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SUBJECT: INVESTIGATION OF THE CHRONOPOTENTIOMETRIC
METHOD OF ANALYSIS

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FROM: D. J. Fisher

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Distribution

1. R. A. Anderson
2. S. W. Scott
- 3-10. H. F. Carroll

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INVESTIGATION OF THE CHRONOPOTENTIOMETRIC METHOD OF ANALYSIS

D. J. Fisher

In the chronopotentiometric technique - described recently by Delahay and Mamantov (1), Reilley, Everett and Johns (2), and others (3) - the concentration of a particular ion is determined by measuring the time lag in the polarization of a quiet mercury pool cathode when the electrolyzing current through the solution is maintained constant. This time lag is called the transition time, and is caused by the partial depolarization of the cathode by the discharge of the ion in question. Provided there is no kinetic complication in the reduction of the ion, the transition time is related to the concentration of the ion by the equation:

$$\tau = K \frac{C^2}{i^2}$$

where: τ is the transition time,
C is the concentration of reducible ion,
i is the current through the cell,
K is a constant, incorporating a number of constants, including the number of electrons involved in the reduction of the ion, the diffusion coefficient of the reduced ion, and the square of the surface area of the mercury cathode (1).

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The present investigation was undertaken with the idea of applying the technique to analysis on a routine basis, and particularly at low concentrations. Various factors in cell design were studied, as well as the limitations which these factors set upon the use of the method.

Apparatus

The apparatus employed was a modification of that described by Reilley, Everett and Johns (2), and is shown in block diagram in Figure 1. The constant current supply was designed by M. T. Kelley, and is shown in Figure 2. The cells and electrode holders were machined from lucite, and the general design of these is shown in Figure 3. To minimize vibration, the cell assembly support was mounted on rubber shock mountings which rested on a sheet of plywood supported by inch-thick sponge rubber.

Two different lucite cells were employed: one in which the reservoir for the mercury cathode was 3/16-inch in diameter, and second cell in which the mercury cathode reservoir was 14/16-inches in diameter. In both cells, the walls of the cathode reservoir were machined as nearly parallel as possible, and in successive chargings with mercury, the mercury level was maintained the same by pipetting the same volume of mercury into the cell for each sample.

Three different anodes were tried. In the first, the anode consisted of a platinum wire immersed in saturated KNO_3 solution. This external anode maintained contact with the solution in the cell through a salt bridge, the tips of which were 1/4-inch porous glass rod, held in place by teflon sleeves. This bridge was found to have too high a resistance, and so was

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replaced by an agar-agar bridge in which the platinum anode was stuck directly in the top of the glass tube containing the agar-agar. Two different sizes of agar-agar bridges were tried, and it was found that when a large mercury cathode was employed, the transition times obtained with a fixed current depended upon the size of the anode bridge. This effect is shown graphically in Figure 4.

The reference electrode employed was a saturated calomel electrode, located external to the cell, and connected by means of a saturated KCl bridge. The portion of the bridge extending into the sample was constructed of glass tubing, with a small piece of porous glass rod connected by means of polyethylene tubing. To prevent leakage, the polyethylene tubing was heated in a flame until it sealed tightly to both the porous glass rod and to the glass tubing.

Procedure

Solutions of CdCl_2 (using a mixture of 1 M NH_4Cl and 1 M NH_4OH as supporting electrolyte), and solutions of uranium in 0.1 M HNO_3 were run. Transition times versus currents were plotted on log paper for different concentrations. These results are shown in Figures 5 and 6.

In running a chronopotentiogram, the procedure employed was as follows. The cell was rinsed with the solution to be run, and then charged with mercury by pipetting the mercury into the cathode reservoir. In the cell having the 3/16-inch diameter cathode, 0.15 ml of mercury was used.

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In the cell having the 14/16-inch diameter cathode, 1.5 ml of mercury was used. Care was taken to use only pure mercury, and to avoid drawing up any of the surface of the mercury into the pipette. Approximately 10 to 15 mls of the sample were then added and the cell was clamped into place under the electrode holder. The nitrogen sparge tube was introduced below the surface of the mercury, and nitrogen was bubbled through mercury and solution for at least 15 minutes. The tube was then raised above the surface of the mercury, and the nitrogen was continued through the solution for another ten minutes. The nitrogen tube was then raised to just below the bottom of the electrode holder and the flow of nitrogen was cut down somewhat to prevent disturbance of the sample.

At this point, the mercury cathode was examined visually and any bubbles of gas at the interface between mercury and solution were removed by stirring the solution with nitrogen, while at the same time tapping the side of the cell.

