

SCANNING RATES AND THE ROTATING MICROELECTRODE
IN POLAROGRAPHY

By

PHILLIP ALBERT LEWIS

Bachelor of Science

Aurora College

Aurora, Illinois

1942

Submitted to the faculty of the Graduate School of
the Oklahoma Agricultural and Mechanical College
in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

May, 1954

Thesis
1954
L675w
cop. 2

OKLAHOMA
AGRICULTURAL & MECHANICAL COLLEGE
LIBRARY
NOV 1 1954

SCANNING RATES AND THE ROTATING MICROELECTRODE
IN POLAROGRAPHY

Thesis Approved:

Paul Arthur

Thesis Adviser

J. M. Trimble

Faculty Representative

Robert Madison

Dean of the Graduate School

329838

ACKNOWLEDGEMENT

The author wishes to express his appreciation for the guidance and help extended by Dr. Paul Arthur throughout the course of this investigation. The author also wishes to thank Dr. O. C. Dermer and the chemistry department of the Oklahoma A. and M. College for aid, including an assistantship, and Dr. H. M. Trimble for his helpful criticism of the manuscript.

TABLE OF CONTENTS

Chapter	Page
I. Introduction	1
II. Scope of Research	8
III. Experimental Details.	10
IV. Results and Discussion	17
Electrodes	17
Supporting Electrolytes.	26
Scanning Rates	28
Diffusion Currents	39
Half-wave Potentials	44
V. Conclusion	48
Bibliography.	50

LIST OF TABLES

Table	Page
I. Microelectrode Preparations and Statistics	15
II. Half-wave Potentials of Microelectrodes	45
III. Half-wave Potentials of Cadmium Ion with Various Scanning Rates	46

LIST OF ILLUSTRATIONS

Figure	Page
1. A Typical Polarogram	3
2. Polarograph Circuit Diagram	11
3. Rotating Microelectrode Assembly	13
4. Electrolysis in 0.1 M KCl with Several Microelectrodes.	18
5. Electrolysis in 0.1 M KCl with the Copper Amalgam Microelectrode	19
6. Polarogram of 10×10^{-4} M $\text{Cd}(\text{NO}_3)_2$ with the Copper Amalgam Microelectrode	20
7. Polarogram of 4×10^{-4} M $\text{Pb}(\text{NO}_3)_2$ with the Silver Amalgam Microelectrode	22
8. Polarogram of 4×10^{-4} M FeCl_3 with the Gold Amalgam Microelectrode	23
9. Polarogram of 7×10^{-4} M FeCl_3 with the Platinum Amalgam Microelectrode	23
10. Polarogram of FeSO_4 with the Platinum Amalgam Microelectrode	24
11. Electrolysis with the Platinum Microelectrode	27
12. Electrolysis with the Platinum Amalgam Microelectrode	27
13. Polarogram of 10×10^{-4} M $\text{Cd}(\text{NO}_3)_2$ with the Copper Amalgam Microelectrode	29
14. Polarogram of 10×10^{-4} M $\text{Cd}(\text{NO}_3)_2$ with the Copper Amalgam Microelectrode	30
15. Polarogram of 10×10^{-4} M $\text{Cd}(\text{NO}_3)_2$ with the Copper Amalgam Microelectrode	31
16. Polarogram of 10×10^{-4} M $\text{Cd}(\text{NO}_3)_2$ with the Copper Amalgam Microelectrode	32

Figure	Page
17. Polarograms of $\text{Pb}(\text{NO}_3)_2$ with the Platinum Amalgam Microelectrode	34
18. Polarogram of 10×10^{-4} M $\text{Pb}(\text{NO}_3)_2$ with the Platinum Amalgam Microelectrode	35
19. Polarogram of 10×10^{-4} M $\text{Pb}(\text{NO}_3)_2$ with the Copper Amalgam Microelectrode	37
20. Diffusion Current vs. Ion Concentration with the Platinum Amalgam Microelectrode	40
21. Diffusion Current vs. Ion Concentration with the Copper Amalgam Microelectrode	41
22. Diffusion Current vs. Ion Concentration with the Gold Amalgam Microelectrode	42
23. Diffusion Current vs. Ion Concentration with the Silver Amalgam Microelectrode.	43
24. Polarograms of $\text{Cd}(\text{NO}_3)_2$ with the Gold Amalgam Microelectrode	47

INTRODUCTION

The dawn of polarography is usually attributed to Kucera (12) who, in 1903, while employing a dropping mercury electrode (D.M.E.) to study the electrocapillary behavior of mercury in various solvents, noticed peculiar inflections in curves obtained when reducible substances were present. Acting on Kucera's suggestion, Jaroslav Heyrovsky (6) applied the D.M.E. to the study of reducible substances, and found that both qualitative and quantitative applications of the results obtained were possible.

The work received impetus in 1925 from the invention, by Heyrovsky and Shikata (10), of an automatic recording instrument for the new analytical method. The instrument was called a polarograph and the waves obtained were referred to as polarograms. The work continued, on an increasing scale, but still largely due to Heyrovsky and his co-workers, until 1935, when Heyrovsky and Ilkovic (9) explained the significance of the half-wave potentials and wave heights, and placed polarography on a sound theoretical basis. Since that time, polarography has grown on a world-wide scale until today it ranks as a major instrumental method of analysis.

The polarograph consists of a steady direct current source, the potential of which can be varied through a potentiometer. This potential is applied across an electrolysis cell, one electrode of which is very small and polarizable (the microelectrode), the other being larger and non-polarizable. A current-measuring device is also included in the circuit (see Figure 2).

The most widely used microelectrode consists of a small drop of

mercury which is formed and released at the end of a capillary tube, such drops being renewed by maintaining a flow of mercury through the capillary at a constant rate. The non-polarized electrode is either a pool of mercury or some suitable half-cell, such as the saturated calomel electrode. The current measuring device may be a galvanometer of long period, or a recording potentiometer operating across a known resistance in the circuit.

Many workers have used the oscillograph as a measuring instrument with the D.M.E. This has proved useful in studying the reversibility of reactions (8,24), the process of diffusion (5,19,20) and capacitance currents (3). Airey (1) claims no appreciable loss of accuracy with the oscillograph. There is, however, a great deal of experimental difficulty involved, chiefly in obtaining good saw-tooth voltage sources (4,17,18) and synchronization of voltage sweep with drop time (15). Too, the resulting wave is not always simple.

A typical polarogram is shown in Figure 1. As an increasing voltage is applied to the electrolysis cell, a small current flows. This is the residual current. It may include, for the D.M.E., a small electrocapillary effect produced by those ions which lower the interfacial tension between mercury and the solution. Another, more important, contributor to the residual current is the condenser current. This results from the capacitance of the mercury-solution double layer at the interface. In addition, since it is almost impossible to remove the last traces of oxygen and other impurities, there will be a slight faradaic current during the reduction of such impurities.

When the applied voltage reaches the decomposition potential of any electro-reducible substance present, reduction commences. As the voltage is increased, the solution around the microelectrode becomes

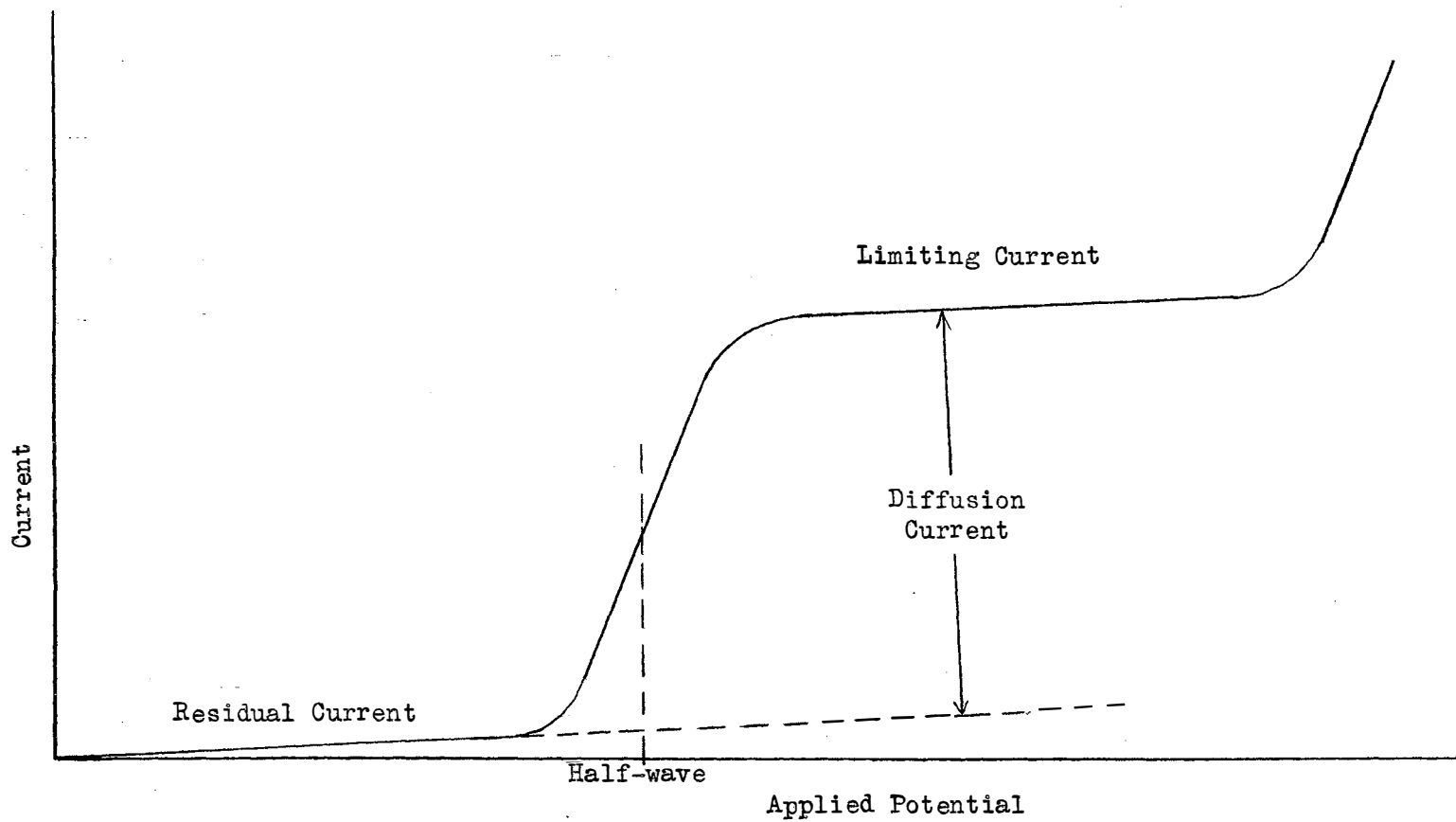


Figure 1 A Typical Polarogram

depleted in reducible ion, until it reaches the state (the limiting current) where reduction is dependent only on the rapidity with which ions can diffuse in to the electrode. This in turn is dependent on the concentration of the reducible substance present. Since the current at this time includes both this so-called diffusion current (I_d) and the residual current, the diffusion current itself is the limiting current minus the residual current.

If the reducible substance were alone in the solution, the limiting current would also be dependent on the migration of these ions, with subsequent variation due to depletion at the microelectrode. In practice, however, the migration current is made negligible by adding an electrolyte (variously called the indifferent electrolyte, the supporting electrolyte, or the carrier) at a concentration of 50 to 100 times greater than that of the reducible substance.

Another capillary action may take place if the concentration of the reducible ion, through adsorption, becomes greater around the microelectrode than in the rest of the solution. This results in a maximum in the limiting current which is not predictable or reproducible. This may be eliminated by addition of surface-active agents, such as gelatin, called maximum suppressors. Although it is concentration dependent, there is no simple relation between the height of the maximum and the concentration of the reducible substance (11).

The D.M.E. continues as the basic microelectrode, not only because of its historical position, but also because of its several advantages. Thus, for example, the surface area is reproducible and easily calculated from the weight of the drop. The surface itself is always smooth and is never completely contaminated by

reduction product, for it is constantly being renewed by the falling away of old drops and their replacement by new ones. Finally, not only will mercury amalgamate with most metals, but also, since the over-voltage of hydrogen at mercury is high, hydrogen evolution does not interfere with work even in fairly acid solutions.

In addition, the underlying theory governing the behavior of the dropping mercury electrode is well understood.

Despite the several advantages of the D.M.E., however, there are many ways in which other electrodes might be much better. The drop itself, with the current increasing as the drop grows, causes the current-voltage curve to contain oscillations. To minimize these, the measuring device must have a long period and/or be damped. Since such oscillations must be averaged and yet meaningful changes in the curve be observable, slow scanning rates must be employed. Currents are not large, but the consumption of high-grade mercury is. In addition, the oxidation potential of mercury is low, which makes it unsuitable for most anodic work.

Various schemes have been tried to overcome these disadvantages, such schemes involving both alterations in the design of the mercury microelectrode and the use of materials other than mercury for microelectrodes.

The use of solid microelectrodes for electrolyses dates back as far as does the development of the dropping mercury electrode. Salomon (23) used stationary electrodes in 1897, but the results obtained were very poor.

In polarography, many stationary electrodes, made of various metals and of amalgamated metals, have been studied (1,2). Such electrodes, employed without stirring, possess the serious disadvantage that the

time required for analysis is too great. The increase of applied potential must be stepwise, with the potential held at each step and time allowed for equilibrium to be established before readings are taken, and the curves then hand-plotted. Attempts to obtain such curves automatically result in the appearance of current maxima (21), although it is claimed that these so-called time maxima may be eliminated by operation at elevated temperatures (25). Any kind of stirring, even by convection, must be carefully avoided.

A great improvement on the stationary electrode is the rotating microelectrode. Nernst and Merriam (16) used a rotating platinum electrode as early as 1905 in studying silver ions, permanganate ions, and halogens. The most commonly used form is probably that of Laitinen and Kolthoff (13), who used a platinum wire 0.5 mm. in diameter, extending 3.2mm. horizontally from the side of a revolving steel shaft (see Figure 3). There has been some confusion in the literature concerning the rate of rotation of the microelectrode, but it is now commonly accepted that speeds above 600 r.p.m. cause little change in the current from that obtained at 600 r.p.m. (22).

