

A NEW POLAROGRAPHIC MICROELECTRODE
EMPLOYING CONTROLLED STIRRING

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EMPLOYING CONTROLLED STIRRING

By

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EMPLOYING CONTROLLED STIRRING

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NATURE OF THE PROBLEM

In 1948, Mr. Roy Maness and Dr. Paul Arthur of Oklahoma A. and M. College became interested in designing a new microelectrode (18) for use in polarography. The purpose in mind was to develop one which would give steady current-voltage curves, would decrease mercury requirements, could be exactly duplicated, and would have at least the range of the dropping mercury electrode (D.M.E.).

Figure 3 shows the form of the electrode and cell they finally designed. The electrode consists of a thin-walled glass tube fitted, by means of a ST 10/30 joint, upwards through the bottom of the cell. The lower end of the male portion of this joint is connected to a "U" tube equipped with a stopcock. Mercury poured into this "U" tube is cleared of air bubbles and adjusted so the upper surface of the curved mercury meniscus is exactly flush with the upper end of the electrode tube, then the mercury is "locked" by closing the stopcock. A stirring tube whose internal diameter is 2 to 5 mm. greater than the external diameter of the electrode tube is brought down over the upper end of the electrode, enclosing about 5 mm. of the length of the latter. This tube, revolved at 600 r.p.m., gives very steady stirring.

Earlier efforts by investigators (Rogers and co-workers (24)) to employ stirring methods with stationary electrodes gave erratic results. The success obtained with the stirring tube arrangement described here was undoubtedly due to the greater control and reproducibility of stirring within the tube, any eddys or fluctuations being of such high frequency that variations were imperceptible.

The first electrode made gave excellent results. The polarograms were free of oscillations inherent in the D.M.E., and very large diffusion currents with extremely small residual currents were obtained. This held promise of greatly increasing the accuracy possible and extending the use of polarography to much more dilute solutions. The amount of mercury required with this electrode was small compared to that required with the D.M.E. Upon further investigation of this electrode, however, it was found that oddities appeared, indicating that something critical was being overlooked.

While the electrode otherwise yielded excellent results, work on this problem had not been carried very far before it was found that the irregularities mentioned earlier were apparently caused by solution creeping inside the electrode tube, forming into droplets, and then bursting out again. This phenomenon seemed to vary as the potential increased, beginning at about -1.2 volts vs. the S.C.E.

The research described in this thesis was undertaken in an effort to investigate more thoroughly the cause of the irregularities obtained with this electrode. Once the nature and cause of the irregularities were determined, various surfaces and modifications of the electrode were investigated and undertaken in an effort to eliminate the presence of these irregularities. After developing the electrode to the point where reproducible results were obtained, some of the variables influencing the behavior of the electrode were determined and evaluated.

HISTORICAL

From the time Heyrovsky (7) introduced the polarographic method of analysis, numerous attempts have been made to develop new microelectrodes to be used in polarography. Various objectives were sought.

1. To eliminate the oscillations which are characteristic of curves obtained with the D.M.E., so increased accuracy of measurements could be obtained and so synchronization of sweep with drop size in certain oscillographic techniques would be unnecessary.
2. To increase the diffusion current without increasing the residual current.
3. To increase range and applicability, particularly in anodic reactions.
4. To make it possible to prepare electrodes of identical characteristics so such new techniques as differential polarography (10) could be more readily applied.
5. To eliminate the need for handling large quantities of mercury.

Such studies led to the development of the streaming mercury electrode of Heyrovsky and Forejt (8) who also employed a streaming amalgam electrode in oscillographic polarography. The results were found to be very satisfactory for oscillographic polarography. Rius and Llopis (23) in 1946 used a device that projected a stream of mercury of constant length into a potassium chloride solution. The current was found to be proportional to concentration.

Riches (22) reported an electrode made of marine barometer tubing with the radius of the orifice greater than the radius of the tube higher up. Greater sensitivity was obtained, but this electrode yielded very high residual currents and was not practical. DeVries and Barnhart (5) constructed an electrode consisting of four dropping mercury electrodes sealed to a common reservoir containing mercury. Sans-Pedrero and Portillo (26) used an electrode containing 15 tips and unsatisfactory behavior was obtained. Residual currents were found to be too large. Bricker and Furman (3) in 1948 also experimented with multiple tip electrodes and found that fluctuations in the diffusion current were obtained due to non-synchronization of the drop times. Stankoviansky (31), on the other hand, reported that he was able to obtain smooth polarograms with a six-capillary electrode in which forced regulation of the drops was utilized. Leveque and Roth (14) used two capillaries with the current measured as a function of the potential between the two electrodes. They were able to determine low concentrations of metal ions having reduction potentials which were very close to one another.

Neiman, Ryabov, and Sheyanova (21) passed mercury through a fritted-glass disk and obtained useful polarograms.

Skobets and Kavetskii (29) investigated forced-drop electrodes which utilized a glass device to force the mercury drop to sever from the capillary. Maxima were obtained when the glass device was too close to the electrode orifice. Airey and Smales (1) separated the mercury drop from the electrode by first weakening the mercury surface tension with an electrical impulse and then moving the capillary slightly in a lateral direction to cause the drop to fall. Reproducible drops were obtained.

Tsimmergaki (32) used an electromagnetic tapper to accomplish enforced removal of the drop. Berman, Saunders, and Winzler (2) have used a vibrating electrode for solutions requiring agitation.

Rogers and co-workers (24) in 1948 studied a platinum electrode rotated at 600 r.p.m. with an automatic polarograph. Skobets and co-workers (27, 28) used stationary platinum electrodes with automatic instruments and obtained maxima on the curve. A stationary platinum needle electrode, an amalgamated gold electrode, as well as rotating platinum and silver electrodes with automatic recording instruments were investigated and moderately successful results were obtained. Skobets, Torov and Ryabokon (30) later found with stationary platinum electrodes that the maxima mentioned above could be eliminated by keeping the solutions at 60°C. Julian and Ruby (9) reported that these maxima can be decreased in magnitude by decreasing the scanning rate. Delahay and Stiehl (4) have investigated rotating platinum electrodes and found that the half-wave potential varies with the type and size of the electrode. They believe this to be due to differences in the surfaces of the electrodes.

Manual manipulation of solid, stationary electrodes has been investigated by Kittelberger and Elm (10), who used a stationary iron electrode. Lydersen (17) found that a waiting period of only one minute was required for the limiting current to reach a steady value, a solid, spherical, stationary, platinum electrode having been used. The electrode was usually platinized.

Rotating electrodes were studied early by Nernst and Merriam (20) and more recently by Laitinen and Kolthoff (12) who used a platinum wire electrode with a manual instrument. Their work has been confirmed by Julian and Ruby (9). Rosenthal, Lorch, and Hammett (25) have used

very rapidly rotating electrodes and have found that a speed of rotation can be reached beyond which the speed of rotation no longer affects the diffusion current. These rotating electrodes have yielded excellent results and show great promise in cases where polarization does not interfere.

Some unusual electrodes of special type have been developed and investigated to some extent. Harris and Lindsey (6) have developed a vibrating platinum microelectrode which yields smooth curves. The electrode was vibrated at a constant frequency of 100 cycles per second. Lyalikov and Karmazin (16) have developed a gas-bubbling electrode. A platinum needle surrounded by an open end tube is dipped into a solution. An inert gas is passed into the tube and allowed to escape in bubbles. By means of this arrangement, the needle was washed with solution as each bubble of gas escaped. A constant depth of immersion of the platinum needle was found to be critical. The diffusion current was found to be proportional to both the concentration of ions and to the rate of bubbling. Further investigations by Lyalikov and Glazer (15) revealed that polarization occurs occasionally, but that it was removed by washing the apparatus in nitric acid or simply short-circuiting the apparatus for approximately five minutes.

Lee (13) has devised a rotating mercury electrode which is capable of determining metal ions at concentrations as low as 0.8 ppm. This electrode consists of a Bakelite cup containing 0.1 ml. of mercury rotated at speeds of 200 to 1800 r.p.m. Maness (18) has investigated a stationary mercury electrode utilizing controlled stirring of the solution under investigation. The electrode consisted of a "U"-shaped tube, one arm of which contained a thin glass tube filled with mercury

until the level was even with the top of the tube. The other arm of the "U" tube contained a stopcock and reservoir for mercury. The stopcock was used to lock the mercury surface in position during electrolysis. The stirrer consisted of a tube fitted over the electrode and rotated at 600 r.p.m. Well-formed polarograms were obtained with this arrangement.

EXPERIMENTAL

Reagents.

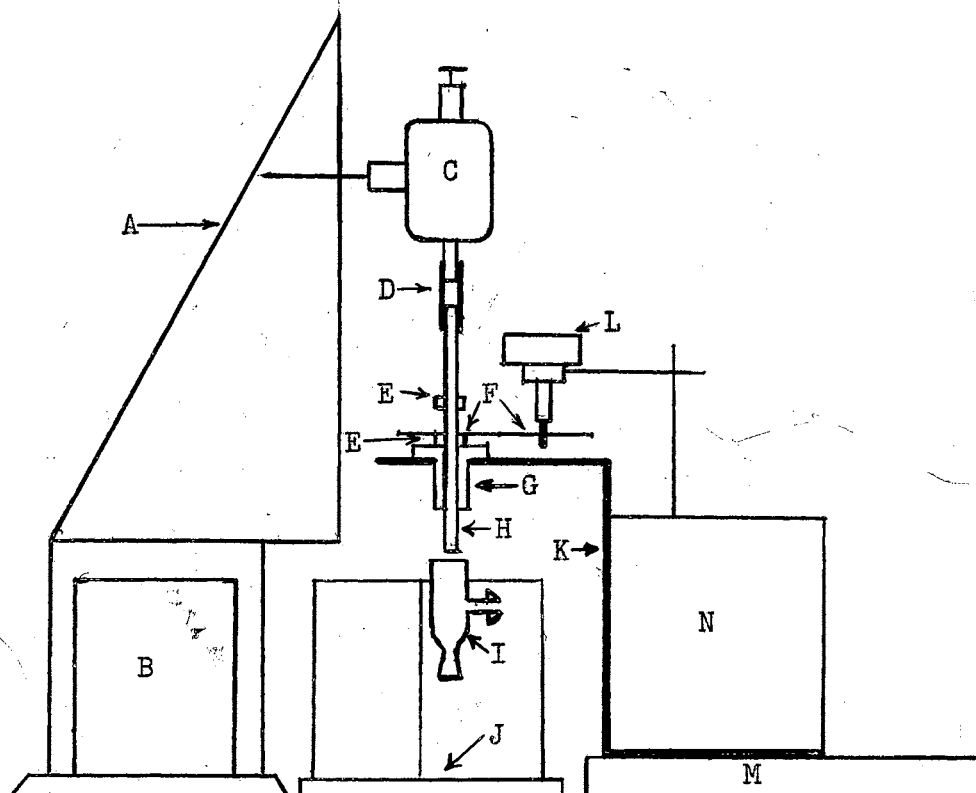
All reagents used were of "Chemically Pure" or "Analytical Reagent" grade. Electrolyses of the solutions using the D.M.E. indicated that the solutions were free of polarographically determinable impurities. Nitrogen used in degassing solutions was purified of oxygen and other impurities by passage through concentrated sulfuric acid, followed by a solution of alkaline pyrogallol, next through distilled water, and finally through a sample of the same solution present in the electrolysis cell.

Apparatus.

The polarographs used in this study were the Sargent Model XXI strip-chart recording polarograph and an experimental polarograph which was so constructed that it was possible to vary the time of electrolysis from 26 seconds to over 5 minutes. The experimental polarograph was assembled from components of a Sargent Model XII photographic recording polarograph.

Checks on significant potentials were made using a Gray Potentiometer. An Eppley standard cell was used for setting the potentiometer.

The assembly of the cell, external saturated calomel electrode, and stirrer tube was used as shown in Figure 1. The stirrer shaft was mounted in a brass bushing, which in turn was mounted in a metal stand attached to a wood base. The wood base was clamped to the table to insure rigidity. The stirrer shaft was held in any desired position by means of an adjustable collar. At the end of the stirrer shaft was the



- | | |
|-------------------------|---------------------|
| A. Stirring motor stand | H. Stirrer |
| B. Weight | I. Cell |
| C. Stirring motor | J. Cell stand |
| D. Rubber tubing | K. Bushing mounting |
| E. Collar | L. Tachometer |
| F. Gear wheels | M. Wood base |
| G. Stirrer bushing | N. Wood brace |

Figure 1. Electrode assembly

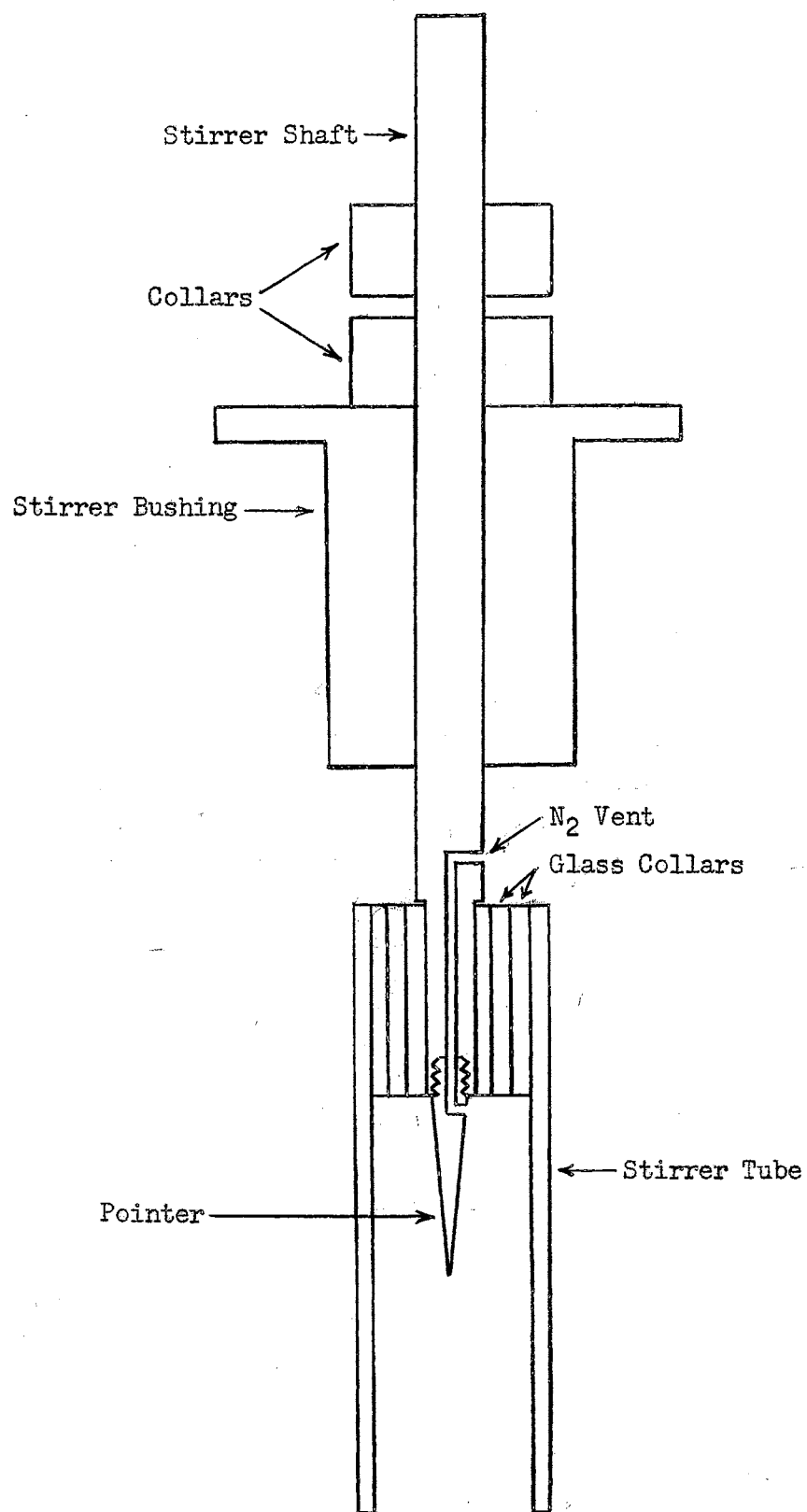
stirrer tube and a sharp point of metal as shown in Figure 2. This pointer was used in setting the position of the mercury surface after first setting the pointer to any desired position. During electrolysis, the pointer was withdrawn from the solution.

The stirrer motor was mounted on an especially braced ringstand which was held in place with a heavy weight on the ringstand base. The shaft of the motor was connected to the stirrer shaft by means of a short piece of rubber tubing. In this manner, transmission of vibrations from the motor to the stirrer shaft was minimized.

The mounting for the cell was constructed by welding three rods to a semicircle of quarter-inch steel plate, a triangle of iron rod being welded to the tops of these three uprights. This assembly was then clamped to the desk. The cell itself was supported by clamps attached to one of the upright rods. The cell, electrode assembly, and standard cell were illustrated in Figure 3.

The stationary electrode used in this study consisted of a glass tube, held in a vertical position, and filled with mercury so that the mercury meniscus was even with the top of the tube. The vertical tube was surrounded by another glass tube of larger diameter which was attached to the stirrer shaft and rotated concentrically about the vertical tube at a constant rate.