With the cell by-passed, the electrolyzing current was adjusted to the desired value, the final exact setting being done by means of the potentiometer across the standard resistance (see Figure 2). After a wait of at least 2 minutes, the Brown recorder was started, and the electrolyzing current was passed into the cell. When the run was completed, the sample was returned to its original condition by one of two procedures, depending upon the ion that was reduced. It was found that with cadmium, it was best to reverse the current through the cell while at the same time bubbling nitrogen

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through the mercury. As soon as the original starting potential was obtained, the cell was by-passed but the nitrogen was continued for two to three minutes. In the case of the uranium samples, only the stirring with nitrogen was employed, the reversing of the current being omitted because of its tendency to produce some sort of non-reversible change in the solution such that further runs on the same sample frequently showed interfering waves. The first curve produced on a new sample was discarded because of the observation that frequently it was distorted or yielded a transition time out of keeping with the results of subsequent runs.

After returning the sample to its original condition, further runs could be made on the same sample. It was found, however, that the lower the concentration of the sample, the fewer were the duplicate runs that could be made on the same sample.

The transition times were determined from the curves by means of the graphical method described by Delahay and Mamontov (1). An example of this method is shown in Figure 7.

Results and Conclusions

Since the transition time varies with the surface area of the cathode, the cell design must be such that this area can be reproduced from sample to sample. The cell design employed in the present work seemed satisfactory, provided the same volume of mercury was employed each time the cell was charged.

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With mercury cathodes of large surface area, the size and the resistance of the anode bridge had an effect upon the transition times obtained. It appeared that the larger the anode bridge, the more sensitive the cell was to lower concentrations of reducible ions. Also, the lower the resistance of the anode bridge, the less distortion there was of the waves at lower concentrations. The former of these effects is illustrated in Figure 4. For work at low concentrations, the best results are obtained with a large cathode and a large anode bridge of low resistance.

One of the factors which place a limitation on the practicality of the method, especially at low concentrations, is the distortion of the waves due to the capacity effect of the ionic double layer at the cathode surface (1). For a given concentration and with a particular cathode area, various transition times may be obtained by changing the current. However, as the current is decreased (thus increasing the transition time) the distortion of the waves increases until a point is reached at which it is no longer possible to determine the transition time from the curve obtained. This effect is illustrated in Figure 8. The size of the cathode and the size and the resistance of the anode bridge affect the amount of distortion obtained. Apparently, for work at low concentrations, a large cathode and a large anode bridge yield the best waves.

In working at low concentrations, since there is a limited range over which transition times can be accurately measured, it is not practical to select a fixed current and to attempt to prepare a standard curve relating transition time to concentration at that one particular current. A glance

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at Figure 6 will show that this would yield a curve in which accurate determinations could be made only over narrow ranges of concentration. A more versatile method is to run a series of different concentrations, each one over the range of currents that yield accurately measurable transition times. Plot these transition times against current on log paper, thus obtaining a series of parallel straight lines. Select a "fixed transition time" in the center region of the curves and draw a straight line parallel to the current axis, intersecting the curves. On another sheet of log log paper, plot concentration versus current at this "fixed transition time". In running an unknown sample, transition times are measured for several different currents, and the results plotted. From this plot the current yielding the "fixed transition time" is obtained, and by means of this current, the concentration of the sample is read from the concentration versus current graph.

References

- (1) Delahay and Mamantov, Anal. Chem. 27, 478, (1955).
- (2) Reilley, Everett and Johns, Anal. Chem. 27, 483 (1955).
- (3) Private communication W. G. Schaap, Indiana University.

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Figure 1
Circuit for Chronopotentiometry

Figure 2
Constant Current Supply

Figure 3
General Design of Lucite Cell

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FIGURE 4
 Cd^{++} IN 1 M NH_4OH + 1 M NH_4Cl
SECOND LUCITE CELL
EFFECT OF ANODE BRIDGE SIZE

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FIGURE 5
Cd⁺⁺ IN 1M NH₄OH + 1M NH₄Cl
EFFECT OF CATHODE DIAMETER

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FIGURE 6
URANIUM IN 0.1 M HNO₃
 $\frac{14}{16}$ " DIAMETER CATHODE
10 mm AGAR-AGAR ANODE BRIDGE

FIGURE 7
GRAPHICAL DETERMINATION OF TRANSITION TIME

FIGURE 8

EFFECT OF CHANGE IN CURRENT LEVEL ON SHAPE OF CHRONOPOTENTIOMETRIC WAVE

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