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INVESTIGATIONS INTO SQUARE-WAVE POLAROGRAPHY. GENERAL REGULARITIES OF THE METHOD

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We have studied the general regularities of square-wave polarography: the dependence of the peaks on the pressure of the mercury column and the properties of the capillary, the possibilities of interpreting the polarograms, the character of the calibration curves, and the special features in the use of the method of additions.

Square-wave polarography is the most sensitive method for the direct polarographic determination of reversibly reduced depolarizers [1]. Before proceeding with the development of methods for determining traces of metals in products of the rare metals industry, we first studied factors affecting the sensitivity of the method. We used the Mervin-Harwell square-wave polarograph (model 3).

Dependence of the Peaks on the Pressure of the Mercury Column and the Properties of the Capillary

It follows from the theory of square-wave polarography [2] that at each moment the variable component of the current is proportional to the surface of the mercury drop electrode. It would seem that the simplest way of increasing the sensitivity of the method is to increase the dimensions of the drop at the instant when the current is measured. However, in parallel with the increase in the useful electrolytic current there is an increase in the interfering capacitance current. In ordinary polarography the ratio of these currents is independent of the drop surface and the increase in its dimensions has practically no effect on the effective sensitivity of the analysis, making it possible to use less refined measuring instruments. In square-wave polarography the interfering capacitance current is cut off [3]. The ratio of the capacitance and electrolytic currents is also independent of the drop surface; however, the efficiency of the capacitance current cutoff and, consequently, the ratio of the capacitance and electrolytic currents in the measured value of the alternating component of the current depends on the drop surface. The less the time constant of the electrolyzer circuit, the more effective the cutoff. In square-wave polarography the increase in the drop surface therefore leads to a reduction in the signal-to-noise ratio and, consequently, to a reduction in the effective sensitivity of the analysis. There is a certain optimum of surface, which depends on the cutoff period of the capacitance current, the amplification factor of the instrument, and other factors.

To find the optimum dimensions of the drop we studied the dependence of the peaks on the internal diameter of the capillary and on the drop period, i.e., on the effective pressure of the mercury column.

A square-wave polarograph can be used to take gated and ungated polarograms. In the first case, the automatic recorder records the alternating component of the current in the electrolyzer circuit two seconds after the previous mercury drop has broken away. By means of a "memory" capacitor the current corresponding to this moment of life of the drop is recorded by the automatic recorder of the instrument in the form of a horizontal line up to the period of life of the next mercury drop. The ungated polarogram is obtained by continuous recording of the current.

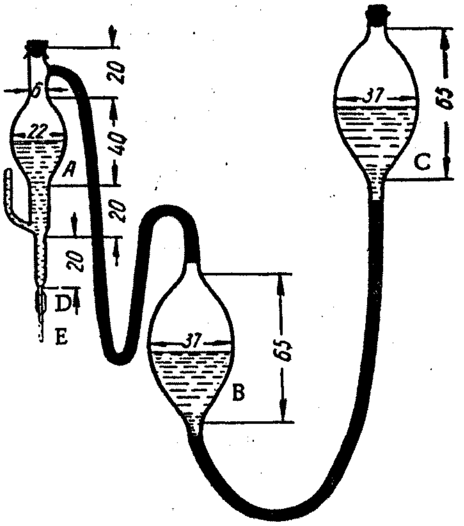

Fig. 1. Capillary apparatus. A) Reservoir with pure mercury and soldered platinum contact; E) thermometric capillary; D) polythene connecting tube; B) and C) bulbs to provide pressure.

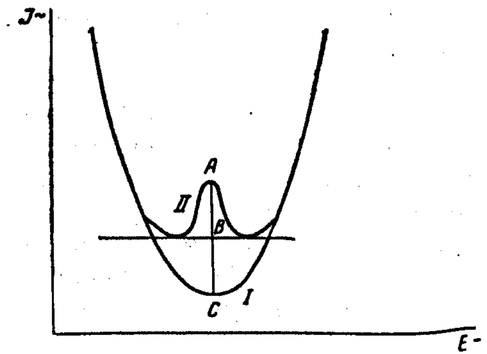

Fig. 2. Error in the graphic interpretation of polarograms (schematic representation); the lower curve is the polarogram of a solution containing the element to be determined; AC is the true height of the peak; AB is the graphic height of the peak.