When temperature control was needed, the cell and the attached calomel electrode were mounted in a jar, the standard taper joint through which the microelectrode was inserted into the cell protruding through a rubber stopper fitted into a hole in the bottom of the jar. The top of the jar was closed by means of a board and a rubber gasket fitted between the jar and the board. The board and gasket contained openings for the cell, the calomel electrode, and the water inlet and



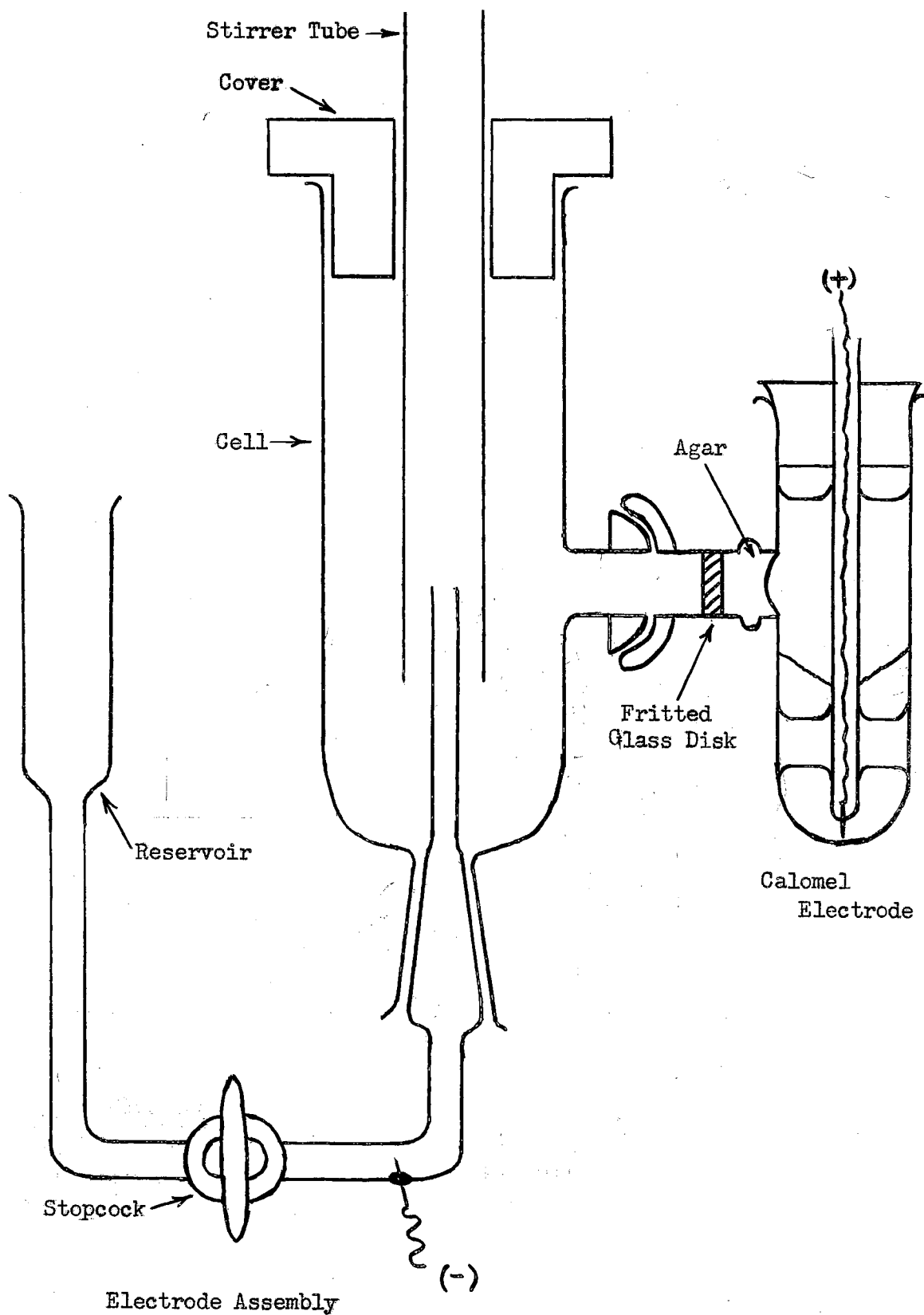


Figure 3. Electrode assembly, cell and saturated calomel electrode.

outlet tubes. Water was circulated from a thermostated bath to the small bath surrounding the cell and calomel electrode. The water in this small bath was kept at $25^{\circ} \pm 0.2^{\circ} \text{ C}$.

At the start of the investigation, the speed of rotation of the stirrer was checked periodically with a Starrett revolution counter. In later work, a Stewart-Warner Model 727-W portable tachometer was attached to the electrode assembly, allowing the speed of rotation of the stirrer to be checked whenever desired.

Procedure.

A typical electrolysis was conducted in the following manner. The saturated calomel electrode was attached to the cell by means of the ball and socket joint. The particular electrode being investigated was next inserted into the cell through the standard taper joint at the bottom. The solution being electrolyzed was then added to the cell until it was in contact with the calomel electrode and extended approximately one-half inch above the top of the microelectrode. The cork cover of the cell was placed in position to close the cell and degassing was started. Degassing was carried out in the usual fashion, using purified nitrogen. After the solution had been degassed, the flow of nitrogen was diverted to flow over the solution. The height of the mercury in the microelectrode tube was then adjusted.

After the mercury level had been adjusted, the stirrer motor was turned on and allowed to rotate for a minute or two before the actual polarograph was recorded. It was found that nitrogen bubbles had a tendency to collect on the stirrer tube. Running the motor for a short time dislodged these bubbles.

When the last electrolysis was completed, the mercury surface was changed and left protruding slightly above the top of the electrode.

The lead to the electrode was disconnected and the electrode carefully lowered from the cell, allowing the excess mercury and solution to drain into a pan. The electrode tip was washed with distilled water and dried with a small piece of filter paper. The electrode was stored with both the reservoir and the tip covered so no dirt could enter. The calomel electrode was then disconnected, the cross arm of the electrode washed with distilled water, and the electrode connected to a reservoir of saturated potassium chloride solution so that the agar plug would remain moist.

It was found that when a new electrode or an electrode which had dried was tested, the first polarogram was invariably erratic. As electrolyses were repeated, the polarograms improved. This erratic behavior on the first polarogram was due to the initial wetting of the electrode with solution. If the electrode was wet with solution before the first electrolysis, the first polarogram was much better. It was found that if, prior to the first electrolysis, the apparatus was set at -1.2 volts and allowed to stand with the current on for a few minutes, the electrode apparently became conditioned. During this conditioning, solution entered the electrode under conditions which were similar to those during an actual electrolysis, as a result of which the film of solution in the electrode tube became stabilized. If the mercury surface was then changed to remove electrolysis products and adjusted, an excellent first polarogram was obtained.

The diameters of the electrode and stirrer tubes were measured using a traveling microscope manufactured by the David W. Mann Precision Instruments Company. With this microscope, distances could be measured accurately to 0.0005 inches and approximated to 0.0001 inches. Four or

five measurements of the diameter of an electrode were made with the electrode fixed in one position, followed by five additional measurements made with the electrode rotated through an angle of approximately 90° from the first position. The average value so obtained was used.

Electrode and Modification of Its Surface.

When a plain untreated glass tube was used as the electrode, solutions containing cadmium ion yielded fairly well-defined waves. The half-wave potential and diffusion current of the cadmium wave were reproducible, and the curve was smooth and free of the oscillations encountered in the use of the D.M.E. Unfortunately, however, an irregularity was almost always observed, this irregularity consisting of erratic peaks in the curve at -1.2 or more volts.

Studies of this irregularity soon revealed the fact that when it was occurring, solution could be seen creeping into the electrode between the mercury and the inner surface of the vertical tube. In an attempt to remove the irregularity due to creepage of the solution into the electrode and thus obtain well-shaped curves, the investigation was conducted with two objectives in mind, i. e., 1) to prevent completely the creepage of solution into the electrode and thus prevent formation of the irregularity, or 2) to facilitate the entry of solution in order to achieve complete wetting of the electrode in the hope of stabilizing the wetting.

In order to achieve the first objective, various substances were placed on the inside surface of the tube in an attempt to prevent the entry of solution. The substances used and the method of their attachment to the glass surface were as follows:

1. Silicone stopcock grease, which was applied by swabbing the inner surface of the tube with a pipe cleaner coated with the silicone

grease. After a thin layer of grease had been applied, the grease and the tube were gently flamed.

2. Paraffin wax, applied by either dipping the end of the tube into a solution of paraffin in benzene and allowing the benzene to evaporate, or by simply dipping the end of the tube into molten paraffin and allowing the paraffin to solidify while the tube was rotated to insure an even coating.

3. Ceresin wax, which was applied in a manner similar to the paraffin wax.

4. Desicote anti-wetting film (General Electric Company Dri-film 9987, a clear, liquid mixture of methylchlorosilanes), applied by dipping the tube into the liquid and allowing the solvent to evaporate and thus deposit a film on the glass surface.

5. Lucite plastic, by forming the plastic into a bushing which was sealed to the tube with red sealing wax.

6. Platinum, by forming platinum foil into a cylinder, inserting it into the tube, and sealing the platinum to the glass by means of heat. Initially, the platinum surface was untreated; while in later experiments, the surface was treated with sodium-mercury amalgam and the sodium dissolved from the amalgam by immersing the tip of the tube in distilled water, thus leaving the mercury wetting the platinum. This platinum surface was further modified so that instead of having a platinum cylinder in the tube, a thin platinum disk was cemented into the tube with silver chloride cement. A hole was drilled through the cement and the platinum disk at its center, leaving a thin ring of platinum exposed to the mercury. This platinum ring was treated as above with sodium-mercury amalgam to improve the adherence of the mercury to the platinum surface.

7. Gold, by cementing a thin gold disk into the tube with silver chloride cement, drilling a hole through the cement and gold disk at its center, and allowing the thin gold ring to amalgamate with mercury.

8. Copper, by placing a cylinder of copper foil inside the glass tube and sealing the copper to the glass by means of heat. Another modification of this surface was made by sealing a thin copper disk into the tube with silver chloride cement and drilling a hole through the cement and copper disk at its center. Both the cylinder and the disk were treated with sodium-mercury amalgam to make the mercury adhere to the copper.

9. Nickel, by placing a cylinder of nickel foil inside the tube and sealing the nickel to the glass by means of heat. The nickel surface was then treated with sodium-mercury amalgam in an unsuccessful attempt to get the mercury to adhere to the nickel foil.

In order to achieve the second objective, various procedures were tried to facilitate the entry of the solution between the glass surface of the tube and the mercury, and various modifications of the tube were attempted. The procedures used and modifications attempted were as follows:

1. Use of detergent, with the solid form being added to the solution in the electrolysis cell, while the tip of the tube was dipped into the liquid detergent and washed with distilled water.

2. Use of the solution to be electrolyzed to wet the various inside surfaces of the tube prior to electrolysis of the solution.

The arrangement of the various surfaces and the modifications of the glass tube are shown in Figure 4.

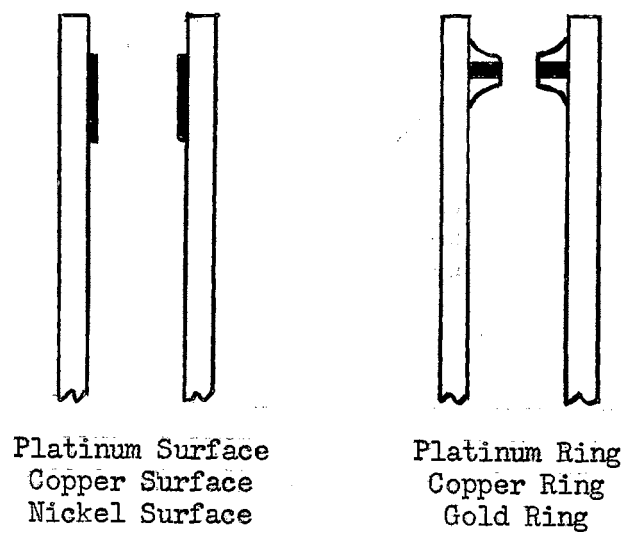
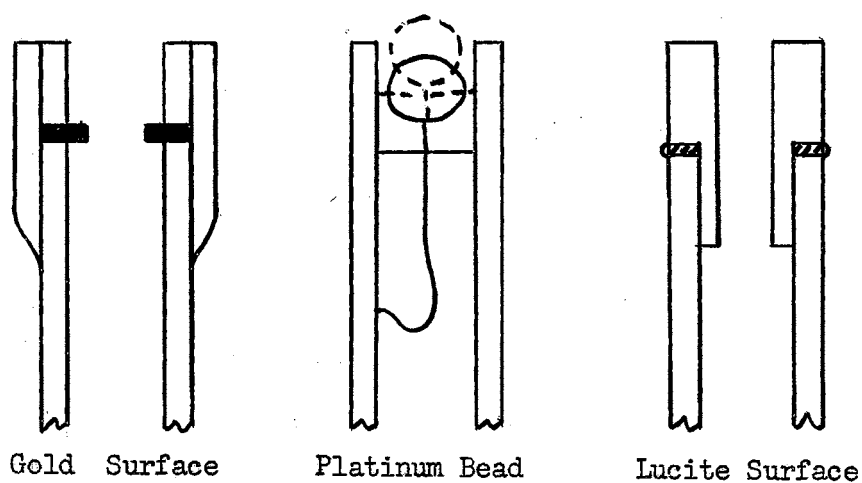


Figure 4. Electrodes

RESULTS AND DISCUSSION

The polarograms obtained with the first form of the electrode tube, an untreated glass tube filled with mercury until its level was even with the top of the glass tube, are shown in Figure 5. As mentioned earlier, with solutions containing only the supporting electrolyte as well as those containing cadmium, the curves obtained were smooth, except for a slight irregularity at -1.2 or more volts. This irregularity, which was found to be caused by solution creeping into the electrode tube, was present on most of the polarograms obtained with this electrode and became progressively more pronounced with succeeding electrolyses.

When the irregularity due to wetting did not occur at -1.2 volts, electrolysis of the solution to a sufficiently negative potential, usually close to that of the decomposition potential of the supporting electrolyte, frequently caused another irregularity to appear, generally in the neighborhood of the decomposition wave.

Prevention of Wetting.

Silicone Surface Electrode Tube. The first attempt to remove the wetting irregularity by preventing the entry of solution into the electrode consisted of coating the inside wall of the glass tube with silicone stopcock grease. This electrode was tested by running eight polarograms on 1 mM cadmium ion solution.

Fairly well-defined waves were obtained, with the limiting current plateau tending to be only slightly irregular. Gentle flaming of the silicone coating to make it smoother and thinner did not greatly alter the results. No wetting was observed until the decomposition potential

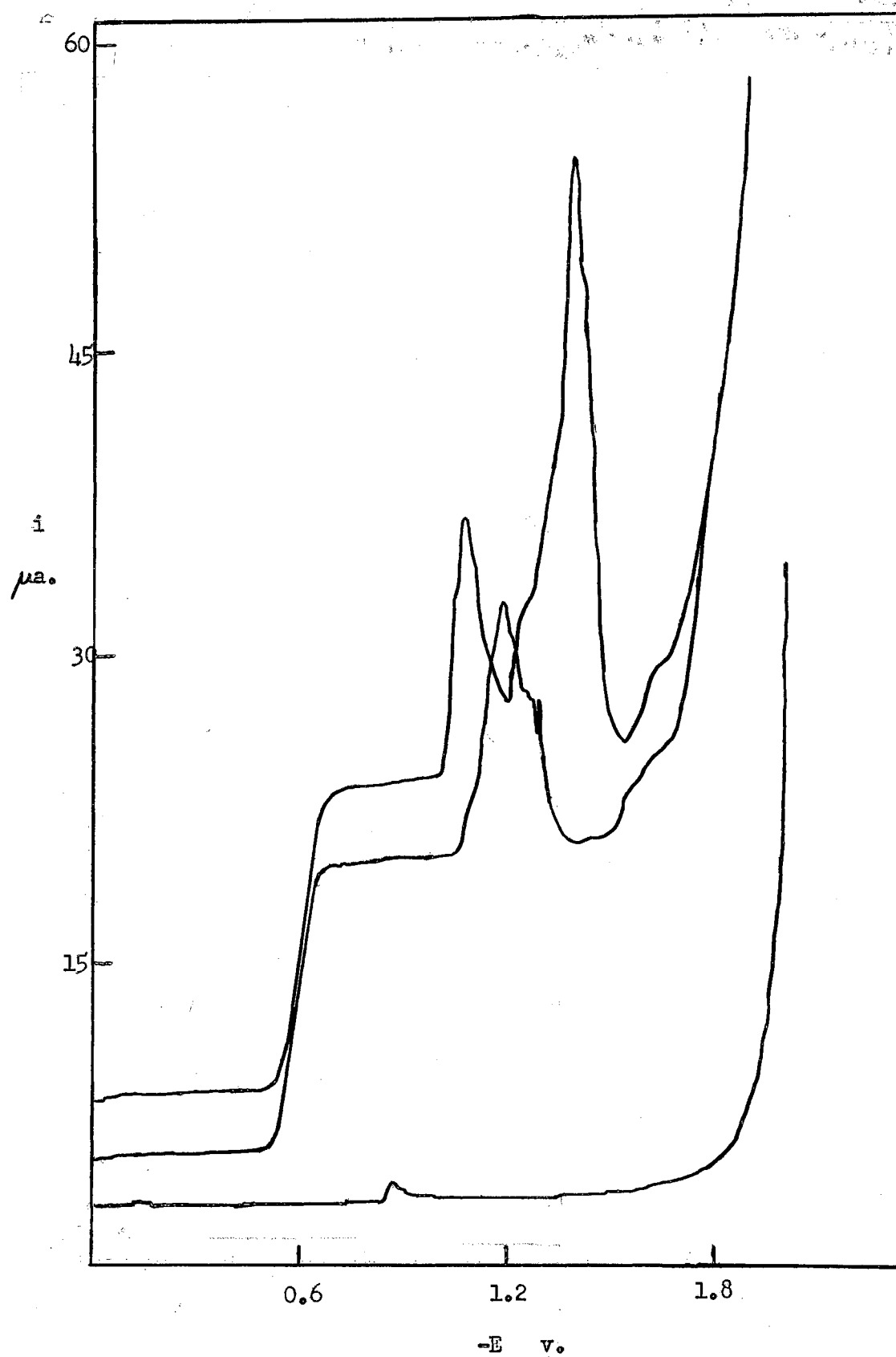


Figure 5. Polarograms obtained with untreated glass electrode tube.

of the supporting electrolyte was approached, when small irregularities and wetting were again noted. The irregularities caused by wetting at approximately -1.2 volts were thus definitely reduced when the silicone coating was used, though the silicone did not remove the wetting irregularities which appeared on the decomposition wave.

Since the removal of the wetting irregularity on the decomposition wave was not accomplished by the application of a coating of silicone stopcock grease to the electrode tube, further investigation with this surface was discontinued.

Paraffin Wax Surface Electrode Tube. The second attempt to prevent the occurrence of irregularities due to the entry of solution into the tube consisted of applying a coating of paraffin wax to the inner surface of the glass tube.

The wax coating was applied either by dipping the tube into molten paraffin or into a solution of paraffin dissolved in benzene and then evaporating the benzene. It was found simpler to dip the tube into molten wax. An even coating of wax was deposited by rotating and inverting the tube while the wax was solidifying.

Cadmium ion solution was electrolyzed using this electrode and the improvement in the shape of the curve due to the use of paraffin may be seen in Figure 6. The irregularity on the limiting current of the wave seemingly was removed; however, further studies indicated that the wetting of the electrode was only delayed through the use of paraffin, since solution was observed to enter the electrode towards the end of the electrolysis. This entrance of solution lead to an irregularity which appeared in the vicinity of the decomposition wave rather than near the usual -1.2 volts position.