The solid rotating microelectrode has certain features not possessed by the D.M.E. There is no drop formation; consequently smooth waves can be obtained with a minimum of damping and the subsequent loss of sensitivity. Scanning rates can be faster and currents are much larger. With platinum, anodic work is possible at quite high voltages. Electrodes do not wear out and are simple to prepare.

On the other hand, disadvantages of solid microelectrodes include the smallness of the hydrogen overvoltage, which limits the usable range to voltages less negative than those obtainable with the D.M.E. In addition, plating of metals onto the electrode during runs changes

its characteristic completely, which means that the past history of the microelectrode is significant, and treatments must be devised to restore the electrode to its original state. Furthermore, the theoretical treatment of results obtained with such electrodes is not satisfactory thus far.

Because polarography is a practical analytical tool, research in this field continues in many laboratories. Such work is designed to extend the applications of polarography to new substances as well as to make existing techniques more convenient and accurate. In general, there are four paths to these objectives. The first involves the electrode itself. Here investigation is aimed at the designing of radically new types of electrodes or the redesigning of existing types. The second path involves investigations of the supporting electrolytes most suitable for given determinations. The third path involves the determination of what substances are capable of being analyzed by existing polarographic methods. The fourth approach is that dealing with any phase of instrumentation, including special techniques, circuits, etc.

SCOPE OF RESEARCH

It is obviously impossible for one investigator to make any kind of exhaustive study along all of the possible paths indicated. In fact, the scope of the field of polarography is such that even one path of research can merely be started in the graduate school experience of one student.

In this study, rotating microelectrodes, standard in size and speed of rotation, were employed. Two objectives were in mind. First, different electrode materials were to be studied in an effort to find a material which would give a wide cathodic range and reproducible results with a minimum of attention. Amalgams were of special interest since from their liquid surfaces any accumulation of metal or other water-insoluble reduction product should be swept away by the stirring action of the electrode as it moves through the solution. Such action would, to a great extent, aid in preventing either electrode blocking or electrode area increase. In addition, the hydrogen overvoltage of any amalgam, and thus the cathodic range, would be expected to be larger than that of any metal except pure mercury itself.

Secondly, the influence of scanning rate was to be studied. It was felt that not only could the time required for analyses be cut down by faster scanning rates, but also the amount of electrolysis product formed would be decreased and the electrode thus made to behave more like the D.M.E. with its constantly renewed surface.

While the time for a run with the dropping mercury electrode is limited by the nature of the drop to rather slow (five minutes or more) or very fast (one-twentieth second) rates, and the stationary microelec-

trode is limited to slow rates by the time involved in coming to equilibrium, there would seem to be no such limitation in the case of the rotating microelectrode. Indeed, once the diffusion layer has been established, the scanning rate should be limited only by the kinetics of the reaction and the response of the recording instrument. In the determination of metal cations, the electrode reactions usually are fast enough. The oscillograph response is so nearly instantaneous as to be adequate in any feasible range of scanning time. Actually, the fastest speed used was three seconds, which is slow both kinetically and electronically.

EXPERIMENTAL DETAILS

Two polarographs, both having, essentially, the circuit shown in Figure 2, were employed. Both may be operated with either upsweep or downsweep voltage scanning. Both have a range of zero to three volts, with preset starting voltages that are either additive or opposed and are continuously variable.

The first instrument, commonly called the experimental model, was designed by Dr. Paul Arthur and built in this laboratory. It has a large selection of scanning speeds, ranging from 26 seconds to 10 hours. Recording may be done photographically or on a Brown potentiometer or on an oscillograph. The mechanical response of the Brown recorder makes it impractical for scanning rates of less than two minutes; the galvanometer used in photographic recording is somewhat more responsive.

The second instrument, commonly called the high-speed model, was also designed by Dr. Arthur and built in this laboratory. This polarograph has two fixed scanning rates, one of three seconds and the other of four minutes 40 seconds, and is adapted for use only with an oscillograph.

Pen- and chart-recording was done with a Brown Elektronik Potentiometer, Model No. 153X12V-X-30. The oscillograph employed was a DuMont Cathode Ray Oscillograph, Model 304H. Photographs of the oscillograph traces were made with an Ibsor D.R.P. camera, with the shutter set at $f/9$ and at a fixed focal length of 13 inches. The camera and oscillograph screen were enclosed in a light-tight box and shield. Eastman Kodak Panatomic X film was used, with enlargements made on F-4 Kodabromide paper.

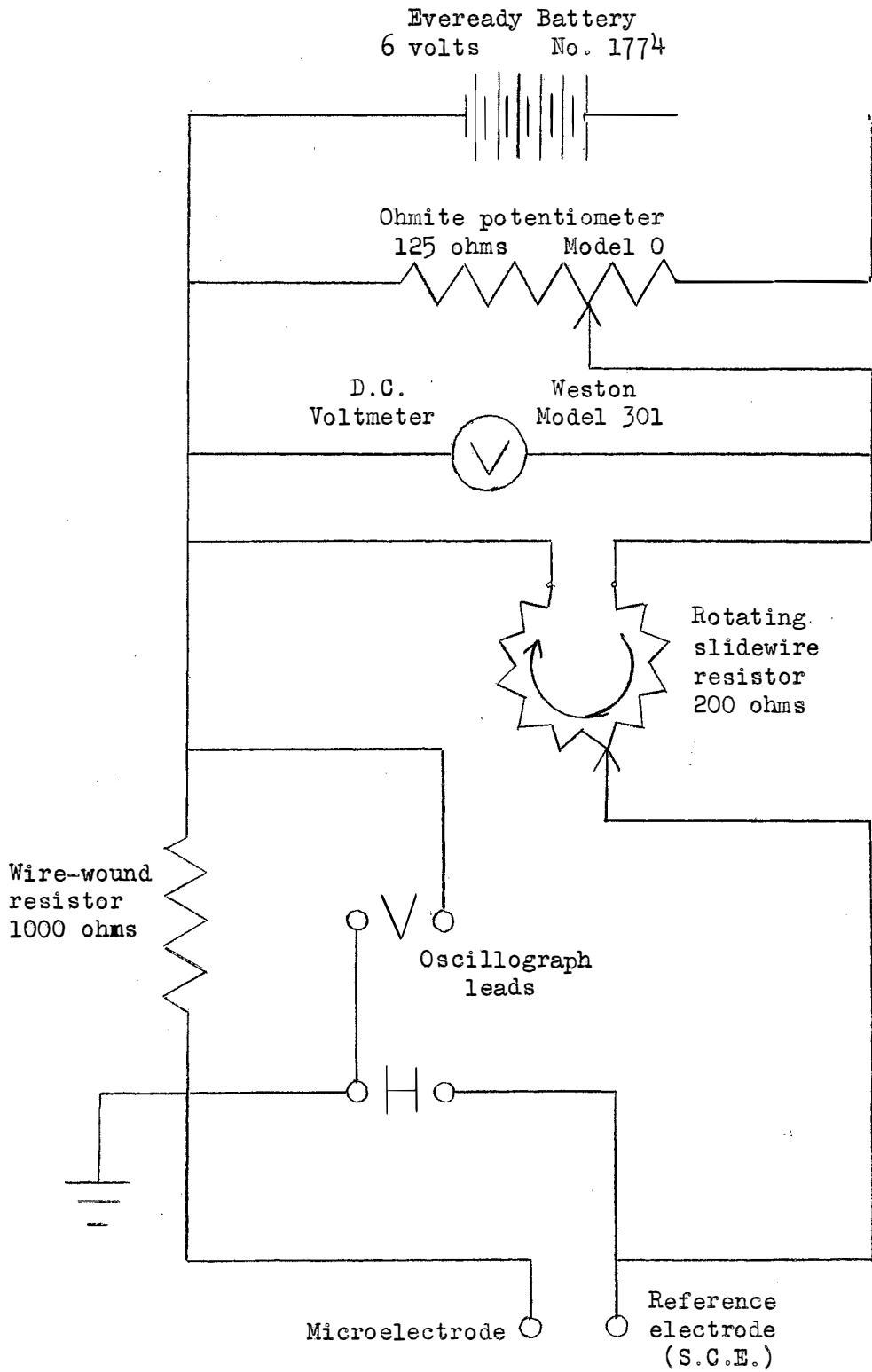


Figure 2 Polarograph Circuit Diagram

The reference electrode was the saturated calomel electrode (S.C.E.); consequently, all potentials listed are with reference to the S.C.E.

Potential calibrations were made using a Wheatstone bridge, essentials of which are a Leeds and Northrup galvanometer, Leeds and Northrup decade box and Gray instrument Co. No. 9244 potentiometer. The potentiometer was itself calibrated against The Eppley Lab., Inc., standard cell No. 452498.

The current axis of the Brown potentiometer was calibrated by using a known resistance in place of the electrolysis and reference cells. The ordinate of the DuMont oscillograph was calibrated in the same way, but the results were not as satisfactory owing to lack of stability in the behavior of the oscillograph. Although the amplification factor of the oscillograph is quite stable under ordinary conditions, it is difficult to detect the effect of a weak tube. On two occasions during this work it became necessary to replace tubes and rebalance the push-pull amplifiers. On one occasion, a number of circuit resistors and capacitors also required replacement.

The basic microelectrode employed was a rotating platinum wire electrode. The platinum wire was imbedded in a hole in the side of a steel shaft and secured with Wood's metal (Figure 3). The shaft was electrically insulated by coating with ceresin wax. A glass bead on the platinum wire insured a reproducible length. The shaft was rotated at a speed of 600 r.p.m. by a 0.050 h.p. Dayton Electric Mfg. Co. motor, the motor speed of 1500 r.p.m. being reduced to the desired speed by appropriate pulleys.

Eight different microelectrodes were used. In addition to the basic platinum electrode, electrodes of copper, gold and silver were

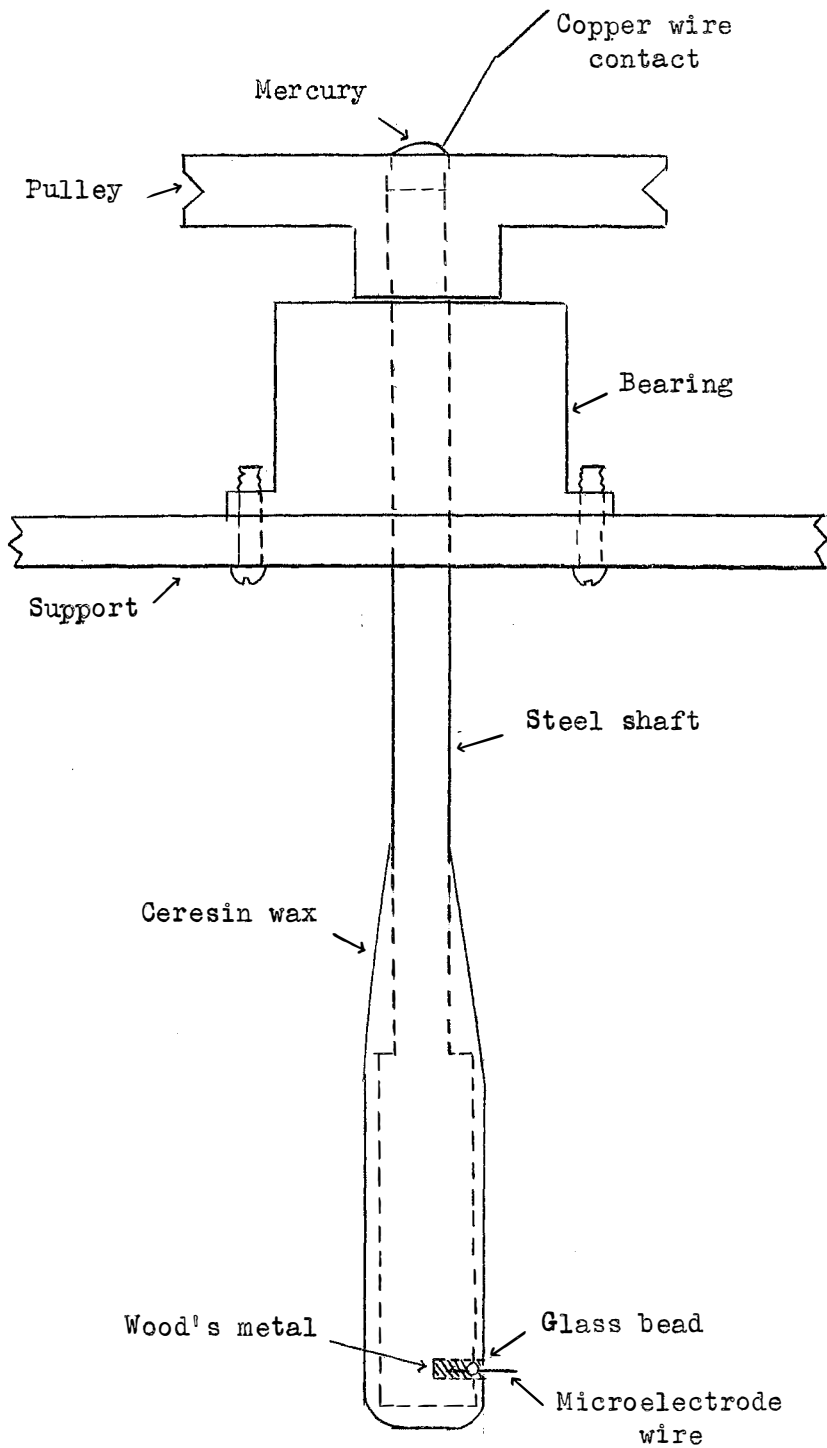


Figure 3 Rotating Microelectrode Assembly

prepared. All four metal electrodes were also used in an amalgamated form. The copper, gold and silver electrodes were made by electroplating the platinum wire electrode with the desired metal. Electroplating was also used, in preference to dipping, for amalgamation, in an attempt to insure reproducibility of surface and uniform thickness of coatings. Electroplating details are found in Table 1.

The microelectrode platings were renewed as necessary. All platings except the gold, which was never renewed, were removed with 50% nitric acid in preparation for replating. This was done more often than otherwise would have been necessary, for it was desired to establish the reproducibility of the electrode preparations.

All reagents used conformed to American Chemical Society Reagent Grade specifications. All solutions were made with distilled water.