Increasing the drop frequency by increasing the mercury level should lead to a proportional increase in the volume of the drop at the start of the measuring period. The surface of the drop is proportional to its volume to the power $^2/_3$ and, consequently, the height of the peak on the gated polarogram should change in proportion to the drop frequency to the same power with change in the effective mercury pressure.

We proved this relationship; in the polarography of an ammonia solution of cadmium chloride of a certain concentration with the same capillary we obtained a peak of height 40 mm with a drop period of 2.7 sec and 32 mm at 3.7 sec. The ratio of both heights is 1.25, and the inverse ratio of the corresponding periods to the power $^2/_3$ is 1.24.

With increase in the drop period we frequently observed an increase in the height of the peak on the ungated polarogram. This may be due to the inertia of the amplification and measuring system of the polarograph.

On comparing the square-polarographic peaks obtained with various calibrated thermometric capillaries (with openings from 0.04 to 0.1 mm), we found that an increase of more than 0.07 mm in the internal diameter of the capillary led, in most cases, to a reduction in the effective sensitivity of the determination. There was then a sharp increase in the fraction of the capacitance current in the measured value of the alternating component of the current and the large slope of the capacitance current curve masked the peaks of the elements being determined on the polarograms. An increase in the clearance of the capillary from 0.04 to 0.07 mm doubled the heights of the peaks.

There are indications [4] that the maximum sensitivity of a square-polarographic determination is achieved without using a gating mechanism. This is evidently a reference to the possibility of obtaining currents corresponding to large drop surfaces. We found that the use of ungated polarograms is sensible when the peak is near the electrocapillary maximum. In other cases the large oscillations on the polarographic curve hinder the interpretation of the polarograms. The maximum sensitivities in the determination should therefore be obtained by using gated polarograms with an internal capillary diameter of 0.07 mm and drop period of 2.9-3.0 sec.

The slope of the capacitance current curve on the polarograms also depends on the state of the internal capillary surface. High capacitance currents are observed during operation of the capillary; this can be shown by an appropriate measurement of the capacity of the drop at the instant when it breaks away. This may be due to the gradual contamination of the internal surface of the capillary. In some cases the quality of the capillary could be restored by washing it with nitric acid, but usually the capillary had to be shortened to some extent, or it had to be replaced.

Figure 1 shows the capillary apparatus; it needs little adjustment and the thermometric capillary can readily be replaced.

The change in the properties of the capillary is accelerated when very negative or very positive voltages are applied briefly to the electrode, and also when fine drops of mercury are frequently broken off. When the solution was to be blown with nitrogen, the electrode was arranged so that the gas bubbles did not break off the

TABLE 1. Graphic Interpretation of Tungsten Peaks in 6 N HCl

Comp. of solution μg/ml			Slope of tungsten peak, mm	Graphic height of peak, mm	
W	Cd	Pb		first method	second method
0.4	0	0	8	35	42
0.4	0.1	0	16	31	44
0.4	0.2	0	24	26	46
0.4	0.4	0	26	20	44
0.4	0.8	0	43	14	54
0.8	1.6	0	55	23	77
0.8	1.6	2.0	49	8	54

TABLE 2. Graphic Heights of Peaks of Cadmium in a 1 M Solution of Ammonia and Ammonium Chloride in the Presence of 0.001% Gelatine and 2% Na_2SO_3

Conc. of Cd, μg/ml	Hgt. of peak in absence of Cu, mm	Hgt. of peak in presence of 4 μg/ml Cu, mm
0.02	16	33
0.04	58	65
0.08	90	99

TABLE 3. Data for the Combination of the Method of Additions and the Method of Variation of Weights

No. of peaks	Weight, g	Addition, μg	Hgt. of peak after correct. for vol., mm
1	1	0	5
2	1	0.1	10
3	1	0.2	17
4	1	0.3	24
5	1	0.4	31
6	2	0	11
7	2	0.1	18
8	2	0.2	25

mercury drops too soon. The capillaries, hydrophobized with methyltrichlorosilane, also changed their properties with time.