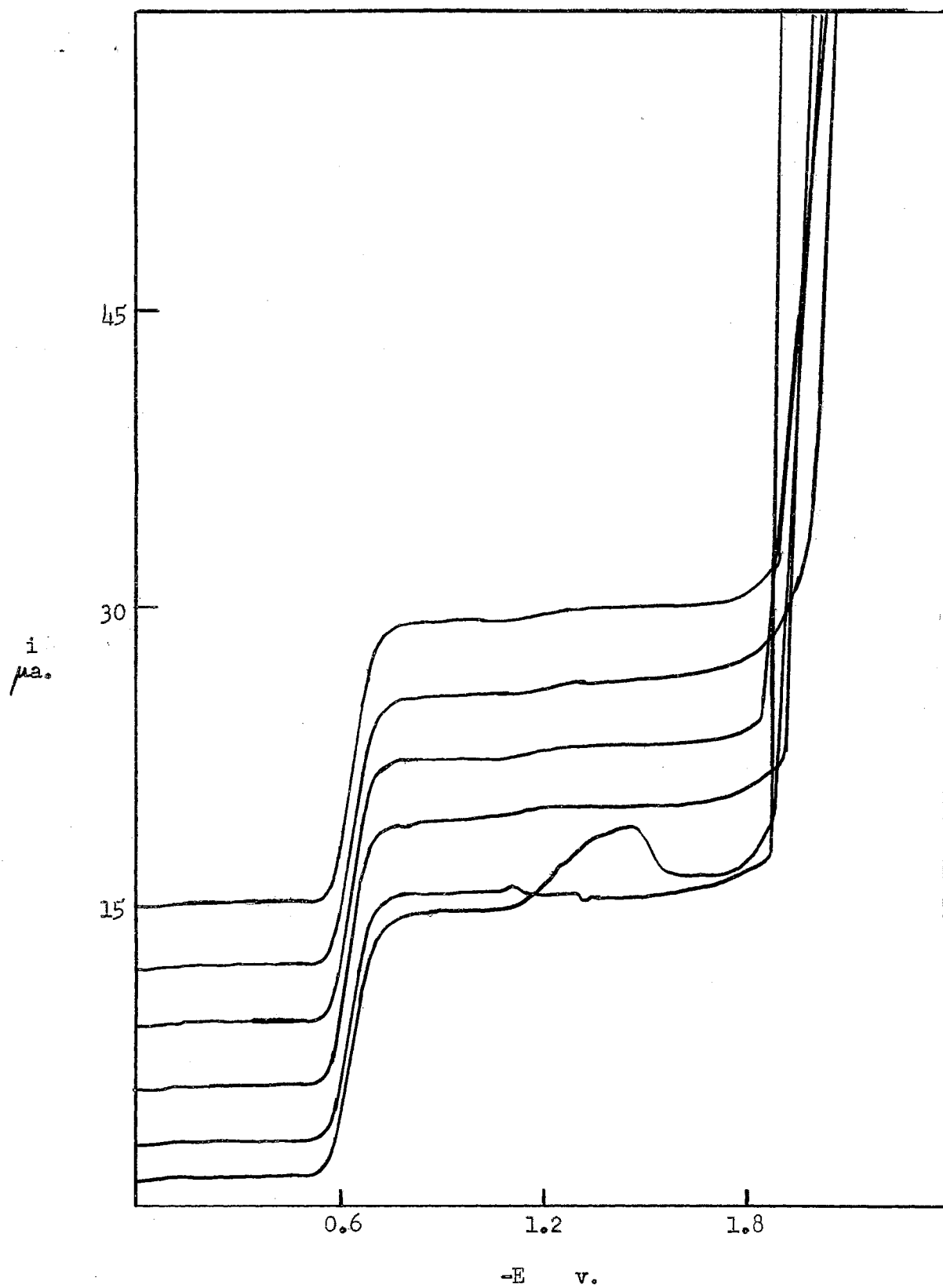


Figure 6. Polarograms obtained with paraffin wax surface electrode tube.

During one electrolysis, when the irregularity began to manifest itself, electrolysis was stopped and the potential allowed to remain constant for a time. When this was done, the current slowly returned to its original value. When the electrolysis was then continued, a well-defined wave was obtained. This phenomenon indicated that the film of solution was stabilizing itself, and these observations led to the formulating of the "conditioning" technique described earlier under "Procedure."

Cadmium ion solution was electrolyzed with this electrode to determine whether the results obtained would be affected by the amount of damping which had been employed during electrolysis. When maximum instrument damping was used, no fluctuations of the current other than those previously mentioned were recorded. As damping was decreased, however, small fluctuations apparently caused by the stirring itself were observed. These fluctuations showed up more clearly when no damping was used.

Solutions of zinc ion and of mixtures of lead and cadmium ions and of cadmium and zinc ions were also electrolyzed with the paraffin wax surface electrode. Well-defined waves resulted. The polarographic constants calculated from these polarograms are given in Table 1.

Table 1

Half-wave Potential* and Diffusion Current of mM Pb⁺⁺, Cd⁺⁺,
and Zn⁺⁺ in 0.1N KCl at Room Temperature

Paraffin Wax Surface Electrode Tube
Outside Stirrer

No.	Sensi- tivity $\mu\text{a./mm.}$	Electrode Size mm.	Pb ⁺⁺		Cd ⁺⁺		Zn ⁺⁺		$\frac{i_d \text{ Cd}^{++}}{i_d \text{ Zn}^{++}}$
			$-\frac{E_{1/2}}{v.}$	i_d $\mu\text{a.}$	$-\frac{E_{1/2}}{v.}$	i_d $\mu\text{a.}$	$-\frac{E_{1/2}}{v.}$	i_d $\mu\text{a.}$	
117	0.15	1.7	0.422	6.75	0.641	4.80			
118	0.15	1.7	0.420	6.60					
119	0.15	1.7	0.426	5.25	0.649	5.55			
104	0.30	1.7			0.617	4.20			
105	0.30	1.7			0.605	4.20			
106	0.30	1.7			0.623	4.20			
107	0.30	1.7			0.635	3.90			
72	0.30	1.7			0.634	6.00	1.071	6.90	0.87
73	0.30	1.7			0.634	6.45	1.041	6.30	1.02
74	0.30	1.7			0.640	7.50	1.052	7.50	1.00
75	0.30	1.7			0.629	4.65	1.032	4.50	1.03
87	0.60	3.4					1.150	36.0	
88	0.60	3.4					1.118	39.6	

*Half-wave potentials given are vs. the S.C.E. and have been corrected for iR drop.

With the cadmium-zinc solution, the ratio of the diffusion current of the cadmium wave to the diffusion current of the zinc wave was calculated as a check on the results obtained. Both ions have approximately the same diffusion coefficient and both are doubly charged. Consequently, if both ions are present at the same concentration, it would be expected that their wave heights would be approximately the same and that the ratio of their heights would be close to unity.

The deviation of this ratio from unity (Polarograms 72 to 75, Table 1) even in cases where there was good agreement in the magnitude of the diffusion currents indicates that some factor other than the setting of the mercury surface is affecting the magnitude of the current

obtained. In the course of these electrolyses, solution was seen to enter the electrode. Since irregularities due to the creeping of the solution tend to confine themselves to the latter half of the polarogram, it might be expected that the zinc wave would be affected more than the cadmium wave. Since these irregularities usually manifested themselves as an increase in the current, this could account, at least in part, for the higher diffusion current of the zinc wave and the consequent low value of the ratio.

Of the eight sets of values obtained with this electrode using a solution of cadmium and zinc ions, the first four are considered reliable since they were calculated from well-shaped curves.

While the use of a paraffin wax surface in the glass tube led to improved behavior of the electrode, the irregularity due to entry of the solution at the decomposition potential was still obtained. The paraffin wax surface was abandoned in favor of a ceresin wax surface.

Ceresin Wax Surface Electrode Tube. The next modification of the glass tube to prevent the entry of solution consisted of coating the tube with a layer of ceresin wax. Ceresin wax has a lower dielectric constant than paraffin wax, and it was expected that the solution would have less tendency to wet the ceresin wax and enter the electrode tube. When this electrode was used with a solution of cadmium ion, well-shaped waves (Figure 7 and Table 2) were obtained.

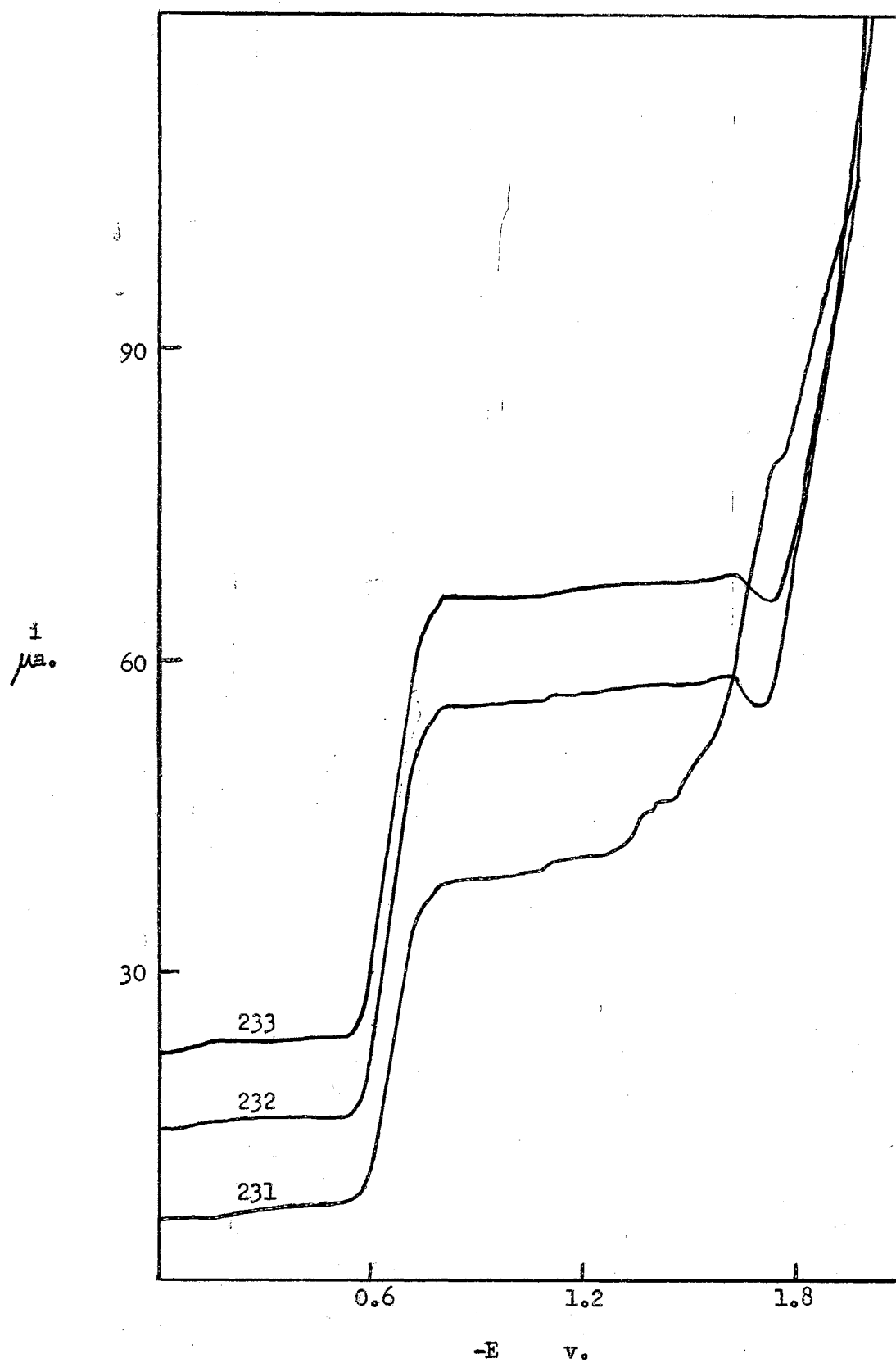


Figure 7. Polarograms obtained with ceresin wax surface electrode tube.

Table 2

Half-wave Potential* and Diffusion Current of 1 mM Cd⁺⁺
in 0.1N KCl at Room Temperature

Ceresin Wax Surface Electrode Tube
Outside Stirrer

No.	$-E_{1/2}$ v.	i_d $\mu a.$
231	0.654	30.6
232	0.632	39.6
233	0.643	42.0

*Half-wave potentials are given vs. the S.C.E. and have been corrected for iR drop.

Of the three polarograms recorded, the first contained a non-representative curve, since, though the wave itself was well-defined, the diffusion current was not of the same magnitude as on the next two polarograms. This behavior, which is due to the initial entry of solution into the electrode, has been observed with many of the other electrode surfaces investigated and its consideration will be deferred until later in the discussion.

On the next two polarograms, after the limiting current reached its peak value, it became constant for a short while, then increased gradually, and decreased suddenly at the transition from the limiting current to the decomposition wave. This behavior in the current caused a dip (Figure 7) to appear on the polarogram. On both polarograms, the bottom of the dip was on a line with the horizontal portion of the limiting current. Of all the surfaces investigated, the ceresin wax surface electrode tube was found to yield the best results.

Desicote Surface Electrode Tube. Another modification of the glass tube to prevent the entry of solution consisted of coating the tube with

Desicote, an anti-wetting agent composed of a mixture of methylchlorosilanes. Tubes of 1.7 and 3.0 mm. diameter were dipped into a solution of Desicote and rotated while the Desicote dried so that an even film resulted. The electrode was then filled with mercury and used with a solution of cadmium and zinc ions.

The results obtained with the Desicote surface electrode tube were fair. The cadmium wave was often not well-formed, containing steps and being rounded so that the limiting current was hard to determine. The solution entered the electrode near the end of the electrolysis, causing erratic behavior and indicating that the Desicote film was not too successful in preventing the entry of the solution near the decomposition potential of the solution.

It was found that immersing the electrode overnight in saturated potassium chloride solution aided in improving the performance of the electrode. This treatment was found to give more well-defined waves than when the electrode was immersed in distilled water. The difference in the behavior after these two treatments might possibly be due to the fact that when wetting occurred, the solution entered a film which was different in nature (the film of liquid between the mercury and the wall of the electrode tube).

Since the behavior of this electrode was inferior to that of the ceresin wax coated electrode, further investigation was discontinued.

Plastic Surface Electrode Tube. A modification of the glass tube to prevent solution entry was made by placing a layer of Lucite plastic on the inner surface of the tube (Figure 4). A hole was bored in a Lucite rod and a half-inch length of the rod was fitted into the tube. The Lucite was cemented to the tube with red sealing wax. This electrode was investigated with solutions of zinc ion and of cadmium with zinc ions.

In almost all cases, the residual current of the resultant wave was inclined, while the limiting current of the cadmium wave contained either a peak at its start or a dip near the zinc wave. On solutions of zinc alone, only an occasional dip was encountered. The limiting current of both waves was inclined and only in isolated instances were the residual and limiting currents parallel to one another. Entry of solution occurred near the decomposition potential, causing the decomposition wave to become erratic.

Due to the poor results obtained, no further investigation of this surface was made.

Platinum Surface Electrode Tube. In another attempt to prevent the entry of solution into the electrode tube, a cylinder of platinum foil was sealed into the tube, approximately 7 mm. from the top. To make the mercury wet the platinum and thus prevent the entry of solution into the electrode tube, the platinum surface was coated with sodium-mercury amalgam. The sodium was dissolved from the amalgam by immersing the tube in distilled water. When the tube was dried and filled with mercury, it was found that the mercury wet the platinum surface. This electrode was investigated with the outside stirrer using cadmium ion solution as well as potassium chloride, lithium chloride, and tetramethylammonium chloride supporting electrolyte solutions.

It was found that a well-shaped cadmium wave was obtained with this electrode even though the limiting current was slightly inclined and contained a dip at the transition to the decomposition wave. The polarographic constants are recorded in Table 3. Electrolysis of the supporting electrolyte solutions also yielded well-shaped curves. When lithium chloride solution was electrolyzed, bubbles of gas were evolved. These supporting electrolytes were also investigated with the D.M.E. and their decomposition potentials measured (Table 4).

Table 3

Half-wave Potential* and Diffusion Current of 1mM Cd⁺⁺ in 0.1N KCl
at Room Temperature with Different Type Stirrers

Platinum Surface Electrode Tube

No.	Sensitivity $\mu\text{a.}/\text{mm.}$	$-E_{1/2}$ v.	i_d $\mu\text{a.}$
Outside Stirrer			
182	0.60	0.656	47.4
183	0.30	0.649	50.7
184	0.80	0.644	46.4
Inside Stirrer			
180	0.60	0.606	17.4
181	0.60	0.594	19.2

*Half-wave potentials given are vs. the S.C.E. and have been corrected
for iR drop.

Table 4

Decomposition Potentials* of Supporting Electrolyte Solutions
Measured with the D.M.E. and Platinum Surface Electrode Tube

Platinum Surface Electrode
Outside Stirrer

No.	Sensitivity $\mu\text{a.}/\text{mm.}$	Supporting Electrolyte	Concn.	$-E_d$ v.
189	0.60	KCl	0.1N	1.86
190	0.60	KCl	0.1N	1.84
191	0.60	KCl	0.1N	1.87
192	0.60	LiCl	0.1N	1.82
200	0.60	Me ₄ NCl	0.1M	1.89
201	0.60	Me ₄ NCl	0.1M	1.92
202	0.60	Me ₄ NCl	0.1M	1.95
203	0.60	Me ₄ NCl	0.1M	1.97

Dropping Mercury Electrode

208	0.06	KCl	0.1N	2.015
209	0.06	LiCl	0.1N	2.230
210	0.06	Me ₄ NCl	0.1M	2.304

*Decomposition potentials given are vs. the S.C.E. and have been
corrected for iR drop.

The effect of coating the glass surface above the platinum cylinder with ceresin wax was investigated using potassium chloride supporting electrolyte solution. On the first electrolysis, the mercury was even with the top of the tube and the solution was in contact with the platinum. The residual current on the resulting polarogram was smooth and slightly inclined until -1.34 volts was reached. The current then suddenly increased and formed a series of steps until the decomposition wave was reached, where the current continued to rise in a smooth manner. On the next electrolysis, the mercury was placed 1 mm. above the top of the tube, and none of the platinum surface was exposed to the solution. The supporting electrolyte curve contained a small step at a potential more negative than that of the sudden rise in the preceding polarogram. A third electrolysis, conducted under the same conditions as the second, yielded a polarogram containing an almost perfectly-shaped supporting electrolyte curve.

From these polarograms, which are shown in Figure 8, it can be seen that the ceresin wax surface above the platinum surface helped improve the behavior of the electrode, though probably not until the wax surface had become wet with solution. The wax had become wet because electrolysis was conducted until the decomposition wave was obtained, which usually resulted in solution entering the electrode.

This electrode was modified by sealing a platinum disk into the tube with silver chloride cement. When the cement had hardened, a hole was bored through it and the disk, so that a ring of platinum was exposed. This electrode (Figure 4) was then treated with sodium-mercury amalgam and the sodium dissolved with distilled water. The resulting electrode was investigated with cadmium ion.

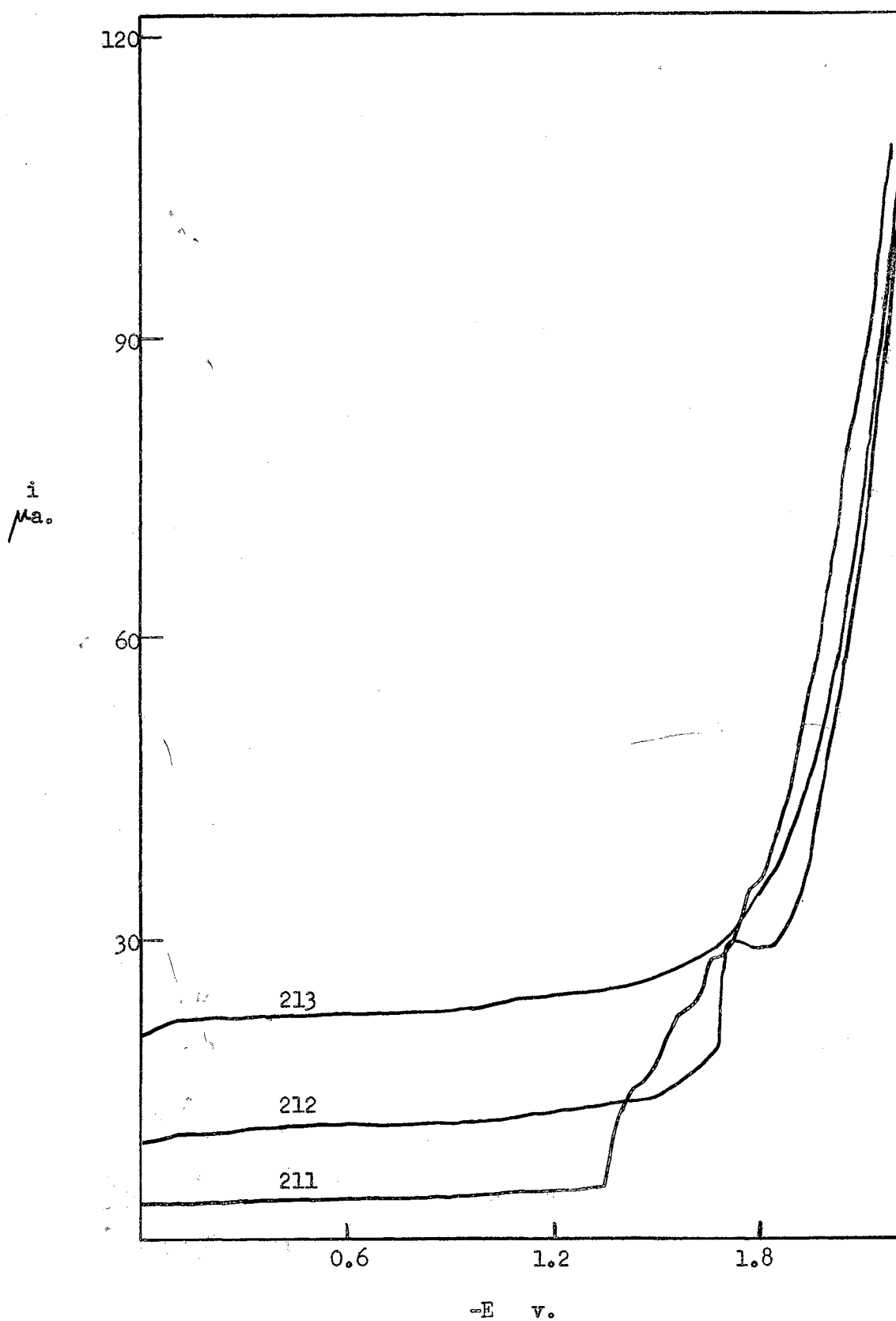


Figure 8. Polarograms obtained with the platinum surface electrode tube containing ceresin wax above the platinum.