All solutions were degassed with nitrogen for at least 15 minutes prior to running polarograms. The nitrogen was first run through alkaline pyrogallol solution, followed by concentrated sulfuric acid, in gas saturation bottles. The solutions were also kept under a nitrogen atmosphere during runs.

The reference cell and electrolysis cell were joined by a ground glass ball-and-socket joint, each sidearm being 40 cm. long. The sidearms were packed with glass wool.

The constant-temperature control was provided by a large central reservoir containing water held at $25.0 \pm 0.1^\circ \text{C.}$, with each individual cell bath connected into the closed circulating system. The constant-temperature water thus provided circulated through a copper tube coiled in a water-filled battery jar which served as a cell bath. A tightly-fitted plywood lid, with holes for the reference cell, electrolysis cell,

Table I
Microelectrode Preparations and Statistics

Electrode	Platinum	Copper	Gold	Silver	Amalgam
Plating solution	---	0.1 M CuSO ₄	0.1 M AuCl ₃	0.1 M AgNO ₃	0.1 M HgCl ₂
Plating time	---	5 min.	5 min.	5 min.	90 sec.
Plating current in ma.	---	0.3	1.2	0.8	0.2
Length in mm.	3.185	3.576	3.279	2.606	---
Diameter in mm.	0.511	0.483	0.526	0.775	---
Area in sq. mm.	5.313	5.610	5.641	6.818	---
Thickness of plating in mm.	---	0.001	0.002	0.041	---

stirrer, and thermometer, covered the cell bath. The thermometer was calibrated against a Bureau of Standards thermometer, and the constant-temperature work was done at $25 \pm 0.1^\circ\text{C}$.

RESULTS AND DISCUSSION

ELECTRODES

All eight microelectrodes enumerated in the previous section (see p.14) were investigated with respect to usable cathodic range by running polarograms on solutions containing only 0.1 M KCL, the supporting electrolyte. Figure 4 shows the shapes of the curves obtained and the relative magnitudes of the residual currents. The decomposition potentials (hydrogen, or carrier electrolyte) agree with those found by Maness (14) for the platinum, copper, gold, copper amalgam and gold amalgam electrodes he investigated, and by Airey (1) for the silver amalgam. From this it can be seen that the amalgamated electrodes all allow operation at a significantly more negative potential than any of the corresponding metal electrodes.

In making these, and other runs with the oscillograph, quantitative results were hard to obtain owing to the instability of the oscillograph. Figure 5 shows two consecutive runs with the 0.1 M KCL supporting electrolyte using the platinum amalgam electrode. This illustrates quite clearly the extent of the drift on the vertical deflection of the oscillograph. Only by making a number of duplicate runs and comparing wave forms obtained on the Brown potentiometer with curves obtained on the oscillograph was it possible to select the photographs uninfluenced by instrument instability. This point will be illustrated again in subsequent sections.

All eight electrodes were used with three polarographically-common cations in a study of the wave forms obtainable. Using $\text{Cd}(\text{NO}_3)_2$ with 0.1 M KCL carrier, the waves were as shown in Figure 6. Typical

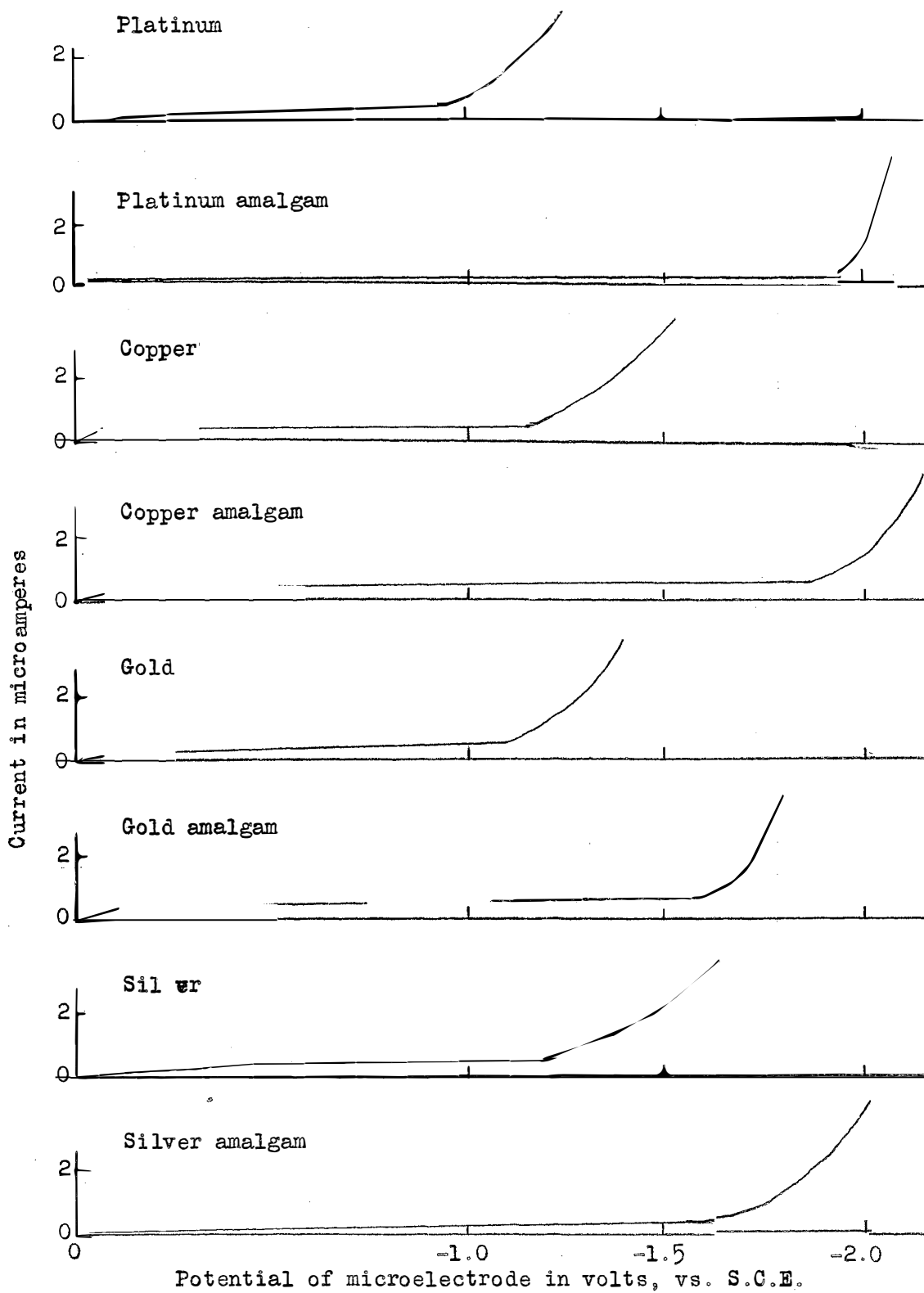


Figure 4 Electrolysis in 0.1 M KCl with Several Microelectrodes

Scanning rate - 3 seconds

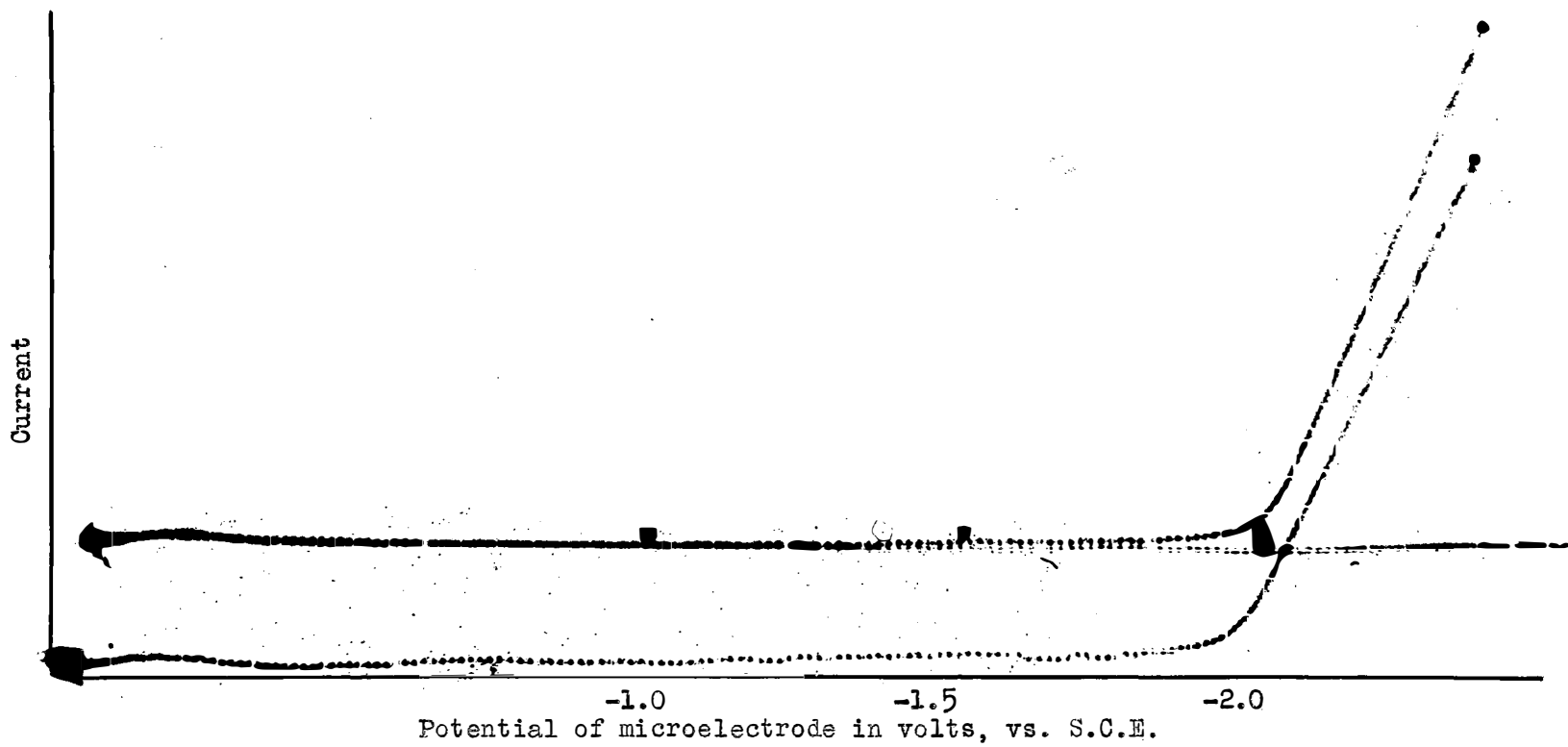


Figure 5 Electrolysis of 0.1 M KCl with the Copper
Amalgam Microelectrode

Scanning rate - 3 seconds

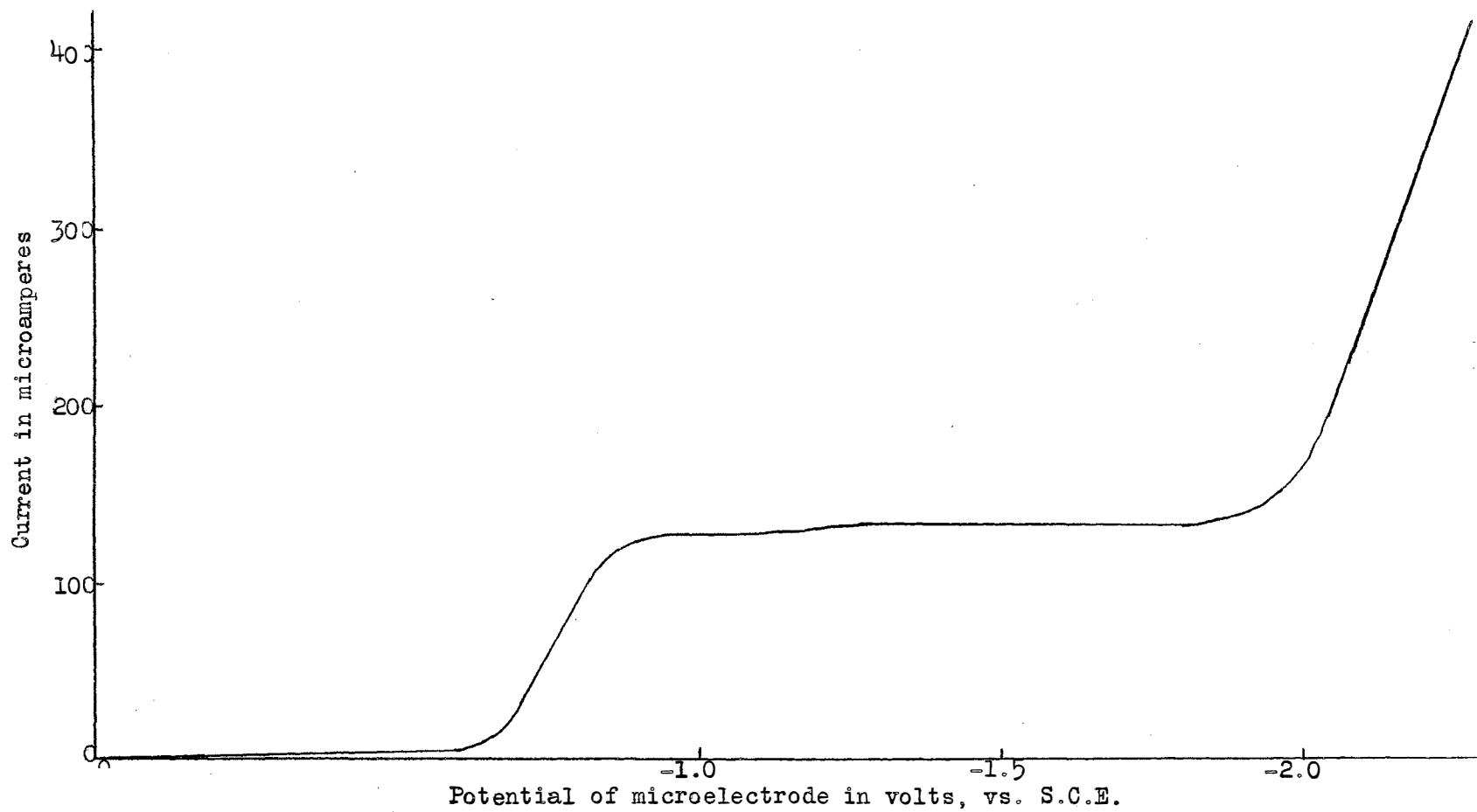


Figure 6 Polarogram of 1×10^{-3} M $\text{Cd}(\text{NO}_3)_2$ at the Copper

Amalgam Microelectrode

Carrier - 0.1 M KCl

Scanning rate - two minutes, 45 seconds

of the waves of $\text{Pb}(\text{NO}_3)_2$ in 0.1 M KCL is Figure 7.