When the electrolyzer circuit was broken at the instant when the drop broke away, a high-quality polarograph timer was switched on; this timer controlled the gating mechanism. A neon indicating lamp then lit up. Sometimes the capillary caused double flashes of the indicating lamp, which was accompanied by irregularities on the polarograms. These phenomena were observed with thermometric capillaries fused onto the capillary apparatus. The breaking away of the drop evidently led to a brief breaking of the mercury thread at the point where the capillary was fused. In some cases, the double flashes were caused by contamination of the end of the capillary and could be eliminated by washing it with nitric acid. Capillaries with a diameter of 0.04 mm gave double flashes more frequently than those with a diameter of 0.07 mm.

Interpretation of Polarograms

The determination of the peak height at a comparatively high concentration of the element to be determined, and in the absence of interfering substances usually presents no difficulties, since both branches of the peak change to lines lying on one horizontal of the straight line or on one straight line with a very small slope to the horizontal. It is much more difficult to establish the height of the peak in a solution with a low concentration of the element to be determined. In the blank solution the inclined section of the residual current curve corresponds to the section of potentials on which the peak of this element was situated. The slope is least at the potential of the electrocapillary maximum, and gradually increases on transition to more positive or more negative potentials. The slope depends on the presence of traces of surface-active substances and oxygen in the solution.

The most accurate way of determining the height of the peak is to determine the difference in currents in the working and blank solutions at the potential of the peak. This principle is used in an automatic concentration measurer with recording of the current at the recorded potential of the peak [5]. The accuracy of such an "absolute" method depends on the reproducibility of the polarographic curve of the blank solution and on the accuracy in setting the potential (especially in those cases where the peak of the element to be determined is masked or is displaced). Fluctuations in the oxygen concentration and traces of surface-active substances, and also other factors, practically exclude the possibility of absolute interpreting when using the maximum sensitivity of the square-wave polarograph.

The simplest method is the graphic interpretation of polarograms based on the rectification of the residual current curve by joining both branches of the peak at the base of the common tangent [6]. In the future we will refer to the distance along the vertical between the apex of the peak and this tangent as the graphic height of the wave. In the literature there is no critical examination of the limits of applicability of the graphic method of interpretation.

We found that the slope of the tangent which is plotted for the graphic determination of the height of the peak depends on insignificant changes in the solution composition, the properties of the capillary, and other factors.

It is best to determine the ratio of the graphic height of the peak to the difference in the ordinates of both points of contact between the tangent and the polarographic curve. In the future we will refer to this difference as a measure of the slope, or simply as the slope in contrast to the angle of the slope (the slope is positive if the ordinate of the point of contact on the side of positive potentials is higher than the corresponding ordinate on the side of negative potentials, and negative in the opposite case).

The permissible ratio of the height of the peak to the slope, i.e., that ratio at which the height of the peak differs by not more than 20-25% from the height of the peak obtained at zero slope, fluctuates, depending on the special features of the interfering elements and on the character of the residual current curve near the potential of the peak of the element to be determined. Graphic interpretation becomes permissible when the ratio of the height of the peak to the slope is 1.5-2.

In some cases, more reliable results can be obtained by determining the height of the peak as the difference in the ordinates between the apex of the peak and the horizontal tangent to one of its bases. In this case, the height of the peak depends to a lesser extent on the presence of one interfering substance in the solution. However, the presence of two interfering substances whose peaks are on both sides of the peak of the element which is being determined can lead to considerable errors in the analysis (Table 1).

The ratio of the height of the peak to the slope can therefore serve as a definite criterion of the resolving capacity of square-wave polarography. The literature also gives other criteria of the resolving capacity, based on establishing the limiting permissible ratio of the alternating components of the diffusion current of the element being determined and the interfering element at the potential of the peak of the element being determined [7,8]. These criteria apply to the absolute method of interpretation and to the operation of an automatic concentration measurer; they do not apply to the graphic method for interpreting polarograms.

The sensitivity of the square-polarographic method is closely bound up with the character of the slope of the polarographic curve. Other conditions being equal, a relatively higher sensitivity in the determination (10^{-7} g-eq/liter) is shown by ions whose peaks are closer to the electrocapillary maximum. We believe that the least concentration which can be determined is that for which the peak exceeds the slope by not more than 1.5 times and the height of the peak at the maximum sensitivity of the instrument is not less than 5 mm.