It was concluded that the platinum surface electrode tube was capable of yielding reproducible results and that in its behavior, it compared very favorably to that of the ceresin wax surface electrode tube. Entry of solution into the electrode did not appear to occur until the region of the decomposition wave was reached. In an effort to prevent solution from entering the electrode in this region, other metal surfaces were investigated.

Gold Surface Electrode Tube. In an attempt to prevent the entry of solution in the region of the decomposition wave, a gold ring was sealed into the glass tube. Two gold surface electrodes were constructed. The first consisted of a gold disk sealed in place by shrinking the glass tube; while in the second, the gold disk was held in the tube with silver chloride cement. A hole was drilled through the center of each disk and the exposed gold surface was left in contact with the mercury overnight to allow the mercury to amalgamate with the gold. The two electrodes are shown in Figure 4.

The first of these electrodes was investigated using a solution of cadmium and zinc ions. Of the seven polarograms recorded with this solution, the first contained three waves instead of the expected two; on the next six, only one wave, corresponding in position to the first wave on the first polarogram, was obtained. During some of the electrolyses, it was observed that gas bubbles appeared on the mercury surface and that solution entered the tube. The decomposition wave of the supporting electrolyte was found to be extremely erratic, containing both steps and peaks.

When electrolysis was conducted without the stirrer in motion, the first and second waves were obtained.

When a solution containing only zinc ion was electrolyzed with stirring, two waves were obtained instead of the one expected. Addition of a slight amount of solid zinc salt to the solution showed that the second of the two waves obtained with the zinc solution was due to the zinc ion, since this wave increased in height. When solid cadmium chloride was added to the solution of cadmium and zinc ions (the one which had yielded three waves), the second of the three waves was found to be due to cadmium. The half-wave potentials of cadmium and zinc were more negative than the values reported in the literature of the D.M.E. and, in addition, more negative than values which had been obtained with any of the electrodes used in this study. In order to determine whether the small wave was due to lead ion present as an impurity in the potassium chloride supporting electrolyte, a slight amount of solid lead salt was added to the solution. A wave due to lead was obtained, but it occurred at a potential more negative than that of the small wave. This small spurious wave was never identified; therefore, there is some reason to suspect that it might be due to cathodic reduction of some of the silver chloride cement.

During the electrolysis of the cadmium and zinc ions solution, it was observed that a dark substance or deposit appeared on the mercury surface. This behavior occurred three times, but the nature of the deposit or its cause could not be determined.

Wetting of the electrode with solution having been observed when the above runs were made, it was decided that the gold was not well sealed to the glass. The second of the gold ring electrodes described earlier was therefore constructed.

When solutions of zinc ion and of cadmium and zinc ions were electrolyzed with this new electrode, results were better. The zinc

wave was fairly well-defined and its polarographic constants could be readily determined. With the cadmium and zinc ions solution, the two expected waves were present. Solution was observed to enter the electrode until it reached the gold ring, but not beyond.

It was observed in drying the electrode with filter paper, however, that some grayish substance resembling the silver chloride cement was removed from the electrode. Particles of this substance could also be seen on the mercury displaced from the electrode during surface renewal. This grayish deposit, which had also been observed with the platinum ring electrode containing silver chloride cement, seemed to appear whenever the mercury was left in contact with the cemented gold surface. In order to prevent formation of this substance when the electrode was not in use, therefore, the mercury was kept below the gold disk.

So many of the polarograms obtained with the gold surface electrode contained irregularities that the solutions were again electrolyzed with the D.M.E. in order to determine whether any polarographically determinable impurities were present. The results showed that none were present. Owing to the fact that it appeared impossible to make the electrode yield reproducible, well-formed waves, experiments with it were discontinued.

Copper Surface Electrode Tube. A copper surface was next investigated in an attempt to prevent the solution from entering the electrode tube. A cylinder of copper foil was inserted into the glass tube and sealed in place by heating the glass. The copper surface was treated with sodium-mercury amalgam and the sodium dissolved with distilled water. The electrode was investigated with the outside stirrer using potassium chloride supporting electrolyte solution.

The results obtained with this electrode were somewhat disappointing. It was found that even with only the supporting electrolyte present, an appreciable current was obtained at the start of the polarogram, followed by a wave which was well-defined on some polarograms and quite erratic on others. Since the electrode would not work even on supporting electrolyte solutions, no electrolyses were tried with reducible ions present.

Another copper ring electrode, therefore, was constructed by cementing a copper foil into the tube with silver chloride cement. When the cement hardened, a hole was drilled through the cement and the copper disk, exposing a thin ring of copper. The electrode was then treated with sodium-mercury amalgam and the sodium dissolved with distilled water. This electrode was investigated with cadmium ion solution in potassium chloride.

The results obtained with this modification of the copper surface electrode were even poorer than had been obtained with the first one. An Ohm's-law type of curve was obtained during the first portion of the polarogram, while the curve consisted of a series of haphazard up-and-down deflections on the remainder. Wetting the copper ring with solution prior to electrolysis was found not to improve the results. In view of the erratic behavior of the electrode, further investigations with the copper surface electrode tube were therefore discontinued.

Nickel Surface Electrode Tube. The use of a nickel surface to prevent entry of solution into the electrode tube was the last one investigated. The nickel surface electrode tube was constructed by sealing a cylinder of nickel foil to the inside surface of the glass tube. This surface was then treated with sodium-mercury amalgam and investigated with potassium chloride supporting electrolyte.

The results obtained with this electrode were as disappointing as those obtained with the copper surface electrode. A typical supporting electrolyte curve could not be obtained. The current was increasing at the start of the electrolysis in some cases, and shortly after the start in others. The current then became relatively constant for a short time, after which the decomposition wave was obtained. A smoother curve was obtained with the nickel surface electrode than with the copper surface electrodes.

Due to the poor results obtained with the nickel surface electrode, further investigations were discontinued.

Facilitation of Wetting.

The surfaces thus far discussed were selected in an attempt to prevent the entry of solution into the electrode tube. Not all surfaces tested were able to accomplish this. Some of them prevented the entry of solution until the decomposition wave of the solution was reached, where they were no longer effective. Other surfaces were even less successful. The one investigated which was capable of preventing the entrance of solution completely (i. e., the gold ring type) yielded such poor results that well-defined waves could not be obtained consistently.

Nevertheless, the first objective had largely been obtained. The entry of solution over the polarographically useful range of this form of stationary microelectrode had been prevented and the resultant polarograms were free of irregularities. The attainment of the second objective, namely, to facilitate the entry of solution in order to achieve complete wetting of the electrode in the hope of preventing further wetting and the occurrence of the irregularity as a consequence of it, was then undertaken.

Use of Detergent. The first procedure attempted to facilitate the entry of solution consisted of the use of detergents. Both the addition of solid detergent to the solution undergoing electrolysis and the dipping of the electrode into liquid detergent were tried.

An untreated glass electrode tube was investigated with cadmium ion, cadmium and zinc ions, and potassium chloride supporting electrolyte solutions containing a small amount of detergent (Atlantic Refining Company Ultrawet K). Results were very poor, the behavior of the electrode being very erratic. With solutions containing reducible ions, non-reproducible waves were obtained, while the supporting electrolyte solution alone yielded waves when none should have been present.

In the final experiments involving the use of a detergent, an untreated glass electrode was dipped into the liquid detergent, after which the electrode was washed several times by filling with distilled water and allowing the water to drain through the tip. The top portion of the electrode tube was wet with distilled water prior to each electrolysis of zinc ion solution.

The results indicated that the shape of the wave had improved. While decreases in the limiting current were still obtained at the start of the decomposition wave, the residual and limiting currents were horizontal and the wave was well-shaped.

On the first polarogram of this series, solution was seen to enter the tube when the decomposition wave started. The current increased and at the point where the current became constant, bubbles of liquid were seen in the capillary tube, after which the tube suddenly became wet. When the current again increased, the bubbles of liquid moved towards the top of the electrode tube. It was observed that the mercury was now

above the top of the electrode tube. When electrolysis was finally completed, the inner surface of the tube was wet with liquid 3.5 to 5.0 cm. below the top of the electrode. This large amount of wetting did not occur when the tube contained a ceresin wax surface.

Wetting With Solution. In the course of investigating the performance of the paraffin wax surface electrode, it was observed that while irregularities due to the creeping of solution into the electrode were eliminated, occasionally a poorly-shaped wave was obtained.

At first, it was thought that the use of a wax surface would yield improved results only in a majority of cases and that one had to resign himself to a poorly-shaped wave every now and then. Later investigations indicated that this was not the case. No matter what was tried to prevent the entry of solution, it was found that when electrolysis was continued until the decomposition wave was reached, solution invariably entered the electrode. It was also noted that the later polarograms in any series of runs were relatively free of any undesirable oddities caused by wetting, provided that the solution was always electrolyzed to approximately the same applied voltage (Figure 9). It was finally concluded that the entry of solution occurring on the first electrolysis was beneficial. While the initial entry of solution caused irregularities due to the erratic entrance of solution into the electrode, once the first electrolysis had been completed the mercury was left surrounded with a relatively stable film of solution. It was this behavior that suggested the "conditioning" treatment described earlier under "Procedure."

The polarographic constants of the waves obtained with wetted and nonwetted electrodes are shown in Table 5. These results illustrate the influence of the entry of solution on the polarographic constant,

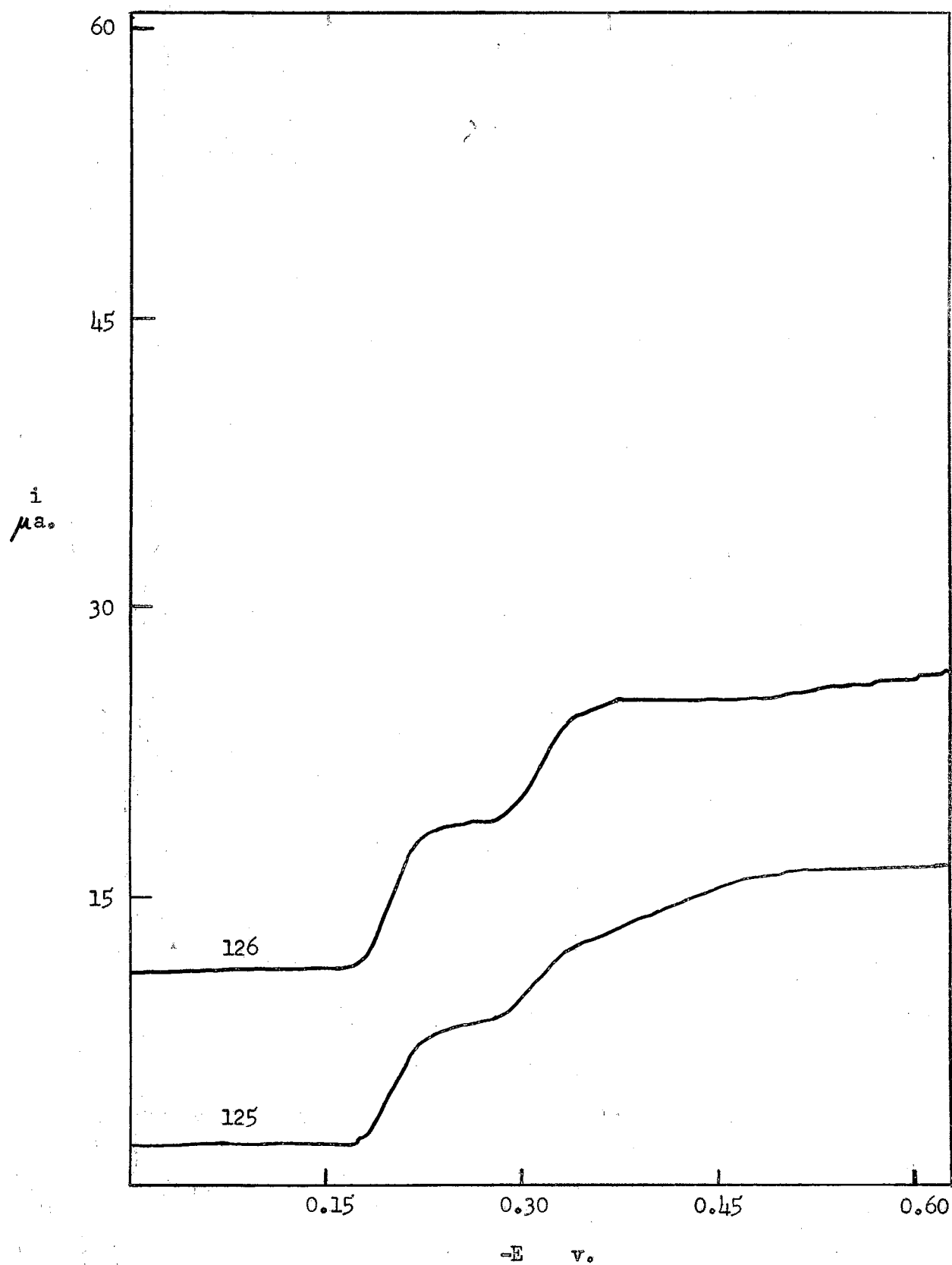


Figure 9. Polarograms showing the influence of wetting.

particularly on the diffusion current. It will be noted that the ratio of the lead diffusion current to the cadmium diffusion current is affected greatly. These values, which should be the same in both cases, are not the same owing to the fact that the entry of solution into the electrode has affected the magnitude of the diffusion currents, especially that of the cadmium.

Table 5

Half-wave Potential* and Diffusion Current of 0.1mM Pb⁺⁺ and Cd⁺⁺ in 0.1N KCl at Room Temperature

Paraffin Wax Surface Electrode
Outside Stirrer

No.	Pb ⁺⁺		Cd ⁺⁺		$\frac{i_d}{i_d} \frac{Pb^{++}}{Cd^{++}}$
	$-E_{\frac{1}{2}}$ v.	i_d $\mu a.$	$-E_{\frac{1}{2}}$ v.	i_d $\mu a.$	
125	0.403	5.70	0.616	3.60	1.58
126	0.408	7.50	0.632	6.60	1.14

*Half-wave potentials given are vs. the S.C.E. and have been corrected for iR drop.

A series of electrolyses were conducted with the untreated glass tube electrode being wet with distilled water and solution prior to electrolysis. It was found that results were much more constant when the electrode tube was wet with solution than with distilled water. Similar behavior was obtained with the ceresin wax surface electrode tube.

Wetting of the electrode with solution prior to electrolysis was also found to improve the results obtained with the platinum surface electrode. When the same procedure was tried with the Lucite surface surface and gold surface electrodes, the results were not improved.

Influence of Variables.

The influence of the following variables affecting the polarographic constants was investigated with the electrodes used in this study:

1) diameter of glass tube, 2) speed of stirrer, 3) diameter of stirrer and position, 4) non-renewal of mercury surface, 5) type of stirrer, 6) position and setting of mercury meniscus, 7) elevation of mercury surface, 8) change of pH of solution, 9) temperature coefficient, 10) scanning rate, 11) stirring of mercury surface, 12) decreased reducible substance concentration. The influence of all variables was not determined with each electrode used. The influence of most of the above variables was investigated with the ceresin wax surface electrode since its behavior was found to be the best of all electrodes tested.

Diameter of Glass Tube. In order to determine the effect of the diameter of the electrode tube on the magnitude of the diffusion current, five tubes of different diameters were coated with ceresin wax, and a cadmium ion solution was electrolyzed to test the behavior of the electrodes.

In the initial study, the same stirrer tube was used with each electrode tube. As a result, the effect of the electrode size on the diffusion current was influenced by the size of the stirrer tube. In an attempt to overcome this effect, a constant ratio of electrode tube internal diameter to stirrer tube internal diameter was maintained while a second series of electrolyses were run.

Average values for polarographic constants, as calculated from the well-shaped waves, are given in Table 6, while the relation between electrode tube internal diameters and diffusion currents is shown in Figure 10.

Table 6

Influence of Electrode Diameter on Diffusion Current
of 1mM Cd^{++} in 0.1N KCl at 25°C .