Behavior of the ferric ion was not as uniform for the various electrodes tried. The platinum, copper, gold, silver, copper amalgam and gold amalgam microelectrodes gave a wave typified by Figure 8, while the silver amalgam and platinum amalgam waves show the two-step appearance of Figure 9.

The first step in any reduction of ferric ion should be to the ferrous ion. The second wave, then, should be observed only when the decomposition potential of the carrier electrolyte is negative enough to permit the reduction of the ferrous ion. Figure 10 shows the polarogram of FeSO_4 in 0.1 M $\text{K}_2\text{C}_2\text{O}_4$ with the platinum amalgam microelectrode. The half-wave potential agrees with that of the second wave of the ferric ion.

Figure 5 would seem to indicate that the copper amalgam electrode should also show a second wave. However, the half-wave potential ($E_{1/2}$) of the ferric ion with the copper amalgam electrode is appreciably more negative than the corresponding $E_{1/2}$ for platinum amalgam and silver amalgam, and so would be the $E_{1/2}$ for the reduction of ferrous ion with the copper amalgam microelectrode.

Freshly-amalgamated electrodes quite often gave waves with anomalous variations on the first run. Merely removing the solution, washing off the electrode with distilled water, and starting again with a new electrolysis solution eliminated this trouble. This phenomenon was also noted by Cooke (2) in his work with silver amalgam electrodes, and was attributed by him to the presence of cadmium and lead impurities in the mercury. Since the amalgams used in this research were produced by electroplating, it seems more probable that the variations observed

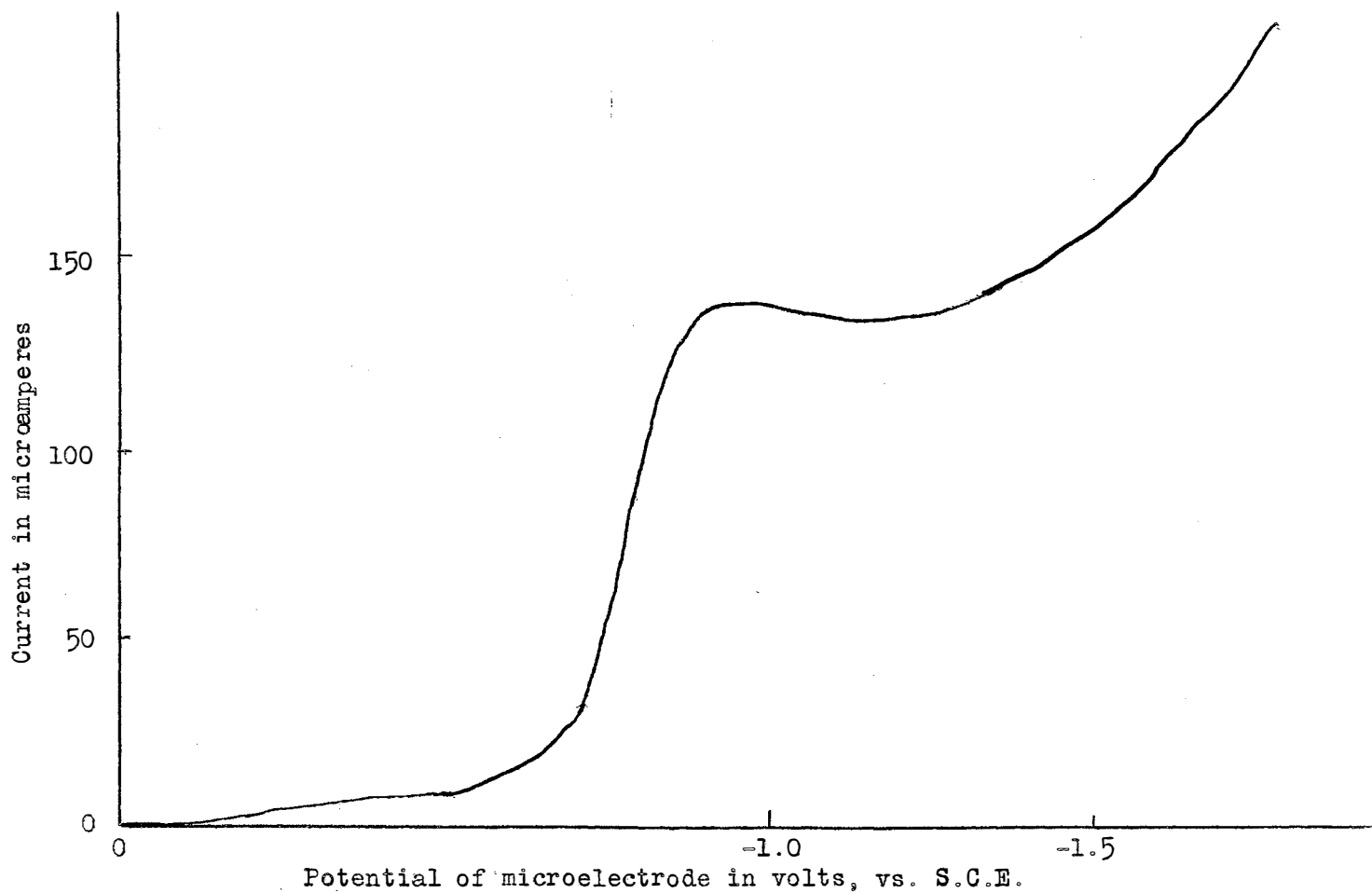


Figure 7 Polarogram of 4×10^{-4} M $\text{Pb}(\text{NO}_3)_2$ with the Silver Amalgam Microelectrode

Carrier - 0.1 M KCl

Scanning rate - two minutes, 45 seconds

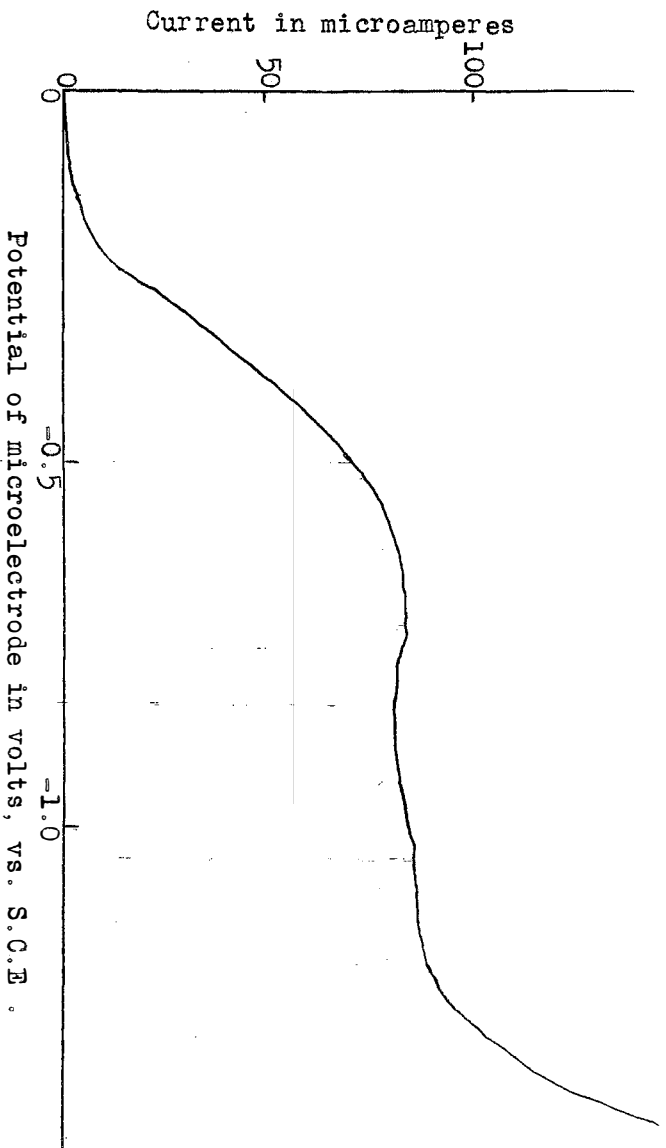


Figure 8 Polarogram of 4×10^{-4} M FeCl_3 with the Gold Amalgam Microelectrode

Carrier - 0.1 M $\text{Na}_2\text{C}_2\text{O}_4$
Scanning rate - two minutes, 45 seconds

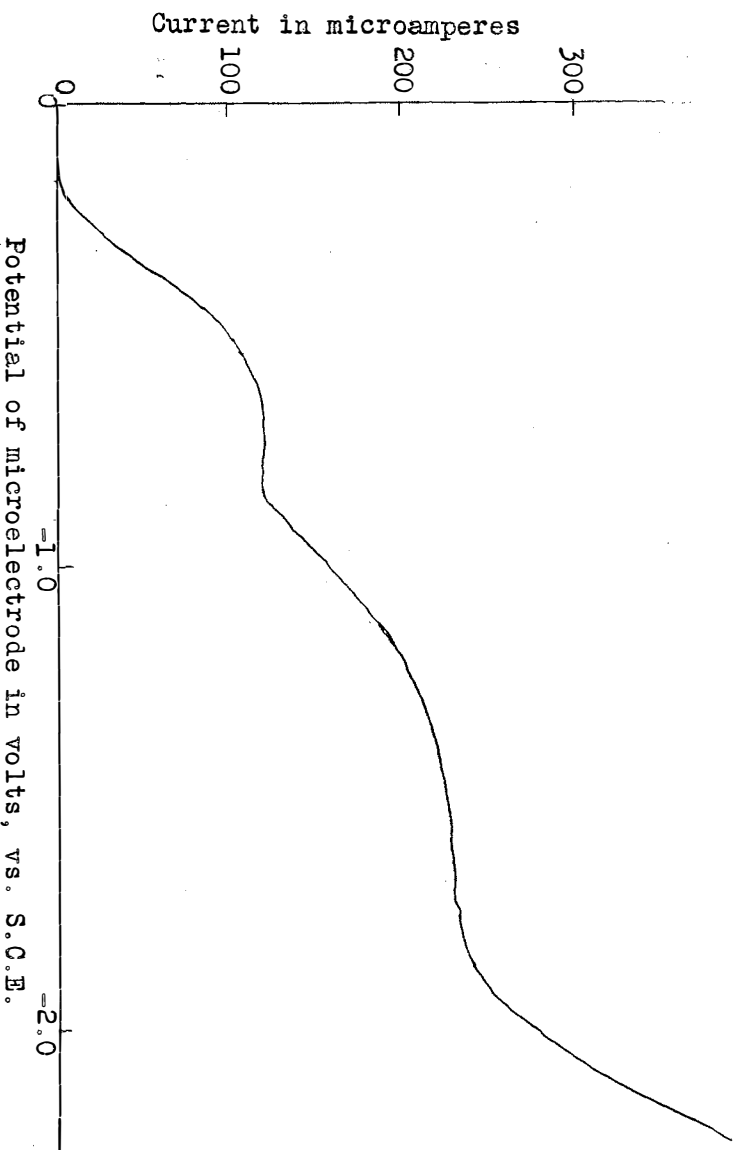


Figure 9 Polarogram of 7×10^{-4} M FeCl_3 with the Platinum Amalgam Microelectrode

Carrier - 0.1 M $\text{Na}_2\text{C}_2\text{O}_4$
Scanning rate - two minutes, 45 seconds

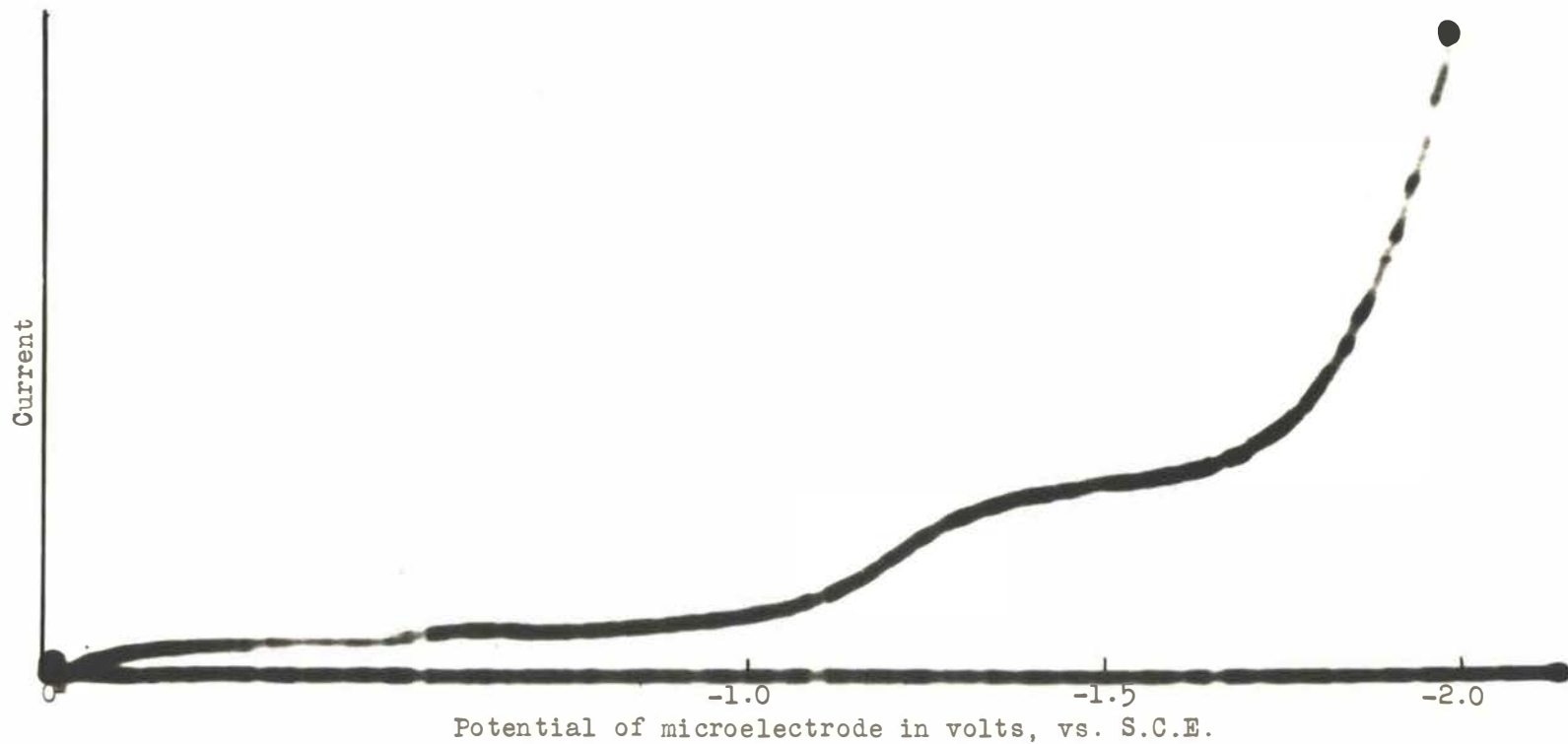


Figure 10 Polarogram of FeSO_4 with the Platinum
Amalgam Microelectrode

Carrier - 0.1 M $\text{K}_2\text{C}_2\text{O}_4$
Scanning rate - 3 seconds

here were caused by other factors. Thus, any mercuric ion not washed off the electrode, mercurous ion present as a result of incomplete reduction, or electrode metal ions (e.g., cupric ions from the copper microelectrode) resulting from a direct oxidation of the metal by mercuric ions, would be expected to give the same type of anomalous waves. This trouble was especially acute with the copper amalgam electrode.