Relationship between the Graphic Height of the Peak and the Concentration

The effectiveness of square-polarographic analysis depends on how accurately we can establish the connection between the graphic height of the peak on the polarogram and the concentration of the element in solution. Two methods are known for determining this connection: the method of calibration curves and the method of additions. The first of them is applicable in the case where the compositions of the standard and working solutions are identical, or when the difference in the compositions has practically no effect on the height of the peak of the required element. In square-wave polarography the polarograms depend to a large extent on the concentration of the main electrolyte, the presence of traces of surface-active substances, and other factors. The method of additions is usually used in square-wave polarography, especially when determining low concentrations. The method of a single addition can only be used when the height of the peak is proportional to the concentration.

It follows from Fig. 2 that the slope of the calibration curve plotted from the graphic heights of the peaks can decrease on transition to low concentrations.

Another case of nonlinearity of the calibration curve is illustrated by Table 2. The nonlinearity of the curve for a solution of pure cadmium is connected with its reduction by traces of electronegative elements present in the mercury. After the addition of an excess of copper to the solution, the calibration curve for cadmium became linear.

In the analysis of low concentrations, the single addition method is insufficiently reliable.

To eliminate errors due to disproportion between the concentration of the element to be determined and the graphic height of the peak at low concentrations, we combined the method of multiple additions with the method of variation of weights. The data for these methods are given in Table 3.

The linearity of the calibration curve only commences for peaks higher than 10 mm. In this region the addition of 0.1 μg is represented by a 7-mm increase in the peak. After subtracting peak No. 3 from peak No. 8, a weight of 1 g in the region of linearity of the calibration curve will be represented by a peak of height 8 mm (with the blank subtracted); the sample therefore contains $0.1 \cdot {}^{8}/_{7}$ μg of the element being determined.

When working with different weights, a correction should be made to allow for the difference in the slopes of the calibration curves.

The proposed method is cumbersome and in practical analysis it is not always convenient. However, by combining the methods of multiple additions with variation of weights it is possible to refine the limits of applicability of the graphic interpretation of polarograms.

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CYCLIC VOLTAMPEROMETRY WITH A PÉ-312 ELECTRONIC POLAROGRAPH

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It has been shown that it is possible to use a PÉ-312 electronic polarograph with a special attachment for the production of cyclic polarograms.

Cyclic voltamperometry with a stationary microelectrode can give valuable information as to the mechanism and kinetics of electrode processes, and it also provides a very simple experimental means for substantially increasing the sensitivity of determination of traces of metals. Cyclic voltamperometry, using a suspended mercury drop electrode [1], has been applied to study the formation of various intermetallic compounds in amalgams, to investigate the mechanism of the reduction of certain organic compounds, and to develop methods for determining ultrasmall amounts of metallic impurities. When studying hysteresis in the autocatalytic reduction of anions, cyclic voltamperometry gives valuable information even when a dropping mercury electrode is used.

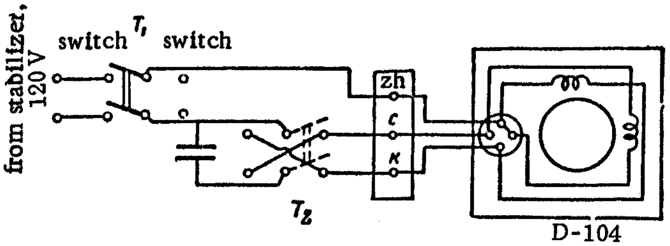

Fig. 1. Diagram for reversal of D-104 synchronous motor.

The PÉ-312 electronic polarograph, developed by the Central Laboratory for Automation [2,3], was mainly intended for analytical purposes. However, this instrument shows a number of obvious advantages over a photorecording polarograph, so that it can be used with advantage in scientific research work.

A factor which limits its field of application is the impossibility of switching it rapidly from recording a polarogram with the electrode polarized in one direction to record a polarogram in the reverse direction, i.e., the impossibility of using it for cyclic voltamperometry.

This disadvantage can easily be remedied. The slide wire and paper chart in the PÉ-312 polarograph are moved by two D-104 synchronous electric motors. In order to make these motors rotate in the opposite direction, it is necessary to switch the phases at c and k by means of the tumbler switches T_2 (Fig. 1). These tumbler