Ceresin Wax Surface Electrode Tube
Outside Stirrer

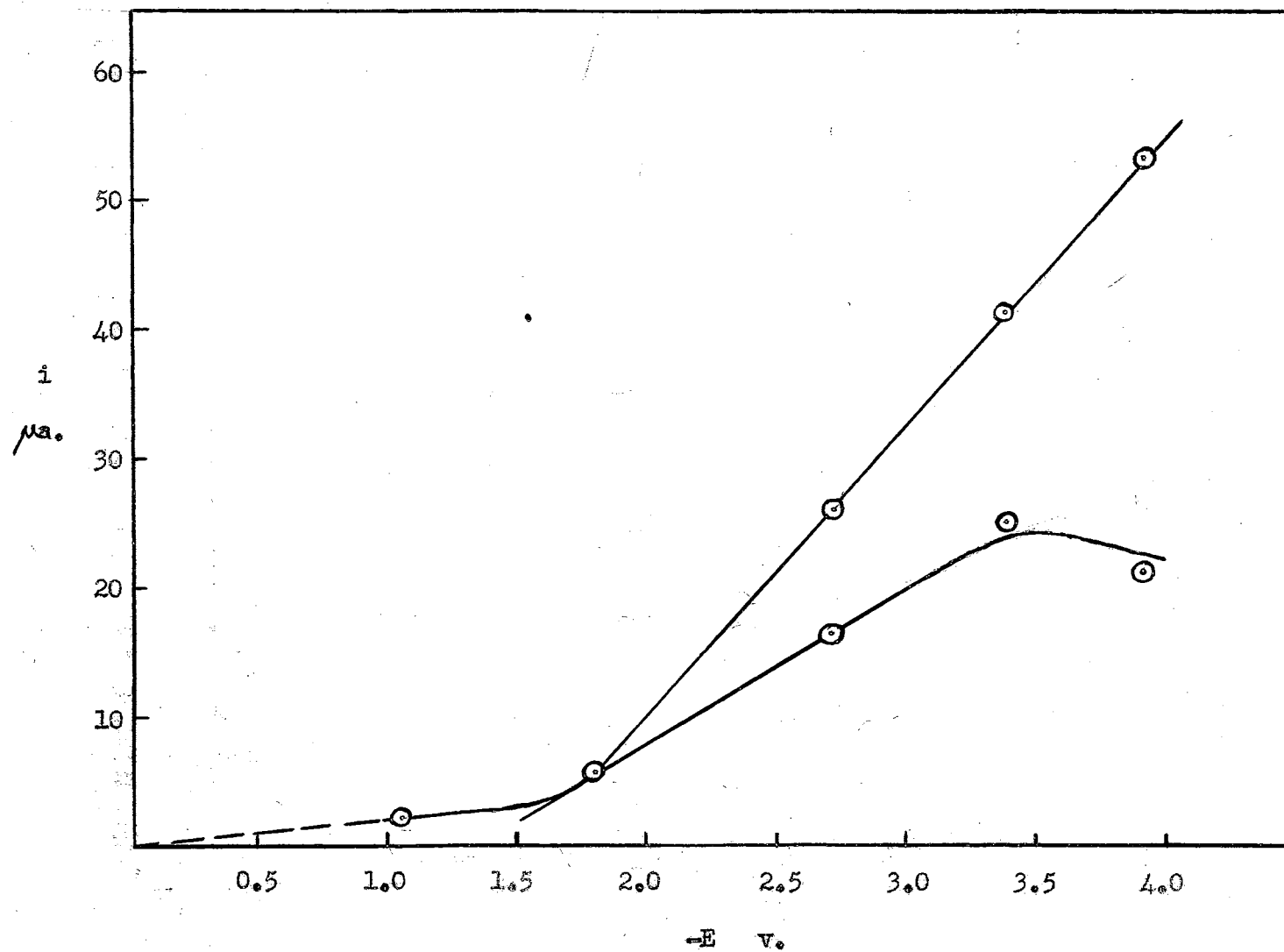
Electrode Diameter mm.	Stirrer Diameter mm.	<u>Electrode Diameter</u> <u>Stirrer Diameter</u>	i_d <u>$\mu\text{a.}$</u>
1.029	7.145	0.144	2.01
1.791	7.145	0.251	5.74
2.710	7.145	0.379	26.0
3.358	7.145	0.470	41.3
3.894	7.145	0.545	53.4
1.791	7.145	0.251	5.74
2.710	7.788	0.348	16.4
3.358	8.146	0.412	25.0
3.894	9.385	0.415	21.2

The results in Figure 10 indicate that the diffusion current increases gradually as the internal diameter of the electrode tube increases. After a diameter of approximately 1.7 mm. is reached, the increase in current is proportional to the electrode tube diameter.

Figure 10 also shows the variation in the diffusion current with the diameter of the electrode tube when a constant ratio was maintained between the internal diameter of the electrode and stirrer tubes. The values in Table 6 show that the ratio of diameters was only approximately constant, but this represented the best choice it was possible to make with the tubing available. The results indicate, however, that the diffusion current increased gradually as the diameter of the electrode increased only until an electrode diameter of 3.4 mm. was reached, after which the current decreased.

The decrease in current with the larger diameter electrode is believed to be due, not to the electrode, but rather to the large

Figure 10. Plot of Diffusion Current vs. Electrode Diameter



diameter stirrer used with the electrode. As will be seen when the results obtained with different diameter stirrers will be considered, the larger diameter stirrer is not as efficient as one of smaller diameter. Hence, it would be expected that the diffusion current would decrease as the diameter of the stirrer increases. This was found to be true with the other larger diameter stirrers; less current was obtained when they were used. The lower efficiency of the larger diameter stirrer is responsible for its diffusion current versus electrode diameter curve being lower than the one obtained with different diameter electrodes and the same size stirrer. With the untreated glass electrode tube, the diameter of the tube did not affect the results if the diameter lay between approximately 1.5 and 3.5 mm. With tubes of diameter smaller than 0.8 mm., difficulty of setting the position of the mercury surface was encountered.

Results obtained with Desicote surface electrodes of 1.7 and 3.0 mm. diameters indicated that the smaller of the two yielded the more consistent behavior, though neither was entirely satisfactory. Both the platinum surface and the paraffin wax surface electrodes yielded well-defined waves regardless of size.

The diameter of the electrode was not found to be critical, provided that electrodes of extremely large and small diameters were avoided.

Speed of Stirrer. In an effort to determine the effect of the speed of stirring on the results obtained, a Welch Scientific Company stirring motor, fitted with an adjusting screw that allowed variation of the speed of revolution, was used to vary the speed of stirring. The motor shaft was connected to the stirrer shaft by a small piece of

rubber tubing. A pulley, to which a gear wheel had been attached, was mounted on the stirrer shaft and a similar gear wheel was attached to a Stewart-Warner Model 757-W portable tachometer mounted on the stirrer support and used to check the speed of rotation. The stirrer motor, attached to a separate ringstand, was not in contact with the cell or stirrer shaft mounting. Constant stirrer speeds of 350 to approximately 1300 r.p.m. were obtainable with this motor.

A solution of cadmium ion was electrolyzed, using the ceresin wax coated electrode and employing stirrer speeds from 400 to 1100 r.p.m. in 100 r.p.m. increments. Since only the polarographic constants of the wave were desired, electrolysis of the solution was stopped at approximately -0.9 volts. Very well-defined cadmium waves resulted, but at speeds of 1000 and 1100 r.p.m., the limiting current of the wave became a little erratic while still remaining essentially horizontal.

The results (Table 7) show that while there is a slight increase in the current as the stirring rate increases, the current stays rather constant. Though the stirrer was rotated at 600 r.p.m. in the investigation of these electrodes, it seems apparent that within the range tested, the stirrer speed does not have to be controlled with very great accuracy.

Table 7

Influence of Stirrer Speed on Diffusion Current
of 1mM Cd^{++} in 0.1N KCl at 25° C.

Ceresin Wax Surface Electrode Tube
Outside Stirrer

No.	Speed R.P.M.	i_d $\mu\text{a.}$	Average* i_d $\mu\text{a.}$
663	400	8.40	
664	500	8.56	
665	600	8.64	
666	700	8.88	
668	800	9.12	
669	900	9.12	
670	1000	9.12	
671	1100	8.80	8.72
660	400	7.68	
	500	8.00	
	600	8.32	
	700	8.72	
	800	8.80	8.30
661	800	8.56	
	700	9.44	
	600	9.52	
	500	9.44	
	400	9.44	9.28
662	400	8.08	
	500	8.24	
	600	8.32	
	700	8.16	
	800	8.00	8.16

*Over 400-800 R.P.M. stirrer range.

In the initial stirring speed experiments, the mercury surface was renewed and set to the top of the electrode tube prior to each electrolysis. Since it had already been shown that the variation in the diffusion current due to the reproducibility of setting the mercury surface was large, a procedure was devised which allowed variation of the stirring speed without requiring renewal of the mercury surface.

With the stirrer rotating at 400 r.p.m., a polarogram was recorded in the conventional manner, except that electrolysis was stopped and the potential allowed to remain constant at -0.9 volts, at which point the limiting current of cadmium had already been reached. The stirrer speed was then increased to 500 r.p.m. and electrolysis was continued at constant potential until the current became constant. This procedure, which was repeated until the stirring speed had been increased to 800 r.p.m. in 100 r.p.m. increments, yielded a short segment of the limiting current at each stirrer speed without requiring renewal of the mercury surface. The residual current obtained with the complete wave at the start of the procedure was used to calculate the diffusion current obtained with each stirrer speed. On the first and third polarograms of this series, the stirrer speed was increased to 800 r.p.m., while on the second, the stirrer speed was initially set at 800 r.p.m. and decreased in 100 r.p.m. intervals to 400 r.p.m. to see if any variation in the diffusion current was obtained. In order to have some means of comparing results, the average value of the current over the 400 to 800 r.p.m. stirrer speed range was calculated (Table 7).

The average value of the current obtained when the mercury surface was renewed and reset between stirrer speed increments agrees well with those obtained when the stirrer speed was increased on the one-mercury-setting electrolyses, while when the stirrer speed was decreased, a higher current resulted. This increase in diffusion current was peculiar since the mercury surface had not been reset and the electrolysis had not been carried to the point where wetting irregularities were usually obtained. Nothing was observed during this particular electrolysis which would serve as a clue to the explanation of such behavior.

At stirring speeds of 1000 and 1100 r.p.m., the limiting current of the cadmium wave was erratic, though still horizontal; and since the stirrer shaft vibrated excessively, higher stirring speeds were not investigated.

The results obtained indicated that the speed of the stirrer was not a critical factor. As long as the stirrer speed was maintained at approximately 600 r.p.m., careful control of the speed was not necessary.

Diameter of Stirrer and Position. In order to determine the influence of the diameter of the stirrer and its position on the diffusion current, stirrer tubes of different diameters were investigated using the ceresin wax surface electrode. These tubes were made of glass, the ends ground smooth, and were attached to the stirrer shaft with collars made of glass and brass. The glass collars were made of the requisite size by using short pieces of close-fitting glass tubing, which were held together by ceresin wax. Ceresin wax was used in attaching the stirrer tubes and stirrer shaft to the collars. The stirrers were positioned so that the bottom of the tube was at various distances, ranging from +0.60 to -1.20 cm., above and below the top of the electrode tube; the positive sign indicates that the stirrer was above the top of the electrode, while the negative sign indicates the stirrer was below. Distances were measured with a cathetometer. A solution of cadmium ion was electrolyzed at 25° C. with the ceresin wax surface using stirrer tubes of various diameters.

The results obtained (Table 8) were generally good, but erratic limiting currents were obtained on many polarograms and determination of polarographic constants was difficult. The erratic results were due to two main causes. First, the glass used in the collars and stirrer

tubes was not always exactly round and secondly, when the tubes were rotated, they did not always run true. This was found to be especially so with the larger diameter stirrer tubes, and the glass collars had to be replaced with collars of brass to improve results.

Table 8

Influence of Diameter of Stirrer and its Position on Half-wave Potential*
and Diffusion Current of 1mM Cd⁺⁺ in 0.1N KCl at 25° C.

Ceresin Wax Surface Electrode
(1.791 mm. Diameter)
Outside Stirrer

Stirrer Tubes**							
	7	9	11	14	16	18	22
Displacement	i_d						
cm.	$\mu a.$						
+0.60		3.10		<u>2.76</u>		4.64	
+0.30	3.70	2.30		<u>3.17</u>	<u>3.90</u>	<u>4.80</u>	
0.00		3.20	3.45	<u>3.68</u>		<u>6.56</u>	<u>4.26</u>
-0.30		5.90	3.45	3.92	<u>3.39</u>	5.20	
-0.60	15.9	6.50		3.96		4.80	
-0.90		7.60		3.92		5.20	
-1.20		9.17		3.76		4.88	
	$-E_1$ $v.$						
+0.60		0.615		<u>0.629</u>		0.643	
+0.30	0.643	0.632		<u>0.617</u>	<u>0.616</u>	<u>0.634</u>	
0.00		0.590	0.621	<u>0.633</u>		<u>0.644</u>	<u>0.618</u>
-0.30		0.615	0.608	0.640	<u>0.619</u>	0.635	
-0.60	0.649	0.625		0.651		0.636	
-0.90		0.606		0.649		0.642	
-1.20		0.613		0.643		0.639	

* Half-wave potentials given are vs. the S.C.E. and have been corrected for iR drop.

**Stirrer tube numbers correspond to outside diameter of standard glass tubing. Internal diameter of each tube was:

No.	Diameter mm.
7	5.001
9	7.145
11	8.827
14	11.255
16	13.457
18	15.913
22	18.608

Representative values of the polarographic constants were selected from all the data obtained with the following criteria in mind: (1) Where well-defined waves had been obtained, all values were used and the average value is given in the table. (2) In the event a given stirrer, set at a given position, yielded only one polarogram containing a well-shaped wave, only the constants determined from the well-shaped wave were used. (3) On polarograms where the limiting current contained several steps showing a gradual increase in current, if the horizontal portion of the wave prior to the first step was of sufficiently long duration, this portion was considered the limiting current of the wave and was used in calculating the polarographic constants. (4) Where none of the polarograms of a series contained a well-shaped wave, the best-formed wave was used to calculate the polarographic constants. These constants are underlined in the table (Table 8) to indicate that their accuracy is lower than the other values.

In spite of the possible error due to vibration of the stirrer in the bushing and to imperfect stirrer tubes, good polarograms were obtained for 22 of the 28 values listed in Table 8.

The selection of 0.3 cm. intervals of displacement of the stirrer tube above and below the electrode tube was purely arbitrary. It was desired to select an interval which was large enough to show significant changes in the current. The 9, 14, and 18 mm. stirrers were positioned over the full range of negative and positive intervals. The 11, 16, and 22 mm. stirrers were set at intervals of -0.3, 1.1, and +0.3 cm. only.

In these experiments it was found that, as the stirrer tube diameter was decreased with the electrode diameter constant, a point was reached where the results became erratic. The 7 mm. stirrer was tested over the

entire range of intervals but only two values are recorded since a peculiar double wave was obtained at other intervals with this electrode. The curve consisted of two waves, a large wave followed by a small one; and while many ways of determining the polarographic constants were considered, it was finally decided that none would yield values of any meaning. Consequently, all values except the two given were discarded.

With the 9 mm. stirrer, the magnitude of the current increased as the stirrer covered a greater portion of the electrode tube. When the stirrer was even with or above the electrode tube, the variation in the current was not regular. This is believed due to the turbulent stirring thought to be present at the bottom of the stirrer. As the stirrer was lowered over the electrodes, the point of turbulent stirring moved away from the top, the solution inside the stirrer tube was rotated more uniformly, and the results became more systematic.

The randomness of the results obtained with the 14 and 18 mm. stirrers indicates that the effectiveness of the stirrer decreases rapidly as the stirrer size increases, owing probably to the turbulence within the stirrer tube. The results in Table 8 show also that the diffusion current was less with the 14 and 18 mm. stirrers than with the 9 mm. stirrer. This was expected, for, barring turbulence, in the exact center of the stirrer the solution may be considered at rest. As we move closer to the glass wall of the stirrer, the speed of movement of the solution increases, the layer of solution touching the stirrer moving at the fastest rate owing to the tendency of the liquid to adhere to the glass. Thus, in going from the center of the solution in the stirrer tube to the glass wall, the speed of the circular motion of the solution increases. Since it has been shown by Muller and others (19) that effective thickness of the diffusion layer is greatly decreased

when the movement of the solution over the electrode surface is fast, and that the diffusion current is thereby greatly increased, the smaller stirrer tubes should give the results observed.

The fact that the current obtained with the 18 mm. stirrer was slightly greater than that obtained with the 14 mm. stirrer appeared to be due to the fact that the 18 mm. tube was somewhat eccentric and thus stirred somewhat more vigorously than usual.

With the 18 mm. stirrer even with the top of the electrode, a greater current was obtained than at any other setting. This was believed due to the turbulence at the bottom of the stirrer.

From the data obtained, it can be seen that the diameter of the stirrer tube and its position with respect to the top of the electrode are somewhat critical. Stirrer tubes must not be too large or too small and must extend an appreciable distance over the electrode tube in order to obtain well-shaped polarograms.

Non-renewal of Mercury Surface. When the mercury surface was not renewed between electrolyses with the untreated glass electrode tube, a new type of irregularity occurred at the start of the limiting current (Figure 11). These new irregularities did not appear to be caused by wetting, but seemed to be caused by some entirely different process. In many cases, non-renewal of the mercury surface resulted in very pronounced anodic currents being obtained, these running in the expected manner into the cathodic wave. The irregularities caused by non-renewal of the mercury surface were eliminated when the mercury surface was changed between electrolyses, as indicated in Figure 12. It should be noted that while renewal of the mercury surface removed the irregularities at the start of the limiting current, it had no effect on the irregularities at the center of the limiting current plateau.

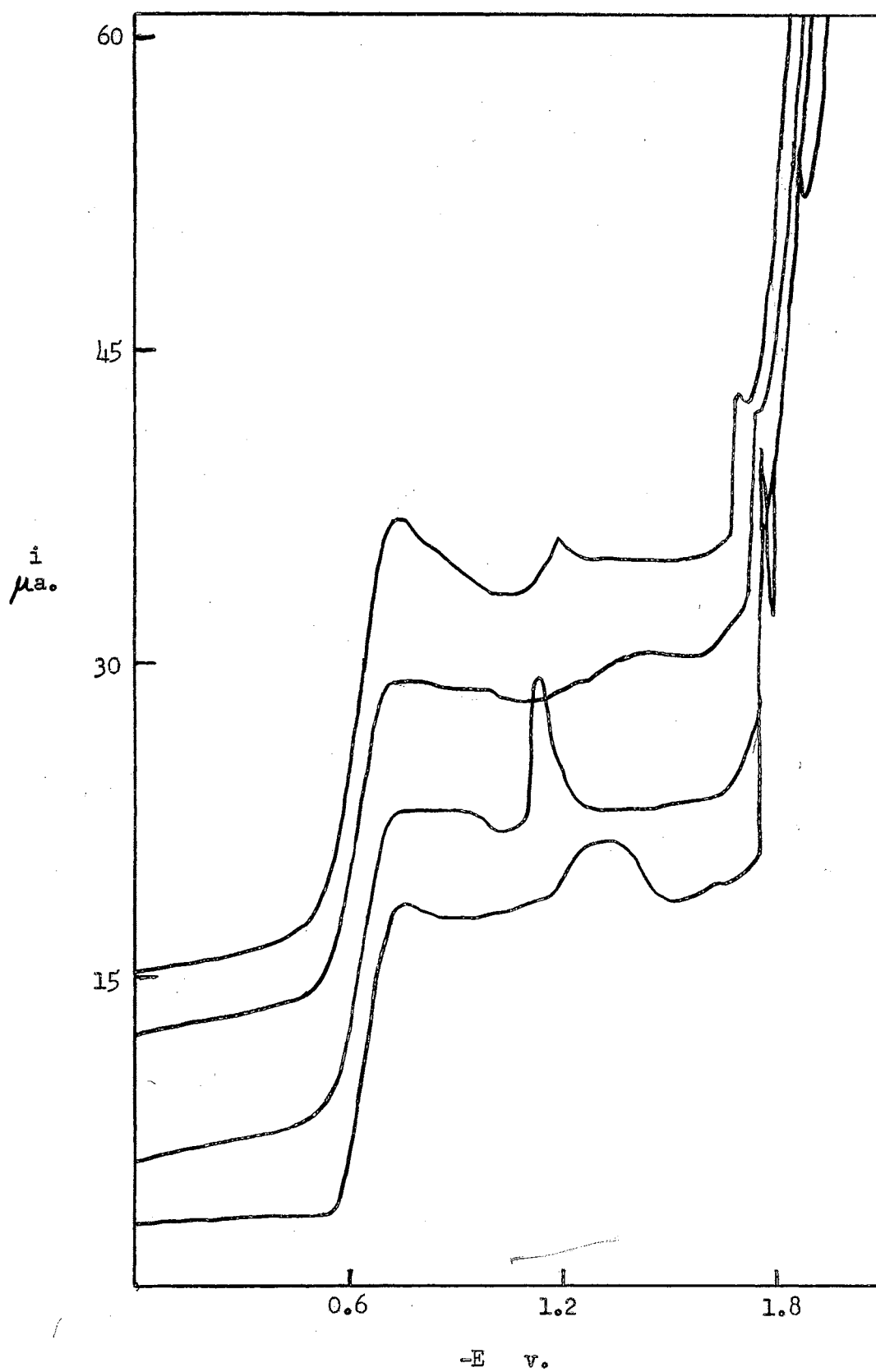


Figure 11. Influence of non-renewal of mercury surface on wave shape.