SUPPORTING ELECTROLYTES

In starting work on the rotating microelectrode, one of the first problems was that of finding a suitable supporting electrolyte. There seemed to be no reason for believing that 0.1 M KCl would be unsatisfactory, but 0.1 M LiCl (7) and 0.1 M $(\text{CH}_3)_4\text{NCl}$ (9) have been used in an attempt to extend the useful range of the dropping mercury electrode to more negative potentials. All three carriers were used with the platinum and platinum amalgam electrodes, and Figures 11 and 12 show the waves in forms easily comparable. Results with the copper electrode were similar to those shown for platinum.

Despite their advantages with the D.M.E., results of this study did not justify using the hydrated LiCl or the very hygroscopic $(\text{CH}_3)_4\text{NCl}$ when KCl would serve at least as well. The study was dropped at this point since this approach did not seem to yield profitable results.

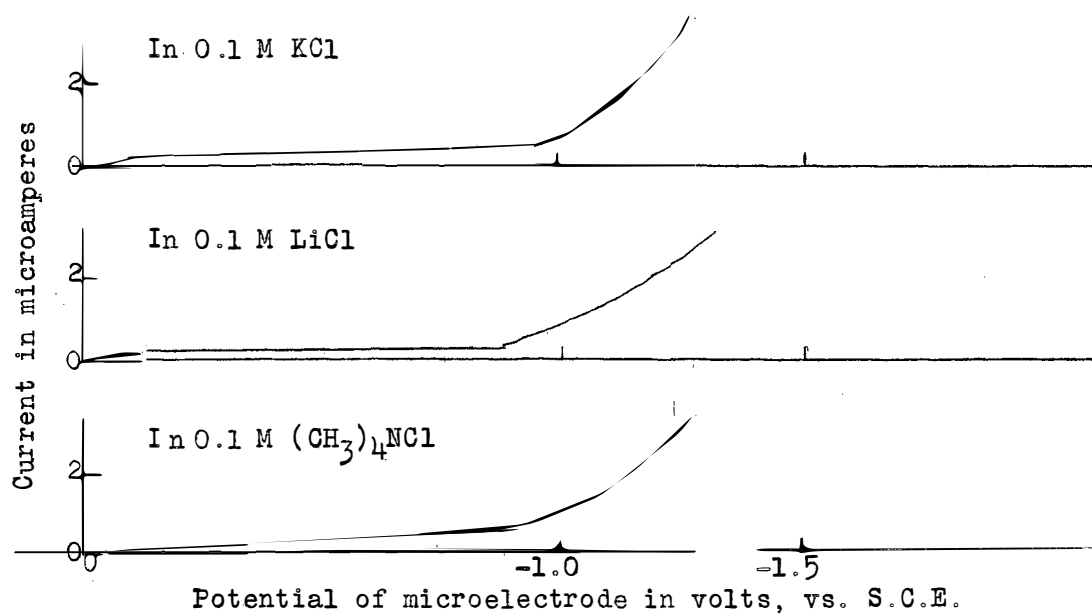


Figure 11 Electrolysis with the Platinum
Microelectrode

Scanning rate - 3 seconds

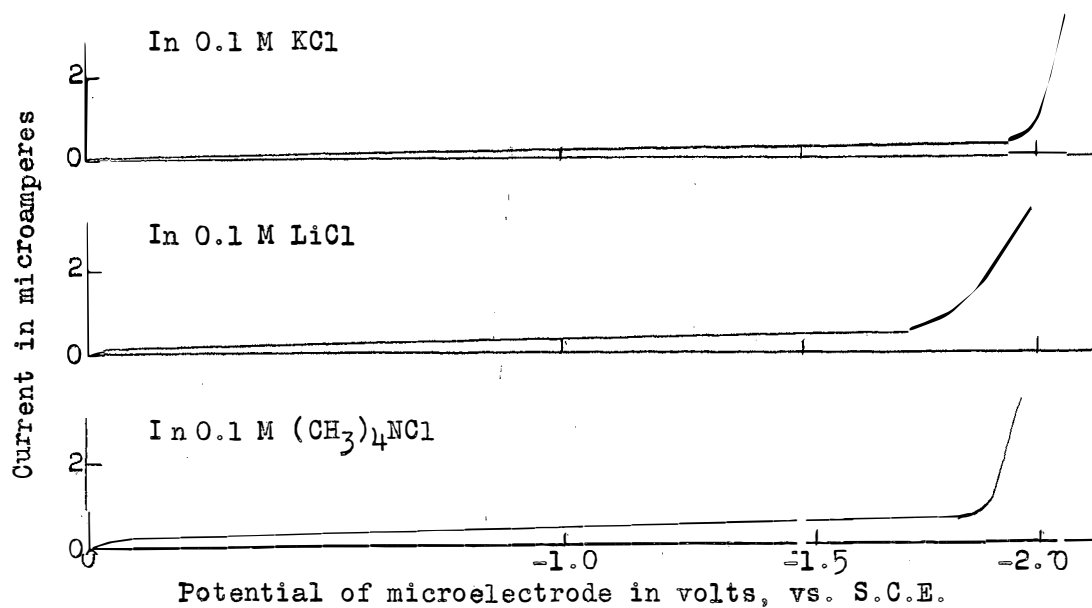


Figure 12 Electrolysis with the Platinum
Amalgam Microelectrode

Scanning rate - 3 seconds

SCANNING RATES

All four amalgamated microelectrodes were studied, each with cadmium, lead, and ferric ions, in an attempt to evaluate the effect of widely different scanning rates on the wave forms, half-wave potentials and linearity of the diffusion current with concentration.

It was hoped at the start of this work that polarograms at all scanning rates could be recorded photographically from the oscillograph. Unfortunately, however, the instability of the oscillograph made it quite unsuitable for slower scanning rates. Figures 13, 14 and 15 show the results of that attempt for 10×10^{-4} M $\text{Cd}(\text{NO}_3)_2$ in 0.1 M KCl with the copper amalgam microelectrode. Figure 13 is at three seconds, Figure 14 at 30 seconds, and Figure 15 is at the two minutes, 45 seconds scanning speed. The instability of the oscillograph is readily seen by comparing Figure 15 with Figure 6, the latter being for the same solution recorded on the Brown potentiometer at the same speed.

It is obvious that the differences noted above were a matter of instrumentation, not of electrode response. On the other hand, Figure 16 shows the same ion under the same conditions using a nine minute 30 seconds scanning rate, the Brown potentiometer being used for recording. In this case, the difference (Figures 6 and 16) is more likely a result of the decrease in scanning rate, and the effect of that decrease on the microelectrode. Since this is more pronounced in the case of the lead analysis, it will be discussed at greater length later.

Since the platinum amalgam electrode was studied most extensively, results of that work will be treated first.

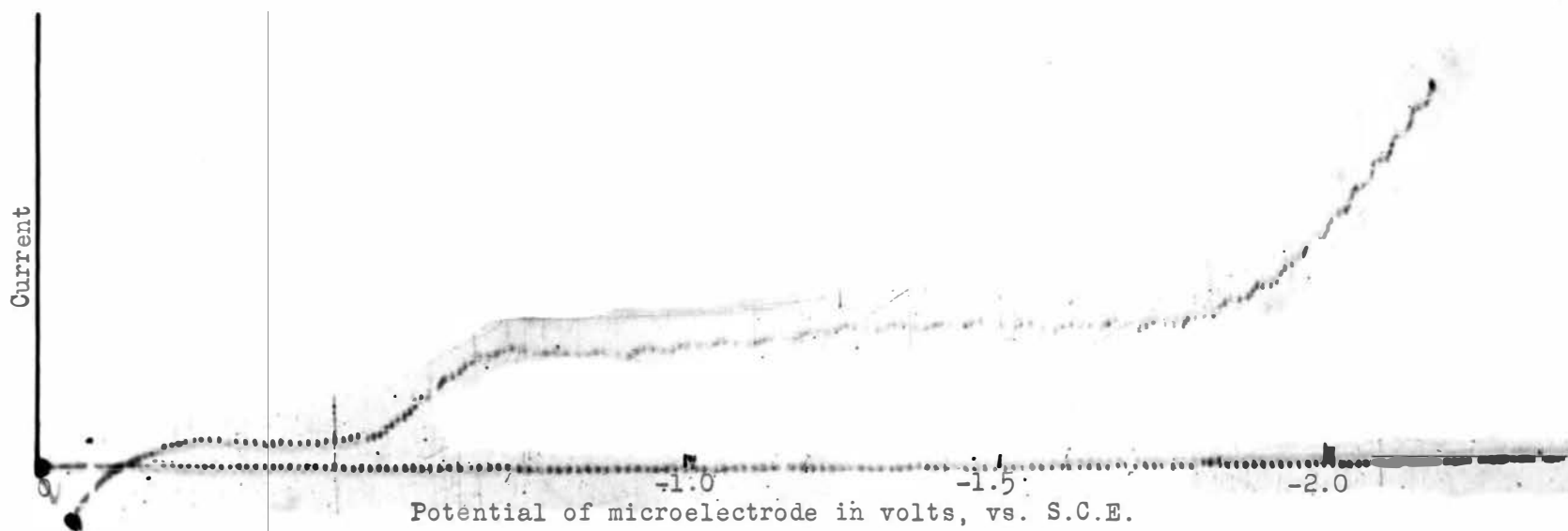


Figure 13 Polarogram of $10 \times 10^{-4} \text{ M Cd(NO}_3)_2$ with the
Copper Amalgam Microelectrode

Carrier - 0.1 M KCl
Scanning rate - 3 seconds

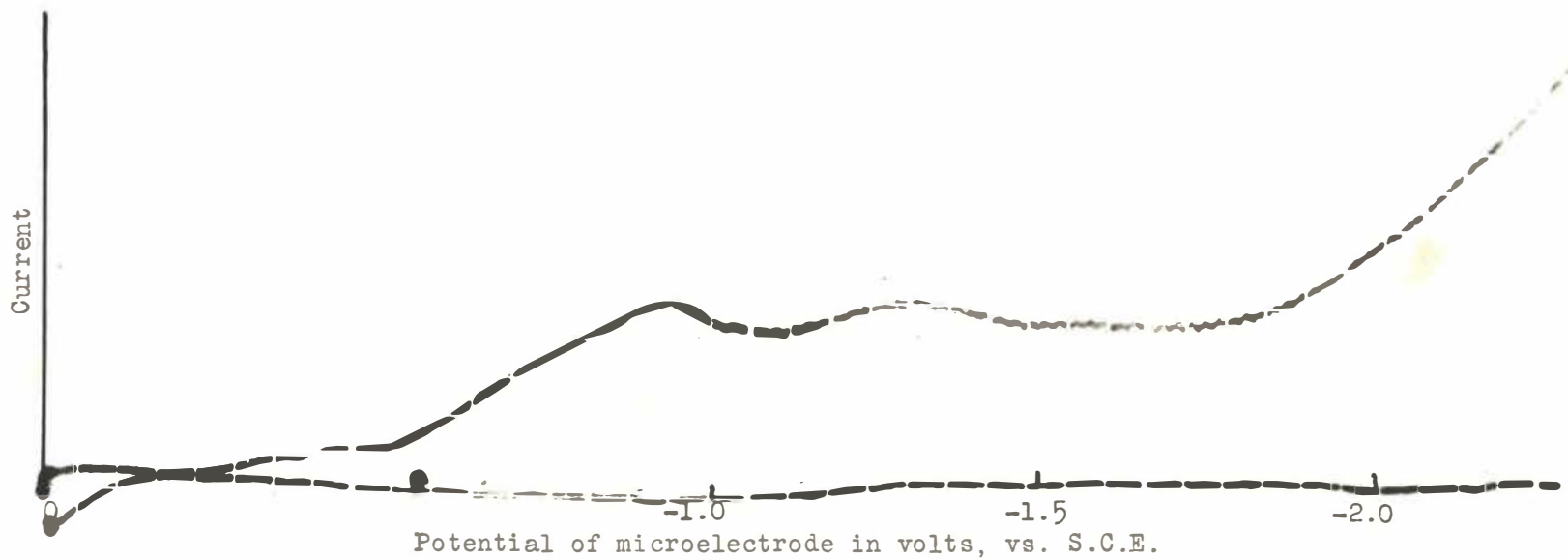


Figure 14 Polarogram of 10×10^{-4} M $\text{Cd}(\text{NO}_3)_2$ with the
Copper Amalgam Microelectrode

