AN INVESTIGATION OF THE POSSIBILITIES OF AMALGAM SQUARE-WAVE POLAROGRAPHY WITH ELECTROLYTIC ACCUMULATION*

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It has been shown that the deviation from linearity of the relation between peak height and electrolysis time, and also the increased slopes of the peaks, prevent achievement of the theoretical limiting sensitivity for square-wave amalgam polarography with preliminary electrolytic accumulation at a stationary electrode.

Barker and Jenkins [1], in 1952, first suggested the idea of combining the two main methods for increasing the sensitivity of polarographic analysis: the apparatus method, based on pulse polarography with elimination of the capacity current, and the electrochemical method, based on preliminary electrolytic concentration of the depolarizer at a stationary electrode. Each of these two methods has been thoroughly investigated on its own, but only two papers [2,3] have dealt experimentally with a combination of the two methods, and, in our view, these are not sufficiently critical.

We have investigated the possibilities of amalgam pulse polarography with a square-wave polarograph made by Mervyn Instruments (Model 3). Various single drop electrodes have been used: a polytetrafluoroethylene piston electrode [4], a mercury microelectrode, deposited electrolytically on a platinum wire [5], or suspended from a gold wire [6]. The solution was stirred by a magnetic stirrer, by a glass stirrer with a mercury seal, and also by a stream of nitrogen, freed from oxygen by passage through a series of absorbers charged with vanadous sulfate solution.

All the experimental work was based on the assumption that the effectiveness of pulse polarography would ensure:

a) the absence of uncontrollable factors which would affect the reproducibility of determinations;

b) the possibility of raising the analytical sensitivity by increasing the time for electrolytic accumulation;

c) the possibility of using the full sensitivity of the instrument when recording anodic polarograms.

Reproducibility of Polarograms; Capacitograms

The reproducibility of the polarograms must obviously depend on the reproducibility of the surface of the mercury electrode. The electrodeposited electrode was reproduced after each experiment by additional anodic oxidation of the amalgam, and its surface did in fact remain unaltered for a very long time. Reproducibility of the surface of the other electrodes was checked by recording capacitograms, i.e., curves showing the relation between drop capacity and time. Capacitograms were recorded at the electrolysis voltage during the whole duration of, or within 0.5 to 1 min after the recording of an anodic polarogram and return of the polarization voltage to the original electrolysis voltage.

When working with solutions not specially freed from surface active materials we noted an initial sharp fall in drop capacity, as described by Barker [2]. The capacity fell by 50% or more within 1 to 2 min after application of the steady value after about 10 min. When the solution was freed from surface active material, by repeated passage through a column of silica gel topped by active carbon, the extent of the fall in drop capacity during the time of

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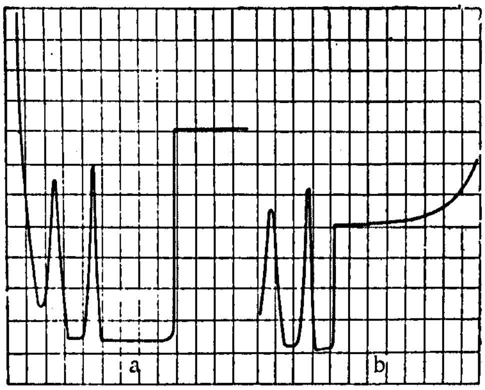
* The basic ideas of this paper were reported to the Second All-Union Conference on Polarography at Kazan in 1962. The paper was submitted to the editor before the publication of the work of S. B. Tsfasman and R.M.-F. Salikhdzhanova [Zavodskaya laboratoriya, XXX, 133 (1964)].



Single crop polarogram of copper (6 μmole /liter) and cadmium (3 μmole/liter) in a weakly alkaline solution of ammonium chloride (1 mole/liter), which had been freed from surface active material by adsorption. The electrolysis voltages were a) −1.4 V and b) −0.9 V. The electrode was of the piston type. The electrolysis time was 5 min. The capacitograms are shown to the right of the vertical lines. The sensitivity was 1:1080.

electrolysis greatly diminished. It should be noted that the fall in drop capacity depended on the electrolysis voltage (see figure), indicating the effect of the voltage for adsorption-desorption of surface active material. This dependence is not mentioned in [2]. We never achieved complete constancy of the drop capacity at the potential for adsorption of surface active material, but it was possible to reduce the fall in capacity to a few per cent during the period of about 10 min required for electrolytic accumulation.

Even with reproducible capacitograms, it was usually found that the anodic oxidation peaks were not completely reproducible. Even when working with the same solution there was generally an initial drift in peak height for the first 2 to 4 polarograms. Subsequently the peak height became steady at a value about 1.2 to 2 times that of the peak in the first polarogram. This drift was observed with all the solutions and electrodes investigated, and this made it difficult to explain. The duration of the drift did not depend on the special purification of the solution from surface active materials. It should be noted that we also observed an initial drift in the reading when using a normal LP-60 electronic polarograph for amalgam polarography with accumulation, though other authors do not agree with this.

A number of factors can affect the reproducibility of anodic polarograms obtained with a well stabilized square-wave polarograph. The rate of voltage change is one such factor. When studying the effect of this on peak height, we found that, starting at a rate of 4 mV/sec, the peak height was proportional to the square root of the scanning rate. This corresponded to the Shevchik equation, which relates the dependence on scanning rate to the amalgam concentration prevailing at the potential of the depolarizer peak. At scanning rates exceeding 4 mV/sec we observed deviations from the Shevchik equation attributable to the inertia of the recording system of the polarograph.