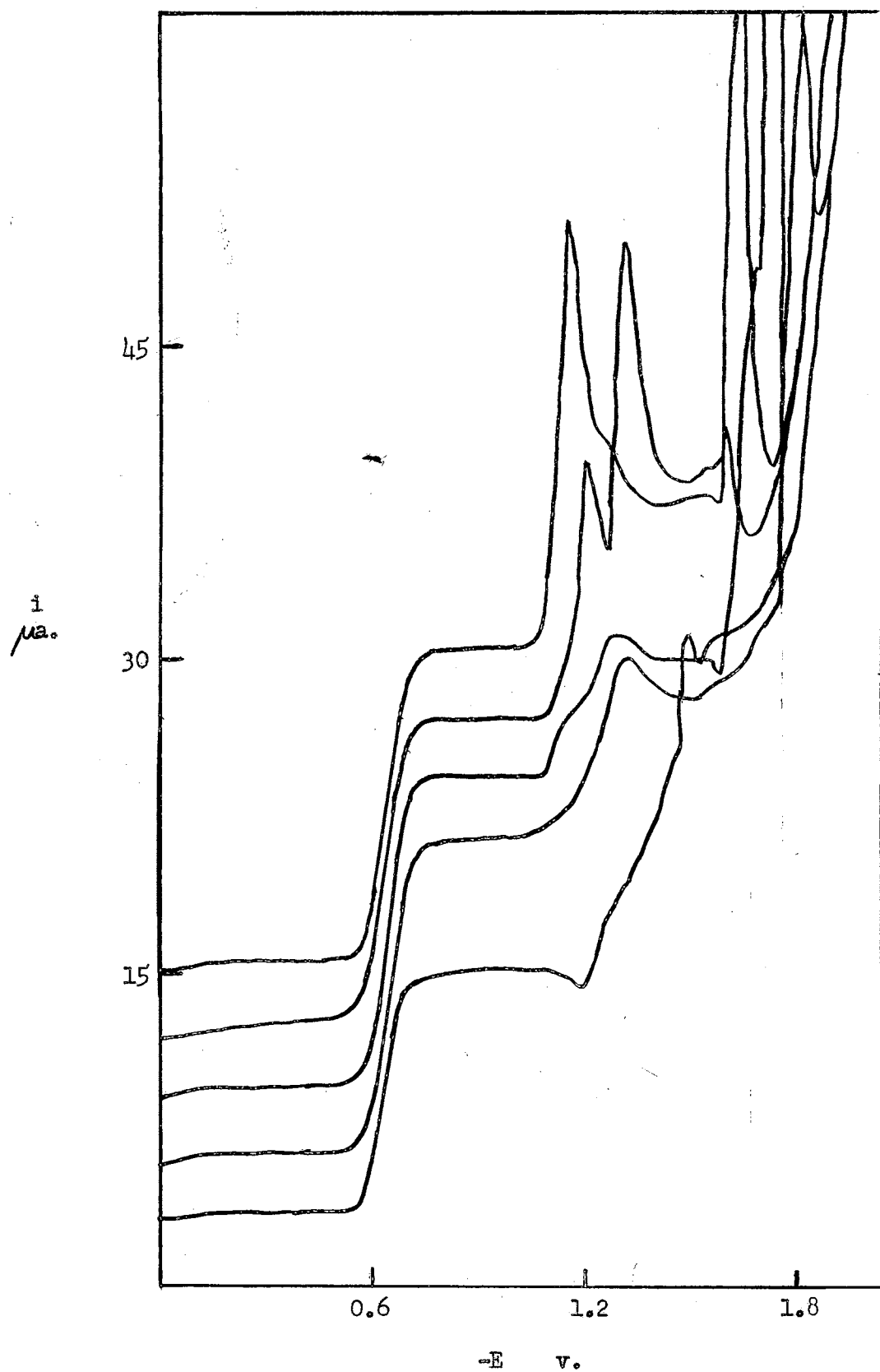


Figure 12. Influence of renewal of mercury surface on wave shape.

Non-renewal of the mercury surface was found to have a great effect both upon the diffusion current and upon the shape of the wave; consequently, it was decided to investigate the cause of this behavior using the ceresin wax surface electrode tube. A series of electrolyses were made, using cadmium ion solution, without renewing the mercury surface prior to electrolysis.

Well-shaped waves were obtained except for the fact that the recorder pen remained at the zero current position of the chart until the decomposition potential of the cadmium ion was reached. The current then increased as the slope portion of the wave was obtained and the limiting current was slightly inclined. Transition of the curve to the decomposition wave was smooth and gradual in some cases, and occurred through a step or rise in current in others, rather than through a dip as had been obtained when the mercury was renewed between electrolyses.

On two of the eight polarograms of the initial series, a rounded peak was present on the zero current line, indicating that prior to the decomposition potential of the cadmium, the current increased and then decreased. On later electrolyses, when the potential was not allowed to reach the decomposition potential of the supporting electrolyte, entry of solution, which usually occurred at the decomposition potential, did not result; and the rounded peak was not obtained. This suggests that the rounded peak may have been due to entry of solution into the electrode, which is somewhat puzzling since solution was not observed to enter the electrode during the early portion of the polarogram. When the solution was later allowed to enter, the rounded peak was not obtained. The cause of the rounded peak, which appeared during only three of the 46 electrolyses conducted, could not be definitely established,

though its absence when electrolysis to the decomposition potential was discontinued strongly suggests that the entry of solution into the electrode was responsible for its presence.

A second series of electrolyses was conducted during which electrolysis was stopped before the decomposition potential was reached. The mercury surface was renewed prior to the first electrolysis only and the cadmium wave was recorded at the center of the chart, thus leaving space for recording any anodic current below the cadmium residual current.

This second series of electrolyses yielded polarograms containing well-shaped waves. On the first polarogram, a conventional wave was obtained since the mercury surface had been changed; while on the next nine polarograms, an increasing anodic current was present below the cadmium residual current. The limiting current of the wave reached its peak value and then alternately became constant and decreased. A point was reached where it became constant until the end of the polarogram. This behavior resulted in the curve having a step-like appearance (Figure 13). The results indicated that if the mercury surface was not renewed, the limiting current of the wave became progressively more erratic on succeeding electrolyses after its peak value was reached.

It was concluded that the anodic current resulted from the dissolution of cadmium-mercury amalgam formed on the electrode during electrolysis. To determine whether the rate of dissolution of the amalgam was dependent on the applied voltage, a series of alternate electrolyses were carried out with cadmium ion solution. During one electrolysis, amalgam was formed; while on the next, the applied voltage was set at a constant value and the dissolution was followed by measuring the anodic current. This procedure was followed using constant applied

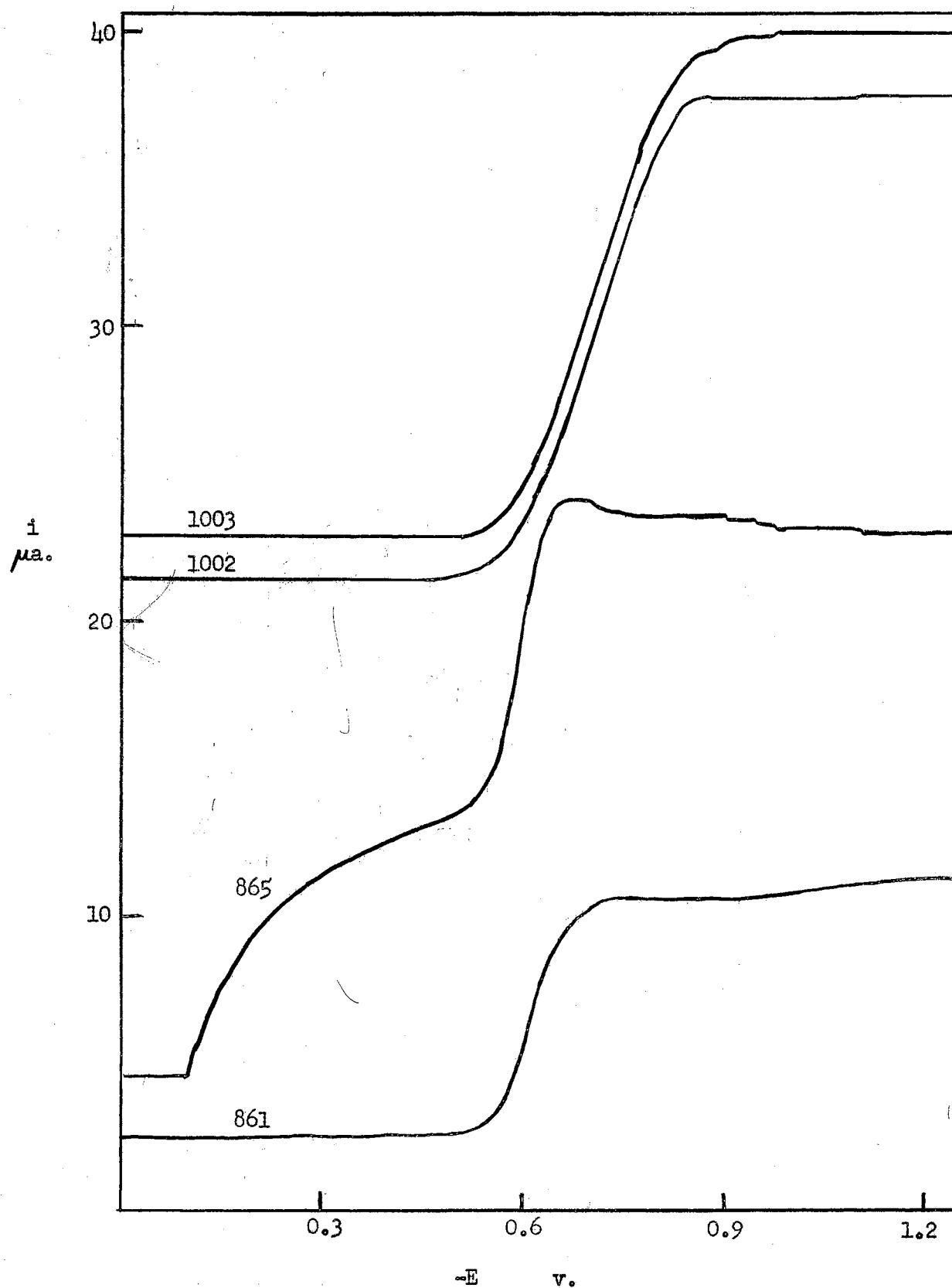


Figure 13. Improvement of wave shape with non-renewal of mercury on elevation of mercury surface.

voltages of 0.0, -0.3, -0.6 and -0.9 volt and the amalgam was considered dissolved when the current, which was increasing at the start of the polarogram, became constant.

The results indicated that as the constant applied voltage increased, the time required to dissolve the amalgam formed decreased. This was indicated by the fact that the decrease of the anodic current became progressively more rapid from electrolysis to electrolysis. When the applied voltage was greater than the decomposition potential of cadmium ion, a constant current was obtained almost immediately at the start of the polarogram. This current corresponded in magnitude to that obtained during a conventional electrolysis at the particular applied voltage used. On electrolyses used to generate amalgam, an anodic current was present or absent depending on whether the preceding electrolysis at constant applied voltage was at a value of the voltage above or below the decomposition potential of cadmium ion.

To ascertain whether the time of electrolysis at constant applied voltage had any effect on the concentration of amalgam formed and thus on the magnitude of the anodic current, a series of electrolyses were conducted with cadmium ion solution. The mercury surface was renewed prior only to the first electrolysis; and at the conclusion of each, the applied voltage was allowed to remain constant at -1.50 volts for varying lengths of time. This procedure was followed with the applied voltage constant for 5, 10, 15, and 20 minutes. The polarograms obtained are illustrated in Figure 14.

The results showed that when the applied voltage was allowed to remain constant for increasing periods of time, greater concentrations of amalgam were formed and the anodic current increased in magnitude as this amalgam was dissolved during the succeeding electrolysis.

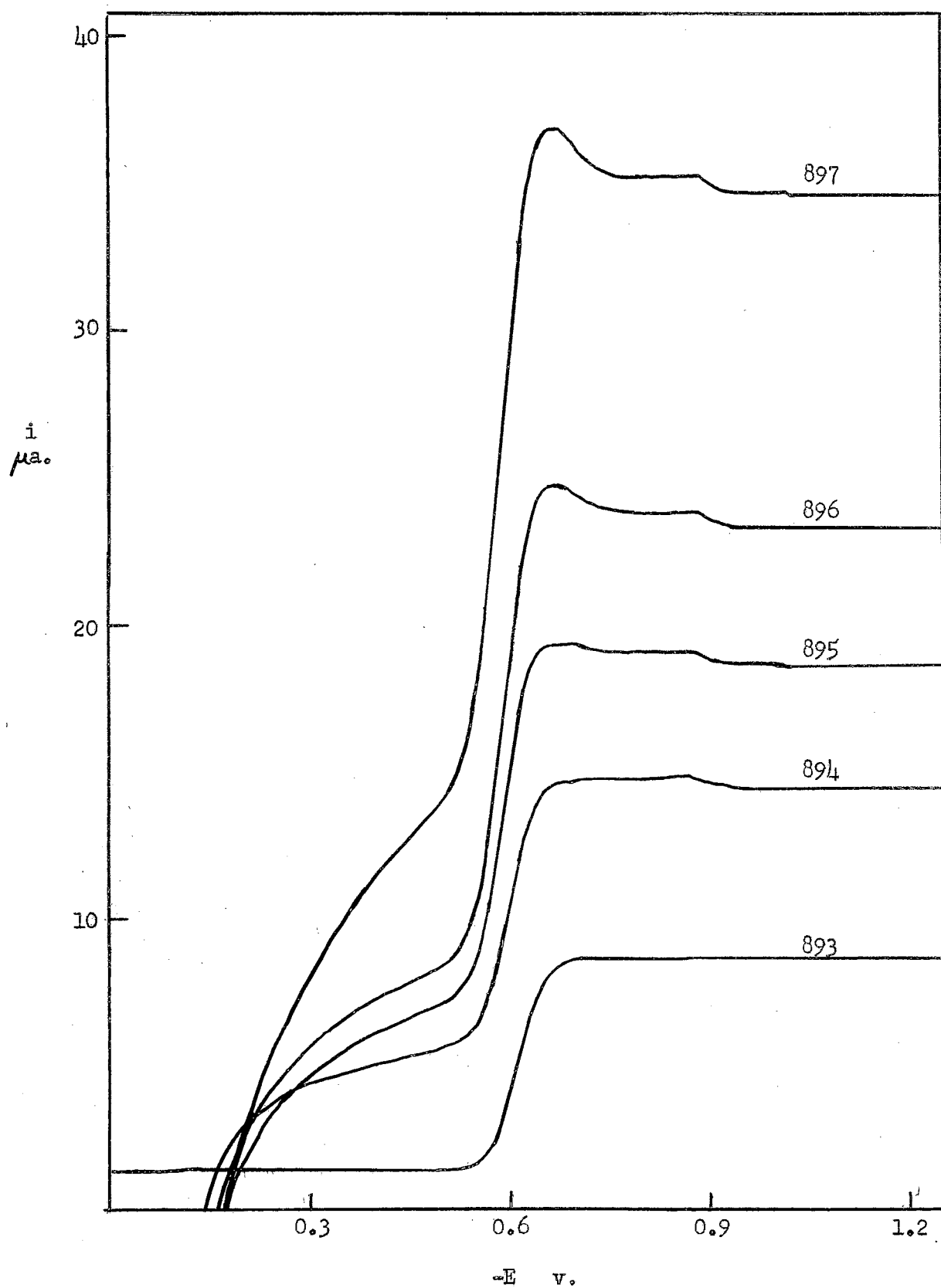


Figure 14. Influence of increased time of electrolysis on wave shape.

It was assumed that amalgam formation was essentially restricted to the surface layer of mercury. The mercury surface was probably only slightly stirred by the motion of the solution. That amalgam deposition was restricted to the surface was indicated by the fact that when successive electrolyses were conducted without changing the mercury, if the position of the surface was adjusted to the top of the electrode whenever that position had altered during the previous electrolysis, the anodic wave was not recorded. Apparently, the slight motion caused by the adjustment of the surface was sufficient to cause the amalgam to be stirred from the mercury surface.

When electrolyses were run without changing the mercury surface, the limiting current of the wave reached its peak value and then alternately became constant and decreased, finally remaining constant until the end of the polarogram (Figures 13 and 14). This behavior resulted in the curve having a step-like appearance, which became more pronounced on succeeding electrolyses.

It is believed that this behavior is the result of the physical arrangement of the electrode and stirrer. When amalgam is formed on the mercury surface and is then dissolved on the next electrolysis, cadmium ions are formed which enter the solution and are dissipated from the solution above the mercury meniscus by the stirring of the solution. The edge of the mercury meniscus is further from the top of the electrode tube than the center of the meniscus. The solution directly above the edge of the meniscus is relatively sheltered from the action of the stirrer. Consequently, when cadmium ions are formed and pass from the surface into the solution, they will not be stirred and mixed with the main body of the solution as rapidly from the solution directly above the edge of the mercury meniscus as from the solution above the more exposed

part of the meniscus. The concentration of cadmium ions in the solution above the edge of the mercury meniscus will become greater than that in the body of the solution as dissolution of the amalgam continues. When the decomposition potential of the cadmium is reached and a cathodic current starts to flow, it would be expected that the cathodic current would be greater due to the greater concentration of cadmium ions in the solution above the edge of the mercury meniscus. Consequently, the current obtained as the slope part of the wave is recorded is greater than that obtained when the limiting current of the wave is finally recorded. After this greater concentration of cadmium ions is depleted, the current would be expected to decrease to the limiting current value. This greater concentration of cadmium ions, formed as a result of inefficient stirring in the sheltered area of the electrode, will in turn cause a greater concentration of amalgam to form on the edge of the mercury meniscus during electrolysis. When this amalgam is then dissolved on the next electrolysis, the concentration of the cadmium ions in the solution above the mercury meniscus edge will be greater than the first time. In this manner, the solution above the mercury meniscus edge becomes more concentrated with cadmium ions on successive electrolyses and the increase in the cathodic current before the limiting current is reached would be expected to become greater, which is found to be true experimentally.

In order to test the above conclusions, the second modification of the platinum bead electrode (Figure 4) was constructed. In this electrode, a bead of platinum which fitted into the electrode tube was so positioned that when the platinum was covered with mercury, the edge of the mercury meniscus was even with the top of the electrode. Since none of the solution adjacent to the mercury surface was now sheltered

from the stirring action, the concentration of cadmium ion in any part of the adjacent solution did not increase above that in the body of the solution. Consequently, the larger current obtained at the start of the limiting current should not have been obtained. It was found (Polarograms 1002 and 1003, Figure 13) that when electrolyses were conducted with this modification of the platinum bead electrode without renewing the mercury surface, the increase in current at the start of the limiting current was not obtained.