Carrier - 0.1 M KCl
Scanning rate - 30 seconds

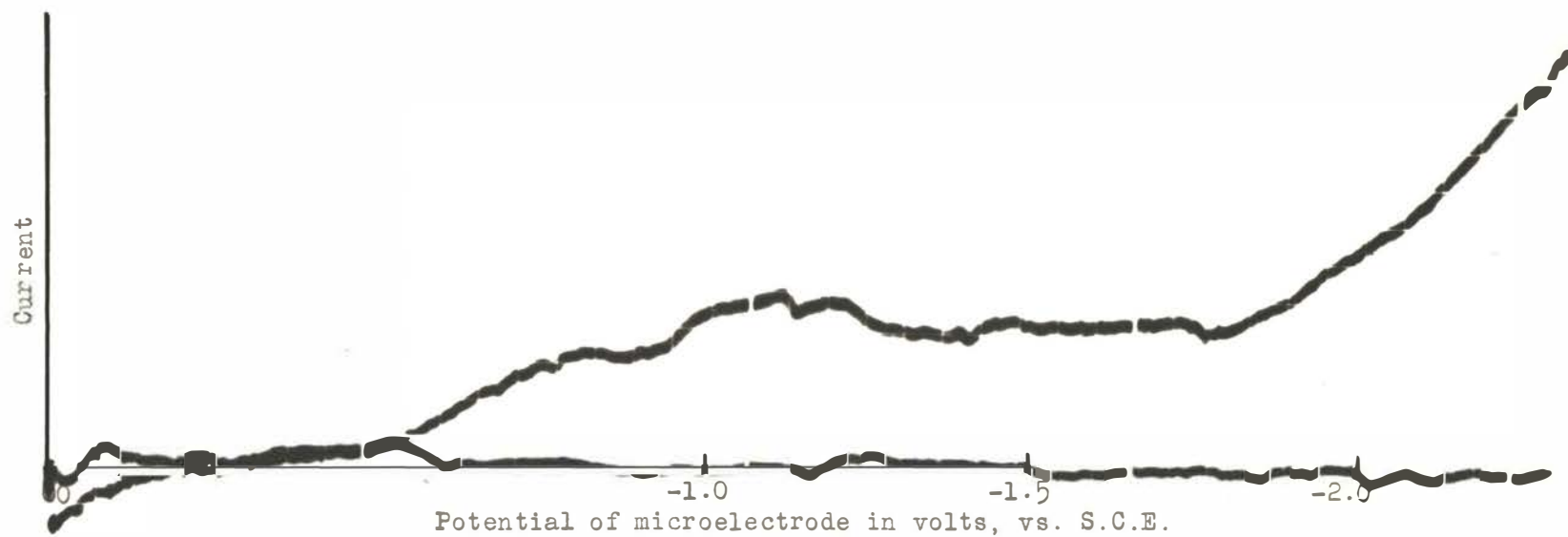


Figure 15 Polarogram of $10 \times 10^{-4} \text{ M Cd(NO}_3)_2$ with the
Copper Amalgam Microelectrode

Carrier - 0.1 M KCl

Scanning rate - two minutes, 45 seconds

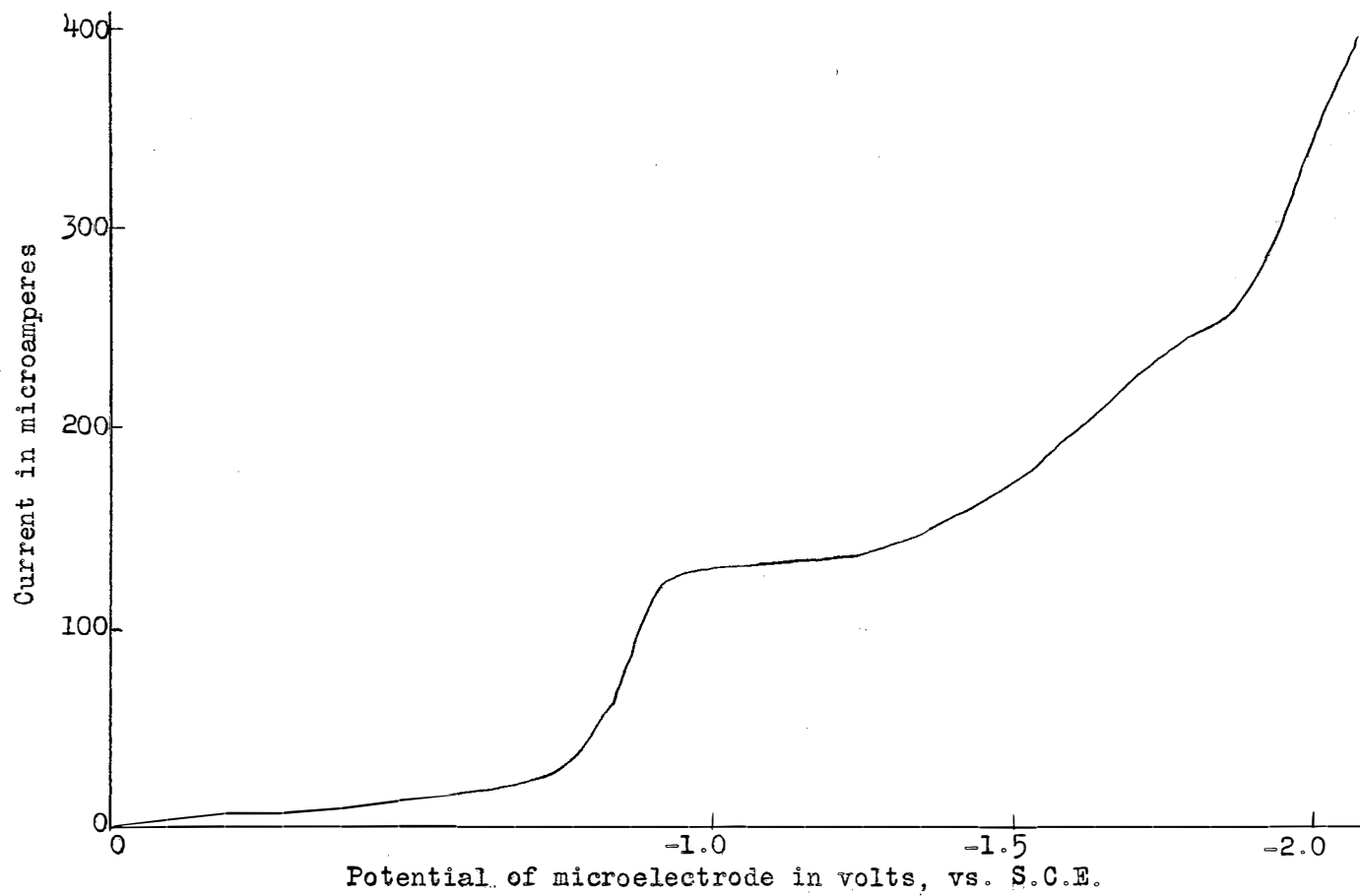


Figure 16 Polarogram of 10×10^{-4} M $\text{Cd}(\text{NO}_3)_2$ with the
Copper Amalgam Microelectrode

Carrier - 0.1 M KCl

Scanning rate - nine minutes, 30 seconds

In these studies, three basic speeds of scanning were used: three seconds; two minutes, 45 seconds; and nine minutes, 30 seconds. With the platinum amalgam microelectrode, an intermediate speed of 30 seconds was investigated, but since there was no change in wave form or other properties, this speed was omitted in subsequent work.

At the two faster rates mentioned, $\text{Pb}(\text{NO}_3)_2$ in 0.1 M KCl gave, at the platinum amalgam electrode, waves of the form shown in Figure 7. The maximum noted in Figure 7 is less pronounced at lower lead ion concentrations. This increase of maximum with increasing concentration of lead ion is characteristic of all electrodes at all speeds.

Figure 17 shows the two extremes of $\text{Pb}(\text{NO}_3)_2$ concentration used in this study for the runs at two minutes, 45 seconds. The two polarograms (curves 2 and 3) for the 10×10^{-4} M $\text{Pb}(\text{NO}_3)_2$ were made in succession without cleaning the electrode after curve 2 was made. By comparing curves 1 and 2, it is readily seen that not only is the diffusion current less regular, but also a slight shift occurs in the half-wave potential as the concentration is increased.

The influence of increased scanning rate upon the diffusion current is illustrated by comparing Figure 17, curve 2, with Figure 18. Both are for lead at a concentration of 10×10^{-4} M, but the scanning rate for Figure 17 was two minutes, 45 seconds, while that for Figure 18 was three seconds. It will be seen from these that the diffusion current at the higher speed is much more well-defined than it is at the lower speed. The second run (curve 3) of the 10×10^{-4} M $\text{Pb}(\text{NO}_3)_2$ in figure 17, which was made immediately after curve 2, gives a clue to the probable reason for these results. It would appear from these studies that at high concentrations and/or slow scanning rates, the

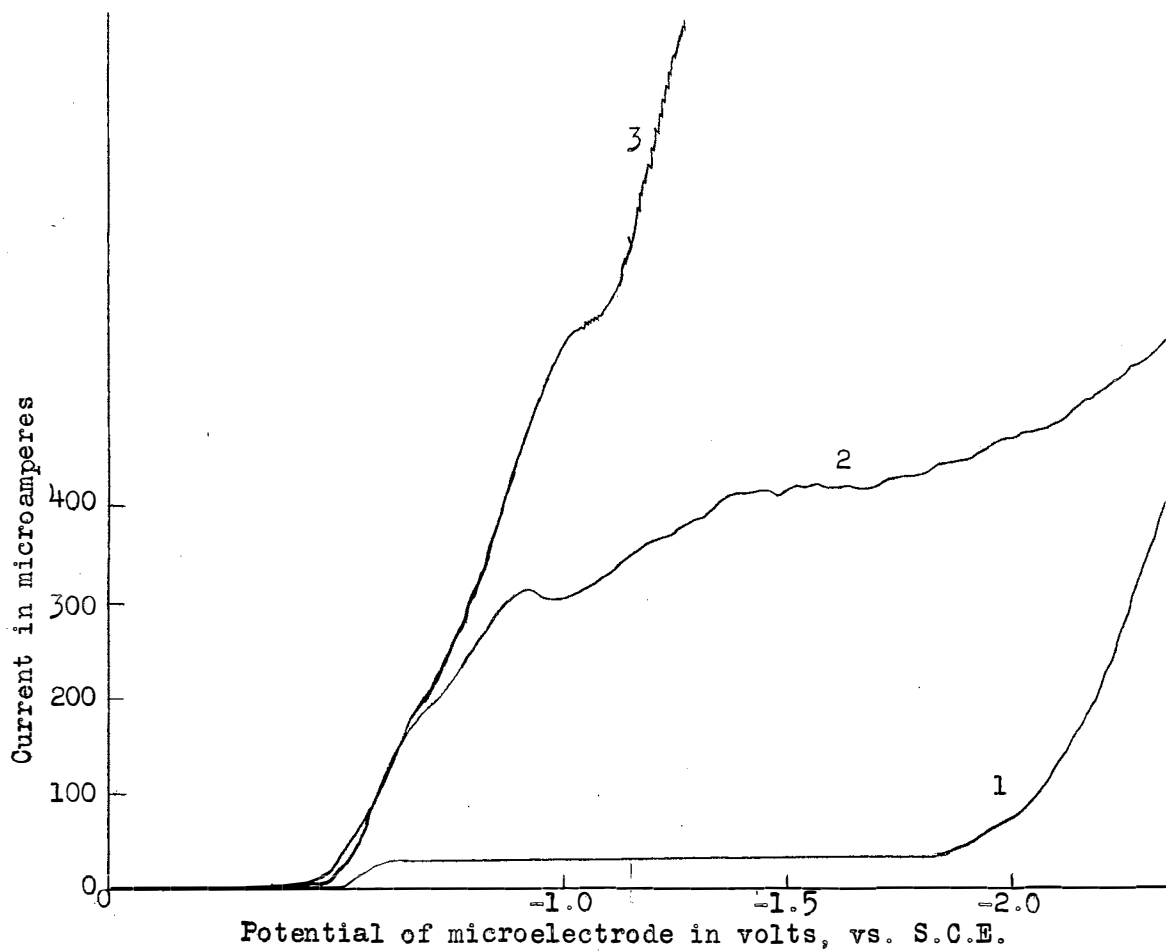


Figure 17 Polarograms of $\text{Pb}(\text{NO}_3)_2$ with the Platinum Amalgam Microelectrode

Carrier - 0.1 M KCl

Scanning rate - two minutes, 45 seconds

- 1 - 1×10^{-4} M $\text{Pb}(\text{NO}_3)_2$
 2 - 10×10^{-4} M $\text{Pb}(\text{NO}_3)_2$ (a)
 3 - 10×10^{-4} M $\text{Pb}(\text{NO}_3)_2$ (b)

