible depolarizers can be determined at concentrations as low as 10^{-8} M, and irreversibly reducible depolarizers can be determined at concentrations as low as 10^{-7} M. More careful removal of the oxygen from the solution is needed before the polarogram is taken. The pulse polarograph is a 60-tube electronic device and is as complex as the square-wave polarograph in operation.

At the International Congress on Polarography, Barker [37] reported on a new high-sensitivity method – radiofrequency polarography. A high-frequency voltage is applied to the cell (from 100 kHz to 6 MHz) and the voltage amplitude is modulated by a square voltage of 225 Hz; a constant voltage is also applied. The square-wave polarograph measures the amplitude of the low-frequency current. The radiofrequency polarographic method can be used to determine reversibly reducible divalent ions at concentrations as low as 10^{-8} M with good reproducibility and irreversibly reducible ions at concentrations as low as 10^{-7} M. According to the authors, the sensitivity can be considerably increased by using electrodes with a large surface, and by improving the electronic circuit.

Oscillographic Polarography

The Heyrovsky and Forejt oscillographic polarographic method using an alternating current has been described in detail in the literature [38, 39]. Here we will examine recent work on the improvement of oscillographic polarography of the $i - E$ curves.

The oscillographic polarography method has high sensitivity and resolving capacity; the polarograms can be recorded rapidly and easily. Good quality instruments are described in the literature and are being produced [21, 40-42]. These instruments are used to determine niobium in steels [43], impurities in germanium [44] and molybdenum [45], uranium in ores [46], nitroglycerine [47], for the analysis of explosives [48], etc. [49-51].

However, in oscillographic polarography, the main interference tending to prevent the sensitivity being increased is the capacitance current, the value of which is proportional to the rate of change in potential. Randles [52] reduced the rate of change in potential, and hence its fraction in the total current of the cell circuit. The use of lower rates of change in potential is limited by the drop period. Randles ensured linearity in the change in potential of the microelectrode by compensating the voltage drop in the cell circuit. This method of increasing the sensitivity of oscillographic polarography has been realized in a number of later investigations [21, 40-42]. For example, Randles [51] uses a mercury drop electrode with a 7-sec period. In the last 2 sec of life of the drop a linear voltage pulse is applied to it and the rate of change in potential (at an amplitude of 0.5 V) is 0.25 V per sec. At higher rates there is more distortion of the oscillographic polarogram by the capacitance current and the actual sensitivity is reduced. When describing the experimental apparatus it would therefore be better to indicate the real sensitivity, which is limited by the interference, rather than the sensitivity of the instrument with respect to the current. The real sensitivity of oscillographic polarographs [21, 40-42, 51], in which the same measures are taken to eliminate the capacitance current and to preserve linearity of the voltage on the cell, should be of the same order.

In 1952, Nigmatullin proposed a different method for increasing the sensitivity of oscillographic polarography.*

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*Reported at a conference of the Kazan State University in 1952.

He used the electrolytic oxidation of certain anions on a platinum electrode to study the practical use of the difference method of oscillographic polarography.

In the difference method of oscillographic polarography the oscillograph screen records a curve of the relationship between the difference in current densities in the two cells and the potential of the microelectrodes. The second cell subtracts the capacitance current or other interfering currents, and does not contain the substance which is being determined. A titration method can be used for quantitative determinations; the substance to be determined is added to the solution of the second cell and the equivalence point is noted from the disappearance of its peak on the oscillograph screen [53].

The difference method was studied theoretically and experimentally by Pozdeev [53, 54], and used to determine small concentrations of ions of certain metals [55].

In his experimental apparatus, Pozdeev [54] used a voltage drop compensator in the circuits of the cells; this ensured good quality of subtraction for high currents in the cell circuits. Synchronization of drop formation and, consequently, reproducibility of the oscillograms, was ensured by periodically shaking the mercury drops with an electromagnetic relay after the end of each sawtooth pulse. The difference in size of the mercury drops (since the capillaries were different) at the moment of application of a sawtooth pulse was compensated by using appropriate current-measuring resistances in the cell circuits. The apparatus also had a three-electrode system. The comparison electrode, which did not carry a current, was a calomel electrode and the polarograms were recorded relative to this electrode. As well as the $(i_1 - i_2) - E$ curves, the derivative curves $(di/dE) - E$ were also recorded, the theory of which was recently published [55]. With this instrument Pozdeev [54] achieved a sensitivity of $3 \cdot 10^{-7}$ mole/liter for Cd^{2+} and Zn^{2+} ions, which is evidently by no means a limiting value.