The tendency for the solution above the edge of the mercury meniscus to become more concentrated with cadmium ions is decreased if the mercury surface is adjusted but not renewed. The amalgam on the mercury surface is stirred when this is done, as is the solution above the edge of the mercury meniscus. If electrolysis is continued for longer periods of time, more amalgam is formed, and on dissolution, the solution above the edge of the mercury meniscus would become more concentrated in cadmium ion. The anodic current would increase in magnitude and the decrease of current on the limiting current of the wave would become more pronounced. This behavior is found to be true experimentally (Figure 14).

Behavior similar to that described was also obtained with the paraffin wax surface when the mercury was not renewed between electrolyses.

The renewal of the mercury surface between electrolyses is necessary if good results are to be obtained. While the amalgam formed during electrolyses may be removed by other methods, changing of the mercury surface was found to be simplest.

Type of Stirrer. To determine the influence of the type of stirrer used, a small glass rod was fitted to the stirring shaft and positioned so that the rod would rotate concentrically with and inside of the electrode tube. This stirrer, referred to as the "inside stirrer," was

tested with the paraffin wax surface electrode using cadmium ion solution. After a well-shaped wave was obtained, the stirrer was fixed to extend 2 mm. into the electrode tube and the surface of the mercury was set at various distances from the stirrer to note the effect on the diffusion current.

From the data (Table 9) it is apparent that a greater diffusion current was recorded when the stirrer was closer to the mercury surface. This behavior was expected since the closer position of the stirrer stirred the solution more vigorously, thus decreasing the thickness of the diffusion layer and increasing the diffusion current. The results also indicate that the setting of the mercury surface and position of the inside stirrer greatly influenced the diffusion current. If the mercury was appreciably below the bottom of the inner stirrer, the diffusion current was smaller; and the limiting current, after reaching its peak value, would gradually decrease until the start of the decomposition wave. To insure the same position of the mercury surface and inner stirrer on a series of electrolyses, the following procedure was devised.

Table 9

Half-wave Potential* and Diffusion Current of 1mM Cd++
in 0.1N KCl at Room Temperature

Paraffin Wax Surface Electrode Tube
Inside Stirrer

No.	Distance Stirrer Extended into Electrode mm.	Distance From Stirrer to Mercury Surface mm.	$-E_{\frac{1}{2}}$ v.	i_d $\mu a.$
143	2	3	0.644	24.3
145	2	5	0.678	18.6
141	2	7	0.637	15.3
142	2	7	0.637	14.4
144	2	9	0.629	10.2

*Half-wave potentials given are vs. the S.C.E. and have been corrected for iR drop.

Two collars, in contact with each other, with the bottom collar touching the top of the bushing, were placed on the stirrer shaft and the shaft positioned so that the glass stirrer rod extended into the electrode tube 6 mm. The top collar was then locked in place and the mercury meniscus was raised until it touched the bottom of the stirrer rod. The stirrer shaft was then raised slightly and a spacer approximately 3 mm. in thickness was inserted between the collars. The bottom collar was then locked in place. This procedure was followed between electrolyses when the mercury surface was renewed prior to each electrolysis and as long as the position of the top collar was not changed, the mercury surface and stirrer rod were set to the same position each time.

This method was used in testing solutions of cadmium ion, of lead and cadmium ions, of cadmium and zinc ions, and of lead, cadmium and zinc ions at decreased concentrations. The resultant polarograms contained well-defined waves, the majority of the curves were free of

irregularities and dips, and the reproducibility of the diffusion current improved. The distance between the stirrer and mercury surface was kept constant in all but two electrolyses and in these two, the change in the magnitude of the diffusion current conformed to expected behavior. The improvement in the shape of the curve, especially the absence of the dip before the decomposition wave, was due to the use of solutions of decreased reducible ion concentration.

The first platinum surface electrode, in which the top of the platinum surface was 7 mm. from the top of the tube, was investigated with a solution of cadmium ion, using the inside stirrer. Well-formed waves were obtained, except that the limiting current, after reaching its peak value, decreased in magnitude. During the first electrolysis, the mercury surface was approximately 6 mm. below the top of the tube and the stirrer 3 mm. above the mercury. On the next electrolysis, the inside stirrer was raised even with the electrode tube and the mercury was positioned 3 mm. below it. The wave height was found to increase slightly; and, even more important, the large decrease in the limiting current after the peak value had been reached was eliminated. Two more electrolyses were conducted with the mercury set even with the top of the electrode tube and the stirrer set 1 mm. above the mercury, and very well-defined waves (Figure 15) were obtained. When the distance from the stirrer to the mercury was kept constant, but the mercury level and stirrer raised, the limiting current did not decrease after the peak value was reached. In addition, the diffusion current first increased and then decreased.

The cause of the behavior obtained when the stirrer was set at different positions is believed due to the isolation of the solution within the electrode from the body of the solution when the inside stirrer tube extends too far into the electrode. As the mercury and stirrer moved

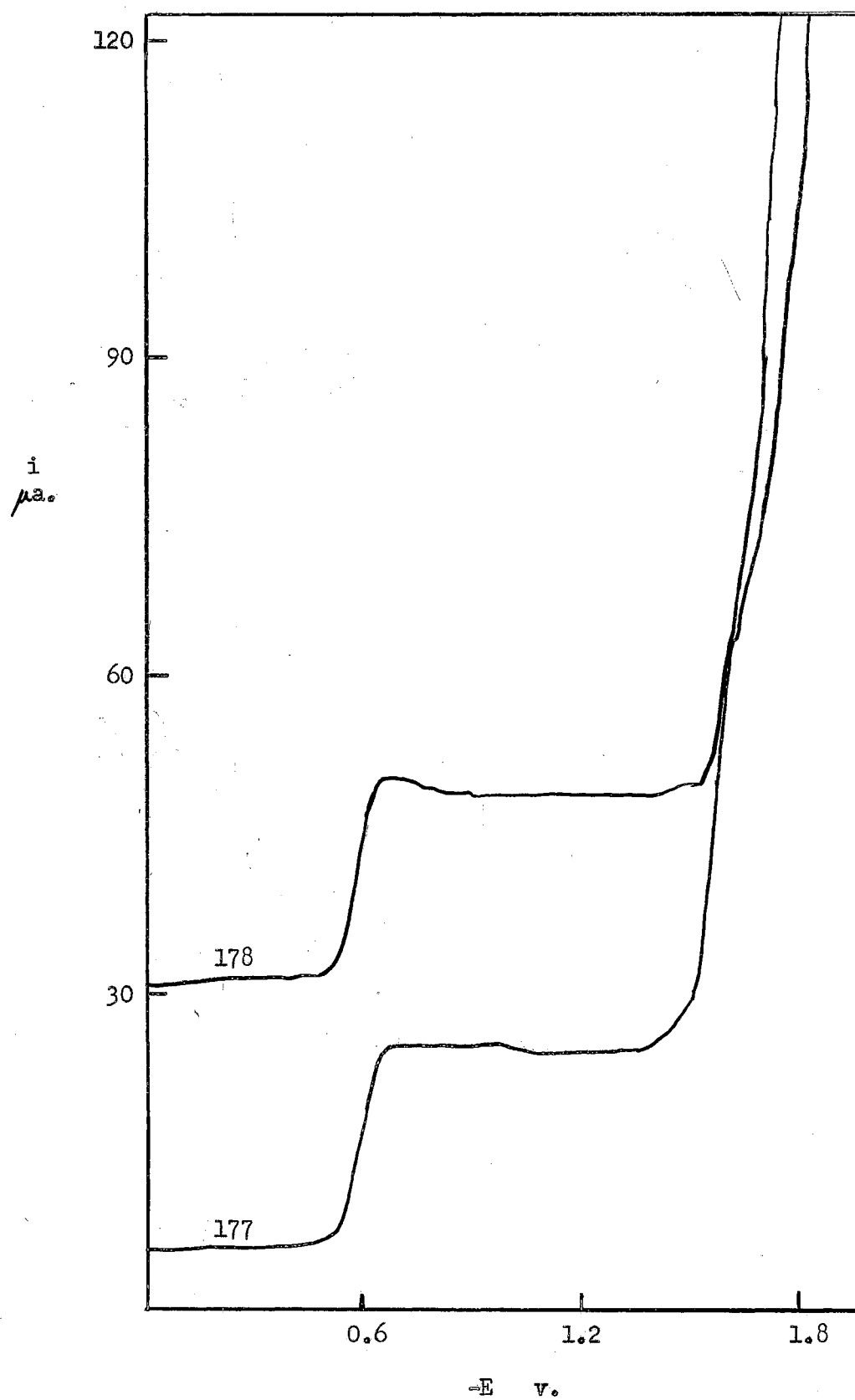


Figure 15. Waves obtained with inside stirrer.

closer to the top, it would be expected that the current would increase because the mercury was being raised from its sheltered place within the tube. The solution above the mercury, which was isolated when the stirrer was inside the tube, was now more exposed and mixing with the bulk of the solution could take place. However, as the stirrer moved out and away from the top of the electrode, the efficiency of stirring of the solution above the electrode decreased and the current would be expected to decrease.

By comparing the diffusion current obtained with the inside stirrer (Polarograms 180 and 181, Table 3) with those obtained with the outside stirrer (Polarograms 182-184, Table 3), under identical conditions, it can be seen that the current obtained with the outside stirrer is greater by a factor of 2.5. The outside stirrer is believed to be the more efficient due to the fact that the electrode tube itself has less chance to decrease the stirring, and probably also because exchange of fresh solution for old, from the main liquid to that inside the electrode tube, occurred more readily with the external stirrer. As a result, the current is greater.

In general, therefore, the outside stirrer was the better. In addition, the construction and manipulation of the outside stirrer is simpler than the inside stirrer.

Position and Setting of Mercury Meniscus. Since the mercury surface was renewed between electrolyses, the reproducibility in setting the mercury surface to the same position for each electrolysis was a factor that would affect the precision with which the diffusion current could be determined. In order to obtain some indication of the reproducibility of setting the position of the surface, a series of nine electrolyses were conducted with the paraffin wax surface electrode using cadmium ion

solution. The first was conducted in the conventional manner, except that electrolysis was stopped and the potential allowed to remain constant at -0.9 volts until the current became constant. This procedure, which was repeated eight times, yielded each time a short segment of the limiting current. The residual current of the first electrolysis was used in calculating each diffusion current. This method of calculation was used since the residual current was constant, while the limiting current was greatly dependent on the position of the mercury surface. The results showed that an appreciable variation in the diffusion current resulted due to the positioning of the mercury surface. This variation was comparable to the variation in the diffusion current obtained when the silicone surface electrode tube was used, and it was almost entirely caused by errors in reproducing the position of the mercury surface.

In an attempt to decrease this variation in the diffusion current and to assure reproducibility in setting the mercury surface, the pointer shown in Figure 2 was attached to the stirrer shaft and its tip was used as a reference point in positioning the mercury. By this means the error in measuring diffusion currents was reduced to less than one per cent.

With an untreated glass tube electrode of 0.8 mm. diameter, setting of the position of the mercury surface was especially important, for if the mercury surface was appreciably (e. g., 5 mm. or more) below the top of the glass tube, no wave was obtained. The wave height was small even with the mercury set at the top of the glass tube. With the smaller area of mercury and consequent smaller current, the variation obtained on successive settings of the mercury introduced a variation into the diffusion current which was quite appreciable.

The position of the mercury meniscus influenced the results obtained with the plastic surface electrode in that the wave was more well-defined

when the mercury was slightly below the top of the electrode.

The setting of the mercury surface is a critical factor due to its influence on the magnitude of the current obtained.

Elevation of Mercury Surface. In an attempt to raise the mercury surface without introducing irregularities due to stirring of the mercury, an electrode was constructed containing a bead of platinum inside and slightly below the top of the tube. The bead of platinum was formed on the end of a platinum wire which projected towards the bottom of the electrode tube (Figure 4). Approximately 2.5 cm. below the bead, the platinum wire was bent and attached to the glass wall of the tube. Directly below the bead, a cross arm of platinum wire held the bead centered in the tube. The ends of the cross arm were attached to the glass wall to insure rigidity. The bead had been positioned so that its top was just slightly below the top of the tube before the wire and the cross arm were attached to the glass.

The platinum bead and the wire below it were then dipped and allowed to remain in sodium-mercury amalgam for a short time, after which the electrode was immersed in distilled water to dissolve the sodium, dried, and filled with mercury. This electrode was then investigated with 1 mM cadmium ion solution, electrolyses being stopped before the decomposition wave was obtained.

Very well-defined waves were obtained with this electrode on the first four polarograms. When the range of the next two electrolyses was extended to record the decomposition wave, the wave was well-defined except for a dip in current before the start of the decomposition wave. When the mercury was lowered to wet the electrode with solution prior to the next three electrolyses, well-defined waves were obtained with no evidence of a dip prior to the decomposition wave. As can be seen in

Table 10, however, the decomposition potential obtained with the wetted electrode is much less negative than when the latter is not wet. The decomposition potential is approximately 0.3 of a volt more positive.

Table 10

Half-wave Potential*, Diffusion Current, and Decomposition Potential*
of 0.1mM Cd++ in 0.1N KCl**

Platinum Bead Electrode Tube
Outside Stirrer

No.	$-E_{\frac{1}{2}}$ v.	i_d μa.	$-E_d$ v.
964	0.650	44.0	
965	0.645	49.2	
966	0.639	51.6	
967	0.649	51.2	
968	0.651	53.2	1.558
969	0.655	50.4	1.533
970	0.643	46.8	1.225
971	0.641	56.0	1.251
972	0.644	58.0	1.252
973	0.700	54.8	1.222
974	0.648	63.2	
976	0.636	46.4	1.487
977	0.639	52.8	1.497
978	0.634	55.2	1.495
984	0.649	33.6	1.418
985	0.647	34.0	1.419
986	0.655	41.6	1.252

*Half-wave and decomposition potentials given are vs. the S.C.E. and have been corrected for iR drop.

**Runs 984, 985, and 986 were made at room temperature. All other runs were made at 25° C.

To determine whether the shift in the decomposition potential was due to solution wetting the platinum bead, on the next electrolysis a portion of the bead was exposed to the solution during electrolysis. Again, a well-shaped wave was obtained, except that the top portion

contained more rounding than had been evident on previous polarograms, and, in addition, the slope of the wave was not as great. While the transition to the decomposition wave had been rounded and gradual when the platinum bead was wet with solution, exposure of the platinum bead to the solution during electrolysis caused the transition to the decomposition wave to be very abrupt. The decomposition potential in both cases was approximately the same. Repetition of the electrolysis with the platinum bead covered with mercury resulted in a well-shaped polarogram. The current obtained with this polarogram was higher than those obtained previously, which was to be expected since the solution had wet the platinum bead before electrolysis.

The electrode was next washed in distilled water and then stored in air overnight to allow it to dry. When it was used the next day, no solution was allowed to touch the platinum bead. Three polarograms were recorded, and all contained a well-defined cadmium wave. The decomposition potential was back to its original larger value, showing again that wetting decreased the usable range of the electrode. The variations in the diffusion current shown in Table 10 were due to variations in setting of the mercury by visual means, as this adjustment was very difficult to make with accuracy.

In an effort to determine whether wetting occurred during electrolyses with this electrode, three more polarograms were run on cadmium solutions containing potassium chloride. The polarograms were all found to contain well-defined cadmium waves. The second electrolysis was allowed to continue to an applied voltage of -2.4 volts. The electrolysis to this extremely negative potential caused seepage of solution into the tube, and marked changes occurred in the diffusion current and decomposition potentials which were obtained on the third polarogram. After

electrolysis, when the tube was removed from the cell, the top carefully dried, and the mercury level lowered, an appreciable amount of solution was found under the platinum bead. The polarographic constants obtained on these electrolyses are given in Table 10.

A second platinum bead electrode similar to the first was made with the top of the bead placed approximately 1 mm. above the top of the tube. The electrode was treated with sodium-mercury amalgam and used in the electrolysis of cadmium ion solution.

A total of seven polarograms made with this electrode all contained well-defined waves. The second polarogram of this set contained two waves, even though the solution undergoing electrolysis contained only cadmium ion. The sum of the two wave heights was slightly higher than the wave height obtained on the previous and succeeding electrolyses. The behavior was present on only one polarogram and its cause could not be determined. The values of the polarographic constants obtained with the second platinum bead electrode are given in Table 11.

If provision is made to prevent the stirring of the mercury surface by providing an internal support for the surface, the elevation of the mercury above the tube is not a critical factor. In fact, such an arrangement seems to have much promise since the entire mercury surface is exposed to stirring.

Table 11

Half-wave Potential* and Diffusion Current of 1 mM Cd⁺⁺
in 0.1N KCl at Room Temperature

Platinum Bead Electrode Tube
Outside Stirrer

No.	$-E_{\frac{1}{2}}$ v.	i_d $\mu a.$
998	0.684	56.0
999	0.656	29.6
1000	0.673	56.8
1001	0.688	61.6
1004	0.680	64.0

*Half-wave potentials given are vs. the S.C.E. and have been corrected for iR drop.

Change of pH of Solution. It was desired to determine whether the pH of the solution electrolyzed had any influence upon the nature of the wave obtained with the stationary electrode. The study of the influence of this variable was made with the ceresin wax surface electrode tube.

Buffer solutions were prepared using lithium chloride as the main constituent. A solution of acid pH was obtained by the addition of hydrochloric acid, while an alkaline solution was prepared by the addition of lithium hydroxide to the solution of the main constituent. In this manner, the buffer solutions contained the same ions. Each solution was adjusted to a uniform ionic strength value of 0.5 by the addition of potassium chloride. The pH of all solutions was measured by means of a Beckmann Model H-2 pH meter. Electrolyses were conducted on these solutions before and after the addition of cadmium salt. In addition to the buffer solutions, the pH of potassium chloride, lithium chloride, and tetramethylammonium chloride supporting electrolyte solutions was measured and these solutions were electrolyzed to determine their decomposition potentials.

Excellent polarograms were obtained with all supporting electrolyte and buffer solutions. The results obtained (Table 12) indicated that there was no significant change in half-wave potential or diffusion current due to change in pH of the solution being electrolyzed. It had not been expected that a significant change would be found.

Table 12

Influence of pH of Solutions on Half-wave Potential,* Diffusion Current, and Decomposition Potential* at 25° C.

Ceresin Wax Surface Electrode Tube
Outside Stirrer

Solution	No.	pH	$-E_{\frac{1}{2}}$ v.	i_d $\mu a.$	$-E_d$ v.	Average		
						$-E_{\frac{1}{2}}$ v.	i_d $\mu a.$	$-E_d$ v.
0.1N KCl	740	6.95			1.449			1.455
	741	6.95			1.461			
0.1N LiCl	742	6.55			1.552			1.569
	743	6.55			1.585			
0.1M Me_4NCl	744	5.36			1.621			1.626
	745	5.36			1.630			
Buffer Solution A	746	2.10			1.088			1.102
	747	2.10			1.115			
	748	2.10			1.199			
Buffer Solution B	749	6.39			1.490			1.487
	750	6.39			1.484			
Buffer Solution C	751	11.73			1.510			1.494
	752	11.73			1.477			
Buffer Solution A + 1mM Cd^{++}	756	2.13	0.663	7.36		0.666	7.28	
	757	2.13	0.669	7.20				
Buffer Solution B + 1mM Cd^{++}	760	6.76	0.641	6.80		0.643	6.95	
	762	6.76	0.644	7.10				

*Half-wave and decomposition potentials given are vs. the S.C.E. and have been corrected for iR drop.