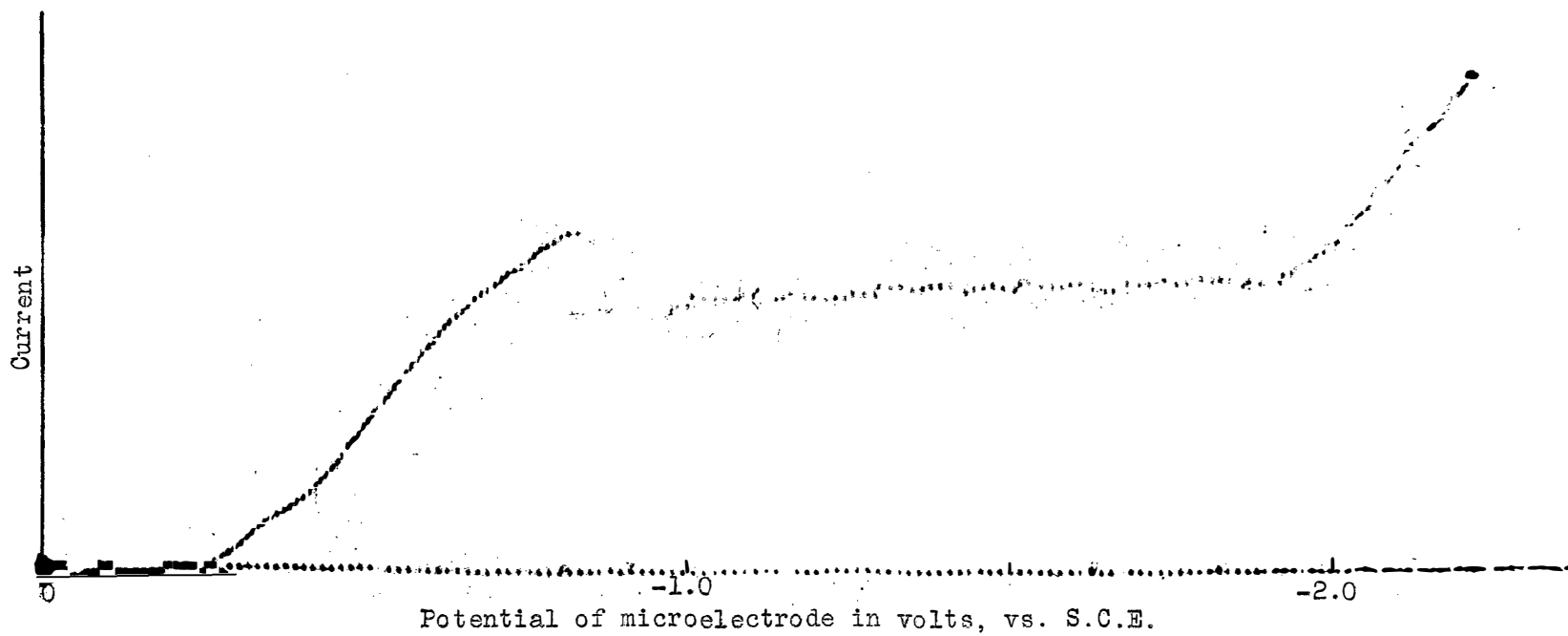


Figure 18 Polarogram of 10×10^{-4} M $\text{Pb}(\text{NO}_3)_2$ with the
Platinum Amalgam Microelectrode

Carrier - 0.1 M KCl
Scanning rate - 3 seconds

electrode becomes completely coated with lead. There is visual evidence for this, for at slower rates the microelectrode becomes appreciably larger, even to the naked eye, and becomes dull black in color. One of the expected advantages of the amalgamated electrode - i.e., the ability to prevent coating by the reduced metal - obviously is not realized in this case. Apparently the lead is not sufficiently soluble, or dissolves too slowly in the mercury of the electrode, to be completely amalgamated. Equally obviously the undissolved metal is held too firmly to be washed off by the stirring action around the electrode, with the result that lead coats the electrode. When this happens, both the effective area and the hydrogen overvoltage of the electrode are changed. Larger currents, and, ultimately evolution of hydrogen at lower potentials than usual thus are only to be expected. With lead ion at the nine minutes, 30 seconds scanning rate, no normal polarogram was ever obtained. This was not surprising since the microelectrode was completely converted to a lead electrode before the diffusion current was reached. This proved to be true even at the lowest lead ion concentration used - i.e., 1×10^{-4} M.

FeCl_3 in 0.1 M $\text{Na}_2\text{C}_2\text{O}_4$ with the platinum amalgam microelectrode is shown in Figure 9. Figure 10 shows the ferrous ion reduction.

The reduction of cadmium ion at the copper amalgam microelectrode has been covered rather thoroughly in Figures 6, 13, 14, 15 and 16. Lead develops a much sharper maximum at high concentrations with the copper amalgam electrode than it does with the platinum amalgam (Figure 19). Figure 8 gives the shape of the ferric ion wave.

The gold amalgam microelectrode is a duplicate of the copper amalgam electrode in wave forms and behavior.

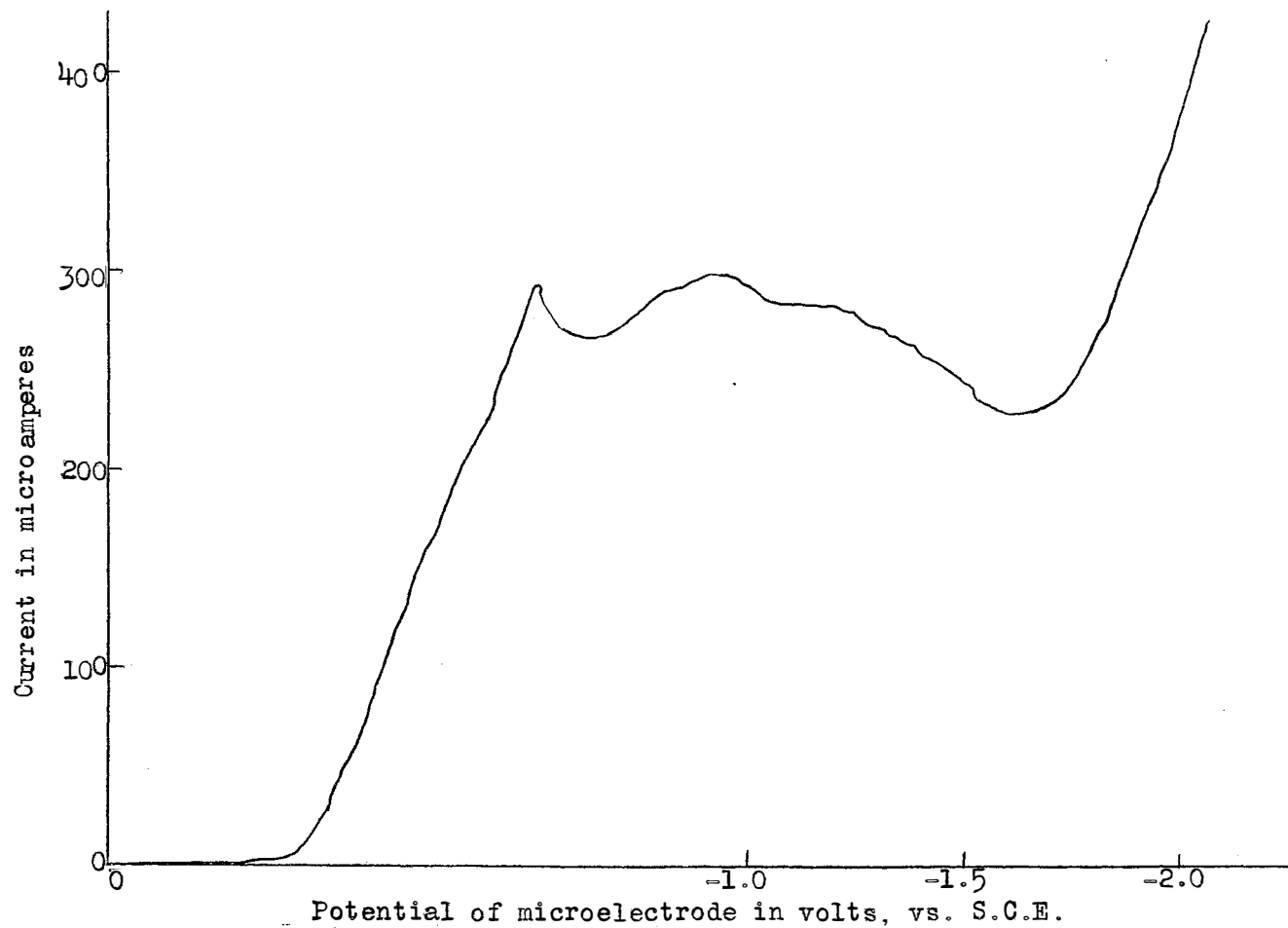


Figure 19 Polarogram of 10×10^{-4} M $\text{Pb}(\text{NO}_3)_2$ with the Copper Amalgam Microelectrode

Carrier - 0.1 M KCl
Scanning rate - two minutes, 45 seconds

The silver amalgam microelectrode gave the orthodox cadmium waves, with the lead ion and ferric ion waves being of the same shape as those obtained with the platinum amalgam electrode.

DIFFUSION CURRENTS

Use of polarography in quantitative analysis depends on the relation of the diffusion currents obtained to the concentration of reducible substance involved. This relationship has been determined for the three ions (cadmium, lead and ferric) used throughout this work with the four amalgamated microelectrodes.

A plot of diffusion current vs. ion concentration for the platinum amalgam electrode is shown in Figure 20. All three are linear over at least a portion of the concentration range used. Although the ferric ion analysis consistently gives a two-step wave, and the half-wave potentials are reproducible, the diffusion current vs. concentration curve is not linear for either wave. The sum of the two wave heights is better, however, and it is this sum which is plotted in Figure 20.

Figure 21 shows the diffusion current vs. concentration curves for the copper amalgam microelectrode. Although the ferric ion gives a one-step wave, the diffusion current is not linear over the concentration range studied.

The concentration range of ferric ion used with the gold amalgam microelectrode was not large enough to give significant results. The cadmium and lead curves are much better (see Figures 22 and 24), although the relationship between I_d and concentration for lead is not quite a straight line function.

Figure 23 shows the diffusion current vs. concentration curves for the silver amalgam microelectrode. The ferric ion curve was obtained in the same manner as the curve for the platinum amalgam electrode.

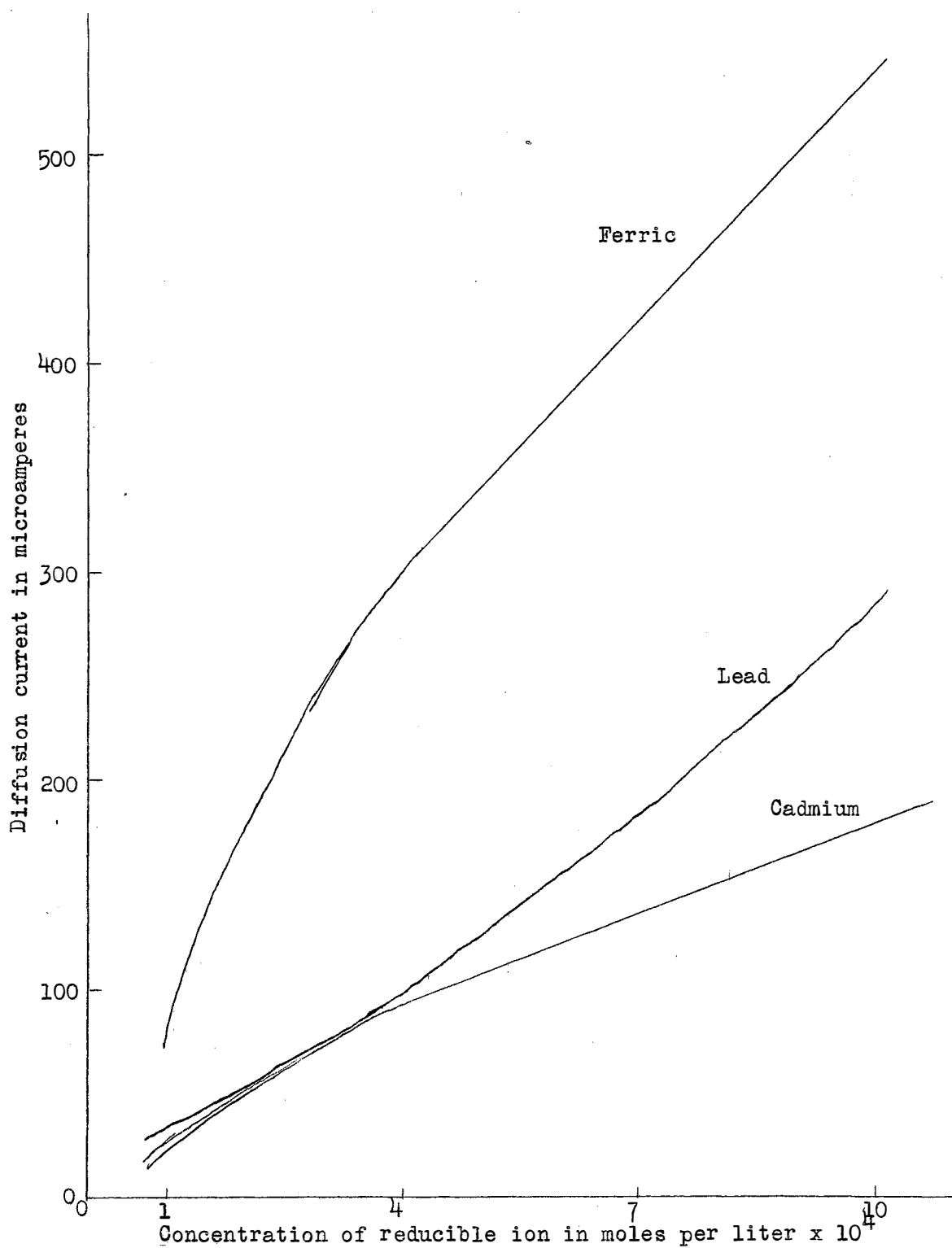


Figure 20 Diffusion Current vs. Ion Concentration with the Platinum Amalgam Microelectrode