Constancy of the electrolysis potential was found to be an important factor affecting polarogram reproducibility. This could be ensured by potentiometric control with a Barker polarograph.

Thus, by observing various simple conditions, and allowing for the initial drift in peak height, it was possible to achieve a reproducibility of 5 to 10% for square-wave polarographic peaks.

The Dependence of Single Drop Polarograms on the Time for Electrolytic Accumulation

Barker [2] did not give a complete analysis of the relation between anodic peak height and the time for electrolytic accumulation. Sturm and Ressel [3] observed a maximum in the *i* versus *t* curves after 5 min, but they did not pay attention to the obvious discrepancy between the experimental and theoretical curves. In theory [7] the accumulation of amalgam in the electrode should be proportional to the electrolysis time up to the point when impoverishment of depolarizer in the solution becomes evident.

We also constantly observed nonlinear *i* versus *t* curves. The linear parts of the curves could be lengthened by adsorptive purification of the solution from surface active materials, by raising the temperature of the solution to 60 to 80°C, by changing the electrolysis voltage, and by other methods. However, it was never possible to extend the linear region beyond 15 to 18 min. It should be noted that the teeth of anodic polarograms of the same solutions, recorded with an LP-60 polarograph, were characterized by *i* versus *t* curves with regions which were linear for several hours.

It is evident that, in addition to less important causes (diffusion of amalgam into the capillary channel of a piston electrode, diffusion of gold to the surface of a suspended electrode, etc), an important role was played here by gradual adsorption of surface active compounds during the course of electrolysis. Indirect evidence for this was provided by the clear dependence of the *i* versus *t* curves on the degree of reversability of the depolarizer reaction at the electrode. For example, in solution in M ammonium chloride, the ratios of the peak heights after 10 and 5 min electrolysis were 1.65 for copper and 1.08 for zinc. A considerable increase in the peak height for both zinc and lead and an increase in the linear portion of the i versus t curve, observed when we changed from solutions with nondeforming anions (sulfate) to solutions with deforming anions (chloride), could also be attributed to the role of surface active agents and to the selective adsorption of chlorides.

We must assume that there can be present in solutions surface active materials of various types with different effects on the character of the i versus t curves. For this reason, even a small decrease in drop capacity during electrolysis may be associated with a marked deviation of the i versus t curve from a straight line. Under conditions of practical analysis it is obviously very difficult to ensure complete removal of surface active materials.

Sensitivity of Amalgam Square-Wave Polarography with Preliminary Accumulation

The mere fact that the i versus t curves are bent, under conditions for the obtaining of reproducible polarograms, should not reduce the possibilities of the method. The sensitivity of the Barker polarograph is better by 2 to 2.5 orders of magnitude than that of a normal polarograph, so that a depression of the concentration effect by two orders of magnitude (in the limit, with a 1 mm^3 drop electrode and 10 ml of solution, this effect may be as much as four orders) should not prevent amalgam square-wave polarography with accumulation from competing successfully with amalgam polarography by means of a normal polarograph.

Extrapolation of data obtained with 10^{-7} to 10^{-6} M solutions of depolarizer actually indicated that it should be possible to determine a 10^{-10} M concentration of depolarizer by amalgam square-wave polarography. However, as will be shown below, such extrapolation is not permissible. It is unfortunate that Barker [2] estimated the sensitivity of the method precisely by extrapolation. Sturm and Ressel [3] did not give one experimental result for the analysis of solutions at concentrations significantly below 10^{-8} M; nevertheless these authors attempted to characterize relative limiting sensitivities for the determination of various elements by comparing specific sensitivities in units $liters \cdot ohm^{-1} \cdot mole^{-1} \cdot cm. 10^{-5}$. However, the limiting sensitivity for determination is not always proportional to the specific sensitivity and is not always related to it.

In square-wave amalgam polarography at stationary electrodes we encountered high peak slopes [8] which were evidently associated with the relatively large surfaces of the stationary electrodes used, as compared with dropping electrodes. It is possible that, in the case of an electrodeposited and suspended electrode, the increased slope may also be due to the action of gold and platinum. Regardless of the cause of this increased peak slope, we found it impossible to use a polarograph sensitivity greater than 1/5 to 1/10 in amalgam polarography, even for elements whose peaks were located close to the electrocapillary maximum.

Combination of the two factors, nonlinearity of the i versus t curves and the increased peak slopes, meant that the sensitivity of amalgam square-wave polarography with accumulation did not in most cases exceed that of normal square-wave polarography by more than one order of magnitude and did not, in fact, exceed the sensitivity of amalgam polarography with a normal polarograph. It is true that square-wave polarography had the advantage of higher resolving power. However, with normal amalgam polarography and accumulation, it is often possible to increase the resolving power by appropriate choice of the electrolysis voltage or by stopping the anodic scan.

Means for increasing the sensitivity of amalgam polarography with accumulation are obvious in principle. They are: improvement in the design of the stationary electrode so as to reduce its capacity and hence the peak slope; improving the efficiency of means for eliminating the capacity current; finding the best means for freeing the solutions from all surface active materials.

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