In order to compare supporting electrolytes, it was desired to have some way of determining the potential to which electrolysis of the supporting electrolyte solution could be carried. The decomposition potential of the solution is usually defined as that potential at which the cation of the supporting electrolyte undergoes electrolysis. For the purpose of this study, the numerical value of the decomposition wave was calculated in the following arbitrary manner. If no wave was present on the polarogram, a line was drawn through the residual current and through the longest straight portion of the decomposition wave, and the potential at the intersection was calculated. If the polarogram contained a wave, a line was drawn through the limiting current of the most negative wave and the decomposition wave, and the potential at the intersection calculated. The same procedure was followed if the limiting current was inclined, or contained a peak followed by a horizontal or inclined limiting current. If a dip or step was present on the limiting current at the transition to the decomposition wave, the dip or step was ignored in calculating the decomposition potential. The line drawn through the decomposition wave passed through the longest straight portion starting from the top of the wave. The decomposition potential was not calculated from polarograms on which the decomposition wave contained irregularities, steps, or other deformations. Since this method was followed consistently, the decomposition potentials are believed to be of value in comparing the behavior of the various supporting electrolytes.

Temperature Coefficient. In order to compare the behavior of the stationary electrode with that of the D.M.E., the temperature coefficient of the electrode was determined. A solution of cadmium ion was electrolyzed at four temperatures ranging from 20° to 35° C. using the ceresin wax surface electrode tube of 2.710 mm. diameter. Three

electrolyses were conducted at each temperature and the polarographic constants obtained are given in Table 13.

The change in diffusion current with temperature was found to be 0.516 microamperes/degree in the 20° to 35° C. range. The temperature coefficient of the diffusion current was found to be 2.2%/degree which is approximately equal to that of the D.M.E. (11).

Table 13

Half-wave Potentials and Diffusion Currents of 1mM Cd⁺⁺
in 0.1N KCl at Various Temperatures

Ceresin Wax Surface Electrode Tube
Outside Stirrer

No.	T °C	$-E_1$ v.	i_d μa.	Average	
				i_d μa.	T °C
955	20.75	0.622	22.8	23.0	20.37
956	20.35	0.625	23.4		
957	20.00	0.628	22.8		
952	25.20	0.629	27.3	27.0	25.23
953	25.25	0.629	27.0		
954	25.25	0.620	26.7		
958	30.78	0.624	28.5	28.3	30.79
959	30.80	0.627	28.2		
960	30.80	0.618	28.2		
961	34.73	0.620	30.3	30.4	34.72
962	34.70	0.629	30.6		
963	34.73	0.626	30.3		

Current increase per degree = 0.516 a./°C.

Temperature Coefficient = % Current increase/degree
2.2%/°C.

Scanning Rate. In an attempt to determine whether the rate of increasing the applied potential had any influence on the results obtained, a platinum surface electrode of 1.5 mm. diameter was investigated, using a solution of cadmium ion, with an experimental polarograph on which it was possible to vary the time of electrolysis. On the first electrolysis, the applied voltage range was spanned in 26 seconds, as compared to the 13 minutes required with the Model XXI Sargent polarograph. On succeeding electrolyses, the applied voltage range was spanned in 52 seconds.

The residual current of the wave was found to be inclined and the limiting current contained a rounded peak on top of which were two sharp peaks. After the rounded peak, the current remained fairly constant until the decomposition wave was reached. When it was attempted to conduct the electrolysis in a reverse manner, going from a high negative applied voltage to zero applied voltage, an almost complete curve was obtained. The two smaller peaks were broader than when electrolysis was conducted in the usual manner. After the rounded peak, the current, instead of remaining constant to form the residual current portion of the wave, kept decreasing until the bottom of the chart was reached. The current remained at the bottom of the chart for a short while and then started to increase slowly until the end of the polarogram. The polarogram obtained is shown in Figure 16.

The explanation of the curve obtained on the reverse run is probably as follows. The application of the large negative applied voltage at the start of the reverse electrolysis resulted in the formation of a large amount of amalgam at the mercury surface. As the applied voltage decreased, the amount of amalgam formed continued to increase until the decomposition potential of the cadmium ion was reached. At this point, amalgam formation stopped and dissolution of the amalgam started. As the

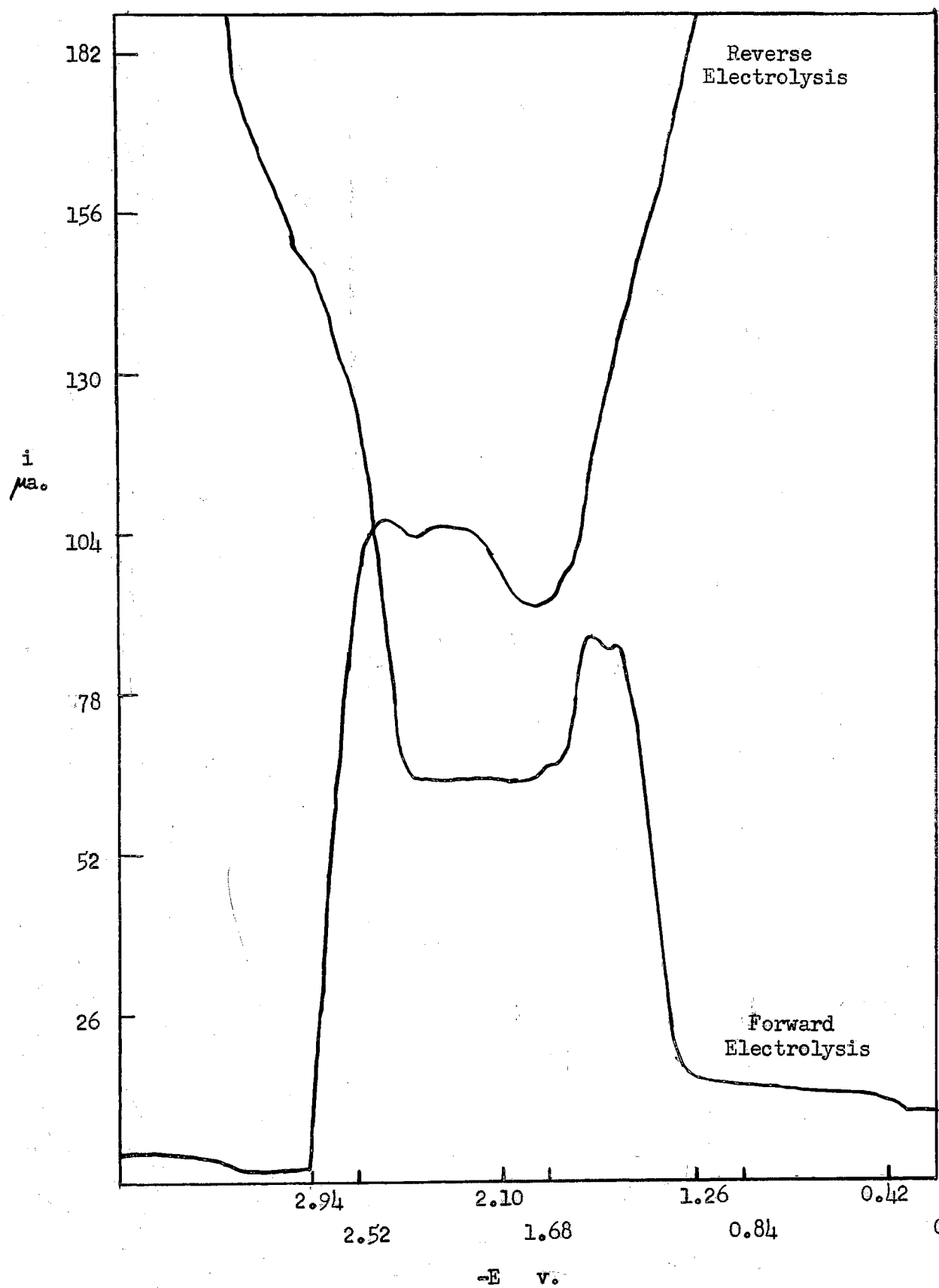


Figure 16. Polarograms obtained using faster scanning rate.

applied voltage decreased from the decomposition potential of the cadmium ion to zero applied voltage at the end of the electrolysis, the rate of dissolution of amalgam became greater and, hence, the magnitude of the anodic current increased. The residual current is absent due to the large magnitude of the anodic current, which is also the cause of the current reaching the bottom of the chart. As the applied voltage decreased, the rate of dissolution of the amalgam increased. A point was finally reached where almost all of the amalgam was dissolved. With no anodic current flowing, the current then increased until its magnitude was approximately equal to that of the residual current.

An electrolysis was made with the same electrode and solution using the Model XXI Sargent polarograph. The peak at the start of the limiting current was much smaller in size, which would indicate that the process causing the rounded peak was influenced by the time of electrolysis.

The scanning rate of the solution was found to affect the results obtained appreciably and is considered to be a critical factor.

Stirring of Mercury Surface. Several electrolyses were made with the ceresin wax surface electrode using cadmium and zinc ions solution with the pointer in the stirrer shaft extended 2 mm. into the mercury. The polarograms obtained were not greatly different from those obtained without the pointer in the mercury, except that the limiting current of the cadmium wave was rounded and inclined and a large dip was present at the transition from the limiting current of the zinc wave to the decomposition wave.

Time did not permit further studies of this procedure and it seems possible that, with suitable stirring arrangements, good results might be obtained.

Decreased Reducible Ion Concentration. When solutions of decreased reducible ion concentration were electrolyzed using the paraffin wax electrode tube and the inside stirrer, the results improved in that the majority of the polarograms were free of irregularities and the dip or decrease in the limiting current occurring prior to the decomposition wave was removed. When solutions of cadmium ion at reduced concentration (0.33 mM) were electrolyzed with the platinum surface electrode, using the outside stirrer, well-defined waves were obtained.

Prior to electrolysis of a lead and cadmium ions solution of decreased concentration, a 1 mM solution of lead and cadmium ions was electrolyzed. The proximity of the two waves made calculation of the polarographic constants difficult, but the half-wave potentials and diffusion currents of the lead and cadmium waves were found to be -0.467 and 64.2 microamperes and -0.761 volt and 57.6 microamperes, respectively. The $E_{1/2}$ values are considered more negative than those reported in the literature for these ions with the D.M.E. In addition, the cadmium ion half-wave potential obtained with the lead and cadmium solution is more negative than the value obtained with the cadmium and zinc solution using this same electrode.

When a 0.33 mM solution of lead and cadmium ions was electrolyzed, the slope portion of the lead wave was found to consist of two parts. All four curves recorded contained a dip before the decomposition wave. The dip or decrease in the limiting current, therefore, does not seem to be eliminated when a solution of lead and cadmium ions at decreased concentration is electrolyzed.

With the Desicote surface electrode, decreasing the concentration of the reducible substance resulted in the elimination of the dip in the curve before the decomposition wave.

As the results indicate, decreasing the concentration of the reducible ion serves to improve the results in some cases. It does not seem to be a critical factor in all cases.

SUMMARY

A new polarographic electrode employing controlled stirring has been investigated and evaluated. It was found that in its original form, which consisted of an untreated glass tube containing mercury surrounded by a rotating stirring tube, the electrode yielded excellent results. However, irregularities appeared on the polarograms indicating that something critical was being overlooked.

It was found on further investigation that these irregularities were due to solution creeping into the electrode tube, forming into droplets, and then bursting out again. This phenomenon seemed to vary as the potential increased, beginning at about -1.2 volts vs. the S.C.E. It was decided to deal with this wetting phenomenon in two ways. The first consisted of an attempt to prevent the wetting of the electrode completely, while the second consisted of an attempt to aid the wetting in order to make its influence constant and thus stabilize the electrode.

The inner surface of the electrode tube was treated with various substances in the hope of preventing or decreasing markedly the wetting of the electrode. Of the substances tested, the best was found to be a coating of ceresin wax. After some of the many variables which affected the behavior of the electrode were evaluated, it was found that consistent and reproducible results could be obtained with great ease. Many of the original objectives sought in undertaking this study were achieved with this electrode. The polarograms were free of the oscillations obtained with the D.M.E., large diffusion currents with small residual currents were obtained, the manipulation of the electrode was relatively simple,

and the apparatus required was not complicated. In fact, in many of its characteristics, this electrode was superior to the D.M.E.

A surface of platinum on the inside wall of the tube formed the second best electrode. This electrode containing the platinum surface was better than that containing the ring of platinum cemented in place with silver chloride cement. The detriment of the ring form seemed to be due to the cement rather than to the electrode material or its position in the tube. In many respects the platinum surface compared favorably with the ceresin wax surface electrode. Its chief drawback was the fact that if the amalgamated platinum became wet with solution, the range was decreased.

The paraffin wax surface also yielded very favorable results. Its ability to resist wetting, however, was not as great as that of the ceresin wax surface.

The silicone, Lucite plastic, and Desicote surfaces were found to be only fair in comparison with the surfaces already mentioned. Consistent results were not always obtained, the surfaces were not as durable, and, in general, the manipulation of these electrodes was more troublesome. Of the three, the silicone surface was best, the Desicote surface next best, while the Lucite plastic surface was not only the least satisfactory, but was also the most difficult to make.

The metal surfaces other than the platinum were found to be the most unsatisfactory of all investigated. This was surprising, since it had been expected that some of them would be capable of yielding satisfactory results. It was concluded that the poor results were not due to the nature of the metals but rather to the method of their attachment to the glass tube. In the case of the gold surface, attachment to the glass was not strong, the gold was slowly dissolved by the mercury, and

there was evidence that the silver chloride was attacked, yielding a grayish deposit. The formation of the grayish deposit occurred with all electrodes in which silver chloride cement had been used. The concept of the cement causing the trouble was borne out by the fact that while the platinum ring cemented in place with silver chloride did not yield good results, the other modifications of this electrode were satisfactory.

With the copper surface, sealing to the glass was difficult due to the formation of the oxide as the glass and copper were heated, and when silver chloride cement was used, the grayish deposit mentioned above was formed.

For much the same reasons as above, the nickel surface was also unsatisfactory. Its polarographically useful range seemed to be the shortest of all the metals investigated.

All of these results indicated that the method of fixing the metal in the tube was the cause of the difficulty. Several of these metals in the stationary electrode might still yield satisfactory results if a suitable means of sealing the metal to the glass tube were devised.

At the start of the investigation of the stationary electrode, wetting of the tube with solution was considered to be injurious, and initially, emphasis was placed on its elimination. It became apparent on continued investigation that the wetting of the electrode could be stabilized sufficiently to give excellent results. Indeed, this was considered one of the main factors contributing to the success of the ceresin wax surface electrode.

Stabilization of the wetting by addition of detergent to the solution was not as satisfactory as dipping the electrode into liquid detergent, then rinsing. The use of detergent improved the results,

but since an external substance was thereby introduced into the solution undergoing electrolysis, the possibility of introducing an interfering impurity was increased.

Deliberate wetting of the electrode with solution prior to electrolysis gave good results. At times, this was done only at the start of a series of electrolyses; at other times, the electrode was wet with solution prior to the start of each electrolysis of a series. Both procedures greatly improved the results obtained.

This wetting with solution was found to improve the behavior of the electrode even when supposedly nonwetting surfaces were used, though it was not successful with some of the metal surfaces, such as copper, gold, and nickel. Much the same effect was accomplished by wetting the electrode as was achieved by the "conditioning" procedure. While the conditioning procedure served to yield better results because it was carried out under conditions similar to those existing during actual electrolysis, merely wetting with solution before electrolysis was faster because this step could be carried out while the mercury surface was being renewed.

A treatment similar to wetting of the electrode with solution prior to electrolysis consisted of storing some of the electrodes overnight in contact with distilled water or potassium chloride solution. It was found that the behavior of the electrode was better when the electrode was immersed in distilled water. Immersion in potassium chloride was suggested by the fact that this was the supporting electrolyte used in the solutions tested.

Having developed several forms of the electrode which were capable of yielding reproducible results, the influence of variables on the

behavior of the electrode were evaluated. At the start, it seemed that the variables were almost without number, since everything seemed to affect the behavior of the electrode.

With electrodes of 0.8 to 3.5 mm. diameter, it was found that the diameter of the tube influenced only the magnitude of the diffusion current. For diameters between 1.5 and 3.5 mm., the diffusion current was a linear function of the diameter.

The speed of the stirrer did not influence the results greatly as long as extremes in speed were not used. The speed of 600 r.p.m., recommended by other investigators for rotating microelectrodes, was found suitable. It was also found that this speed need not be controlled too carefully. However, with low speeds, the magnitude of the current will decrease to the point where the advantages gained with this electrode are overcome. If, on the other hand, the stirrer speed becomes too great, the chance of introducing vibration increases and results become erratic.

The diameter of the stirrer and its position were found to have an influence on the results. If the stirrer diameter was too small, the wave form was affected, while if the diameter was made too large, the efficiency of the stirring decreased. The position of the stirrer with respect to the top of the electrode tube was important due to the turbulence which was present at the bottom of the stirrer. If the stirrer extended over the electrode tube for a distance of 5 mm., constant results were obtained and the influence of turbulence was minimized. The stirrers should be carefully made so that they run true, since uneven motion in the stirrer was found to cause variations in the current.

The earliest experiments indicated that better results were obtained with the electrode when the mercury surface was renewed between

electrolyses. When this was not done, an anodic current as well as an increase in the limiting current of the wave was obtained. As would be expected, the magnitude of the anodic current was found to be dependent on the time of electrolysis and on the applied voltage. The hump often observed at the beginning of the limiting current portion of the wave was apparently due to the construction of the electrode. Because the edge of the mercury surface and the solution above it were protected by the glass electrode tube from the full effect of the stirrer, during the anodic part of the run the solution above the edge of the mercury meniscus became more concentrated with the reducible ion than was the main solution. Until this was electrolyzed out, the current was abnormally large, decreasing, as electrolysis occurred, until equilibrium with the whole solution was attained. When the mercury surface was extended above the tube with the platinum bead electrode, no portions of the solution were isolated from the full action of the stirrer, and concentration of cadmium ion could not increase above that in the body of the solution, and the current could not become greater than the limiting current; consequently, the hump was never observed.

The outside stirrer was more efficient than the inside stirrer as was evidenced by the greater current obtained with the former.

The position of the mercury surface with respect to the mouth of the electrode tube was found to be important. With a small size tube, if the mercury was too far within the tube, practically no current was obtained. When the top of the meniscus was set even with the top of the tube, best results were obtained. The reproducibility of the setting of the mercury surface influenced the results greatly and it was necessary to provide a reference point to set the mercury meniscus when high accuracy was needed.

Elevation of the mercury surface yielded good results once provision was made to support the surface internally by means of the platinum bead mentioned above. Without the support, the surface had a tendency to change position with the potential applied to the electrode. Also, erratic results caused by stirring of the mercury surface were reduced when an internal support was used.

Changes of pH of solutions of inorganic ions had little effect on the results obtained. Temperature was found to affect results moderately. The temperature coefficient of the electrode between 20° and 34° C. was approximately the same as that of the D.M.E.

While the influence of the scanning rate was not exhaustively determined, the rate did affect the magnitude of some of the irregularities obtained with the electrode.

When the concentration of the reducible substance was decreased, the dip often observed in the limiting current before the start of the decomposition wave was removed. This was found to be true when a solution of cadmium and/of zinc ions was electrolyzed, but was not true when a solution of lead and cadmium ions was electrolyzed. Some cations gave no dip at any concentration tried.

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