The difference method and the simpler but less developed experimental apparatus [56] were used to determine small concentrations of Cd^{2+}, Pb^{2+}, and Zn^{2+} ions in a 400- to 3600-fold excess of the more electropositive ions [57], to determine the ions Bi^{3+}, Sb^{3+}, and Cu^{2+}, impurities of the order of 10^{-5}% in sulfur and selenium [59] They were also used to study the effect of oxygen on the electrolytic reduction of Pb^{2+} ions [60] and, in combination with the method of electrolytic accumulation on stationary [58, 61] and rotating [62] mercury electrodes, to determine microconcentrations.

Davis and Seaborn also developed a difference method of oscillographic polarography [63]. They used two identical mercury drop electrodes, a measure which is unnecessary and considerably complicates the work.

Differential Polarography

The method of differential oscillographic polarography, based on the interpretation of $(di/dE) - E$ curves, has high resolving capacity. The signal-to-noise ratio in differential oscillographic polarography is higher, other conditions being equal, than in oscillographic polarography [54]. To a small extent, the amplitude of the differential curve measured between the maximum and minimum points, lying at similar potentials, experiences the effect of the derivative of the capacitance current with respect to potential and is a convenient analytical characteristic. Differential oscillographic polarography is therefore more sensitive than oscillographic polarography.

Using the example of Cd^{2+} and Zn^{2+} ions, Pozdeev [54] showed that the amplitude of the differential curve is proportional to the ion concentration down to $4 \cdot 10^{-6}$ moles/liter. The presence of dissolved oxygen and Cu^{2+} ions does not hinder the determination. A special point on the differential curve is the point with an ordinate $di/dE = 0$, the abscissa E_1 of which, according to Pozdeev [54], is equal to

$$E_1 = E_p + (\Delta v/2),$$

where E_p is the potential of the peak of the oscillographic polarogram, and Δv is the difference in potentials of the two microelectrodes. The point E_1 (and, consequently, the quantities E_p and $E_{\frac{1}{2}}$) on the differential polarogram can be determined with errors of not more than 1 mV.

Discussing ways for developing alternating current and oscillographic polarography, Barker [64] mentioned the following methods for separating Faraday and non-Faraday currents:

1. A difference method of oscillographic polarography using two synchronized mercury drop electrodes and two electrolytic cells, one of which contains an "empty" solution.

2. The application of a sine voltage of low frequency and amplitude to linear scanning. During the scanning the rate of change in the voltage falls to zero once in each cycle of alternating voltage. If the time constant

for the charging of the double electrical layer is low, then the capacitance current will also decrease to zero once in each cycle. The change in the Faraday current during the scanning can be followed from the change in the minimum value of current in each cycle.

3. The use of stepwise voltage scanning. If the time constant for the charging of the double electrical layer is small, then the change in the minimum value of the cell current, with time between two nearest voltage increments of scanning, can be identified with the change in the Faraday current. According to Barker, this method can give almost complete separation of the electrolytic and capacitance currents.

Certain difficulties arise in the analysis of more complex mixtures by the method of oscillographic polarography due to the asymmetric form of the oscillographic polarograms. Barker [64] therefore suggested changing their form by using appropriate shaping circuits. The waves obtained as a result of this transformation are similar in form to an ordinary polarographic wave or its first derivative.

Method of Amalgam Polarography with Preliminary Accumulation

The method of amalgam polarography with preliminary accumulation on a stationary mercury drop occupies a special place among the polarographic methods; this method was dealt with in a recent review [65]. We do not intend to discuss here the problems connected with features of the method and the design of stationary mercury electrodes; we would, however, like to consider the possibilities of polarographic methods in the determination of currents in the electrolytic oxidation of amalgams.

In cases where large samples can be used, the sensitivity of the method is no longer of prime importance, because the concentration of the amalgam (or current of electrolytic oxidation) can be increased by increasing the time of accumulation.

In cases where larger samples cannot be used, a high-sensitivity method should be used to determine the amalgam concentration. The resolving capacity of the method is very important in these and in the previous cases, since the high resolving capacity makes it possible to lower the requirements with regard to purity of the reagents. According to the author, the usual polarographic method gives fairly good results in solving the first group of problems. In solving the second group of problems, the difference method of oscillographic polarography is the most promising, both with regard to its sensitivity and its resolving capacity.

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