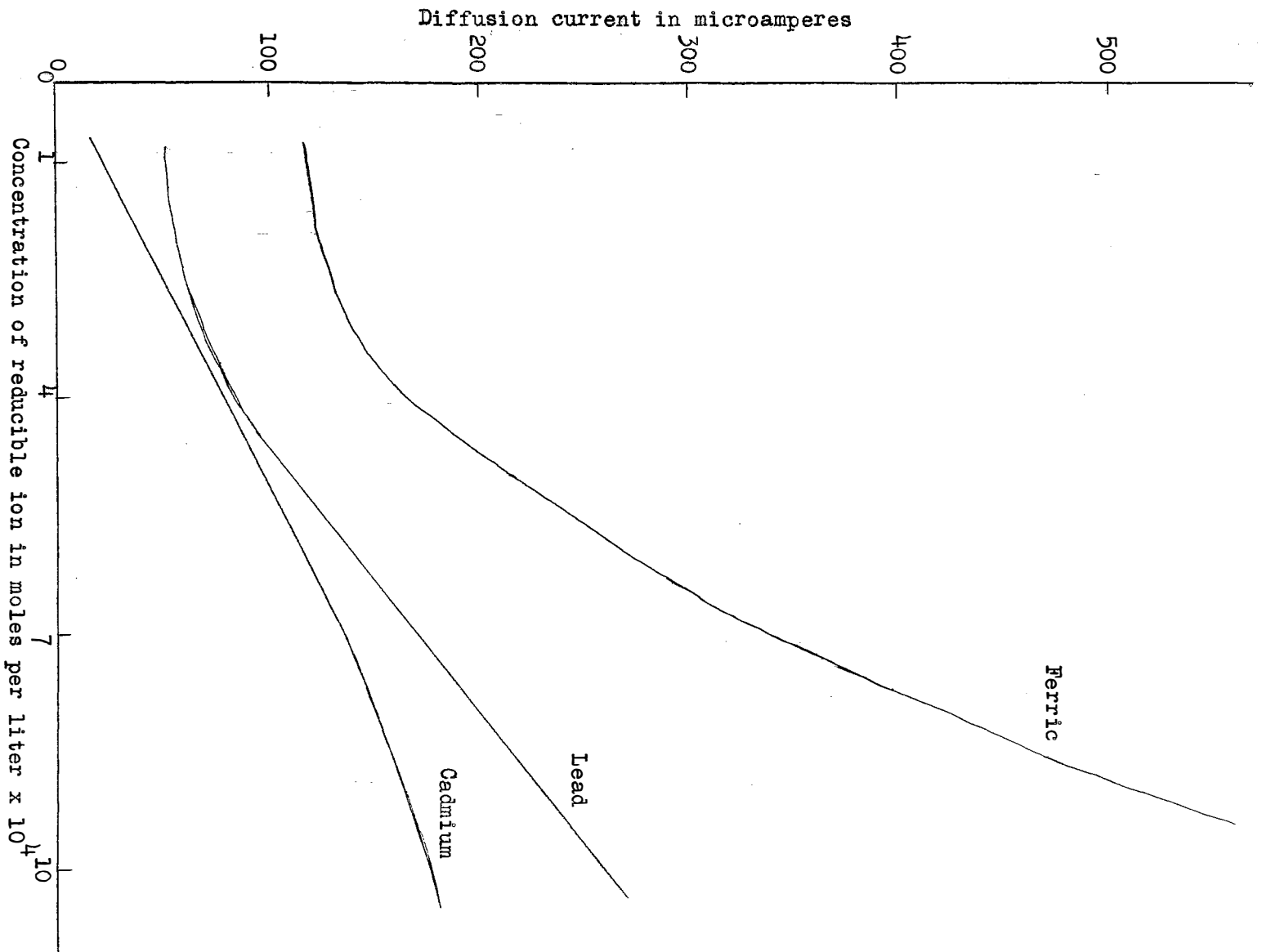


Figure 21 Diffusion Current vs. Ion Concentration with the
Copper Amalgam Microelectrode

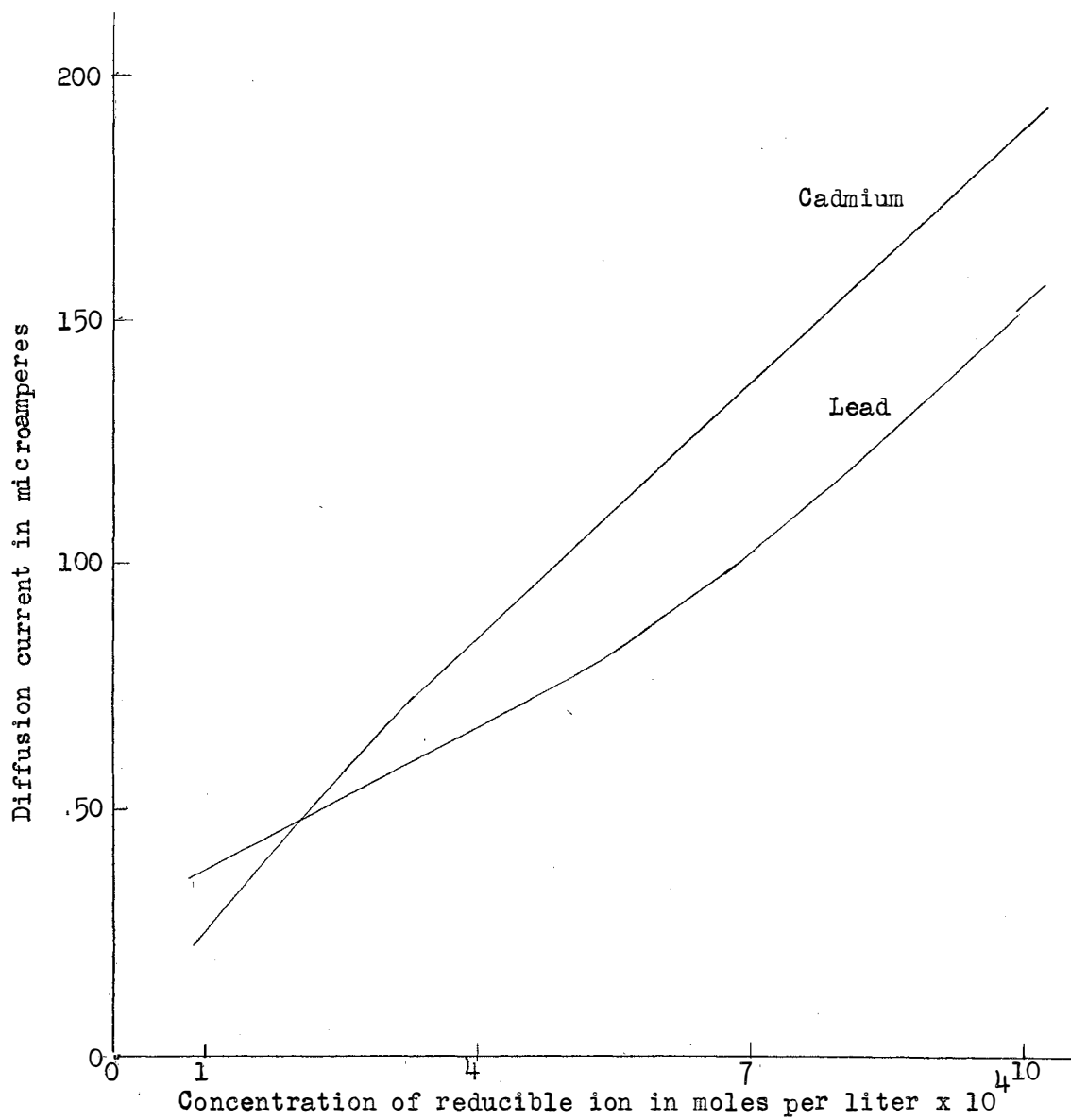


Figure 22 Diffusion Current vs. Ion Concentration with the Gold Amalgam Microelectrode

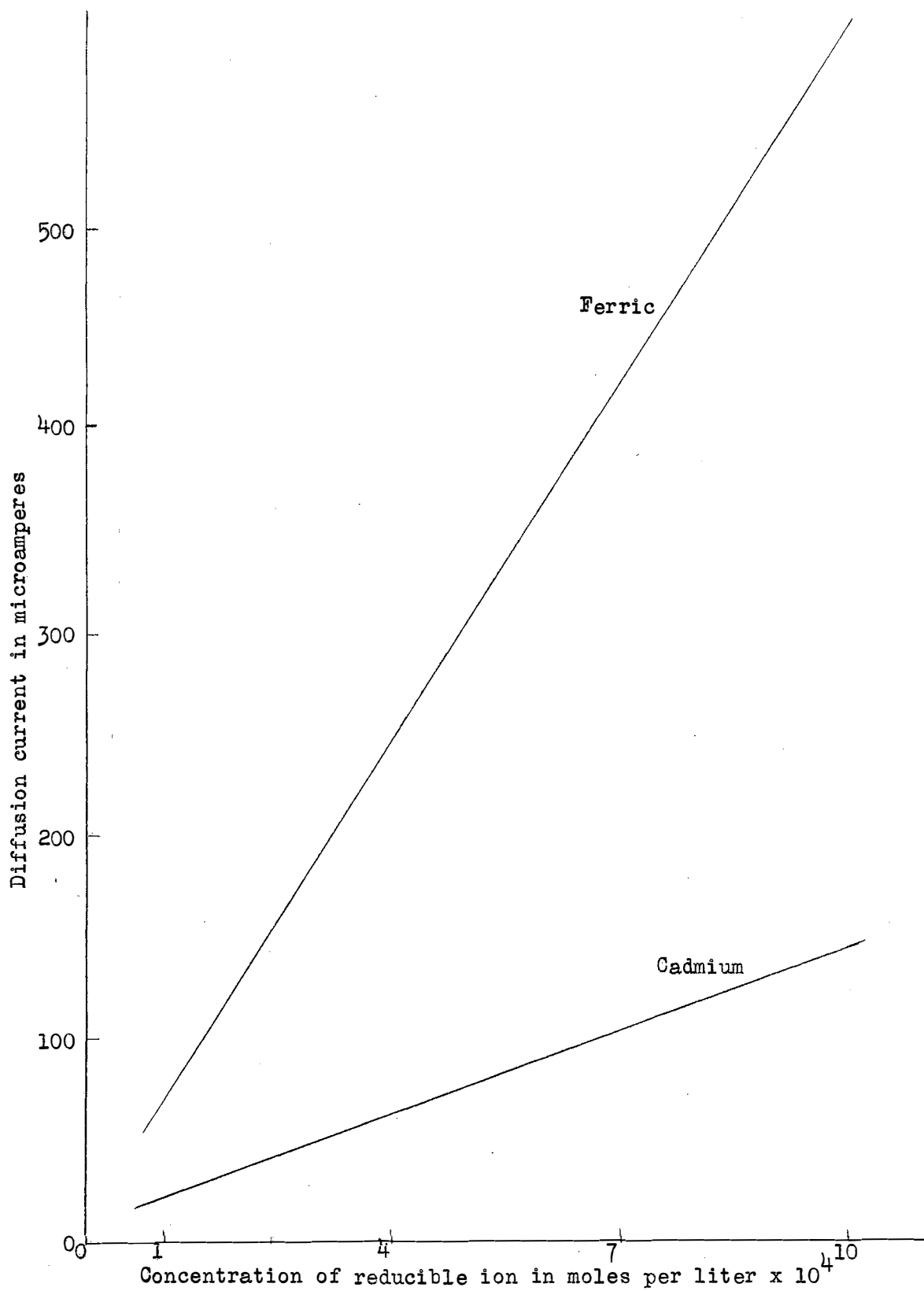


Figure 23 Diffusion Current vs. Ion Concentration with the Silver Amalgam Microelectrode

HALF-WAVE POTENTIALS

There should be two factors controlling the half-wave potentials in these studies. In working with the silver amalgam microelectrode, Cooke (2) found no shift of $E_{\frac{1}{2}}$ with change in concentration of the cobaltic ion. With the cadmium ion, he found a pronounced shift, the $E_{\frac{1}{2}}$ becoming more negative as the concentration was increased. This shift he attributed to the increasing concentration of cadmium metal on the electrode surface. This observation was confirmed by our results for cadmium (see Table 2).

Such results could be expected; for cobalt, being reduced only to the cobaltous ion, does not plate onto the electrode and therefore could not influence the properties of the electrode. Similarly, ferric ion, when reduced only from ferric ion to ferrous ion, would be expected to behave like cobalt. If the wave obtained for iron (the first wave in the case of platinum amalgam and silver amalgam electrodes) involves only the reduction of ferric to ferrous ion, its $E_{\frac{1}{2}}$ should be constant. This proved to be the case. Where there is a second wave, it should represent a reduction of ferrous ion to iron metal, and should behave like cadmium. This is also the case, as is shown in Table 2.

The reduction of lead is not so easily interpreted. Although the product is the metal, the half-wave potential does not change until, apparently, the mercury layer is saturated, at which point the current increases without reaching a plateau (see Figure 17). The cadmium and iron metal layers seem to produce no significant change in the microelectrode area, in marked contrast with the behavior of lead discussed previously (page 33).

Table II

Half-wave Potentials of Microelectrodes, vs. S.C.E.

Scanning rate - two minutes, 45 seconds

Reducible Ion	Microelectrode			
	Platinum Amalgam	Copper Amalgam	Gold Amalgam	Silver Amalgam
Cadmium				
1×10^{-4} M	-0.76		-0.69	-0.82
4×10^{-4} M	-0.80	-0.82	-0.70	-0.86
7×10^{-4} M	-0.83	-0.84	-0.71	-0.90
10×10^{-4} M	-0.87	-0.85	-0.72	-0.96
Lead				
	-0.60	-0.71	-0.61	-0.71
Ferric				
	-0.39	-0.54	-0.33	-0.32
Ferrous				
1×10^{-4} M	-0.91			-0.81
4×10^{-4} M	-1.04			-0.91
7×10^{-4} M	-1.06			-1.05
10×10^{-4} M	-1.11			-1.06

Cooke goes on to make a prediction that is of great interest to this study. He postulates that with higher rates of scanning the total amount of metal deposited during a single run will be less and, consequently, since the concentration of the amalgam formed will be very low, the $E_{\frac{1}{2}}$ should approach that of the D.M.E. This would apply to the cadmium. That such is not the case is shown by the experimentally determined values in Table III and by the curves in Figure 24. At the three second scanning rate the shift in $E_{\frac{1}{2}}$ with scanning rate is slight, al-

Table III

Half-wave Potentials of Cadmium Ion with Various Scanning Rates, vs. S.C.E.

Concentration of cadmium ion	Microelectrode		
	Platinum Amalgam	Copper Amalgam	Gold Amalgam
	4×10^{-4} M	10×10^{-4} M	4×10^{-4} M
Scanning rate			
3 sec.	-0.79	-0.82	-0.69
30 sec.		-0.83	
2 min., 45 sec.	-0.80	-0.85	-0.70
9 min., 30 sec.	-0.81	-0.85	-0.69

though noticeable, for cadmium with the gold amalgam microelectrode. On the other hand, the $E_{\frac{1}{2}}$ values at three seconds are identical with those shown in Table II for the two minutes, 45 seconds scanning rate.

Table III shows more clearly what happens when the scanning rate is changed drastically. There is a slight change, but not the kind of change necessary to substantiate the opinion that the half-wave potential will approach that of the D.M.E. The half-wave potential for the cadmium ion in 0.1 M KCl with the D.M.E. is -0.599 volts, vs. S.C.E.

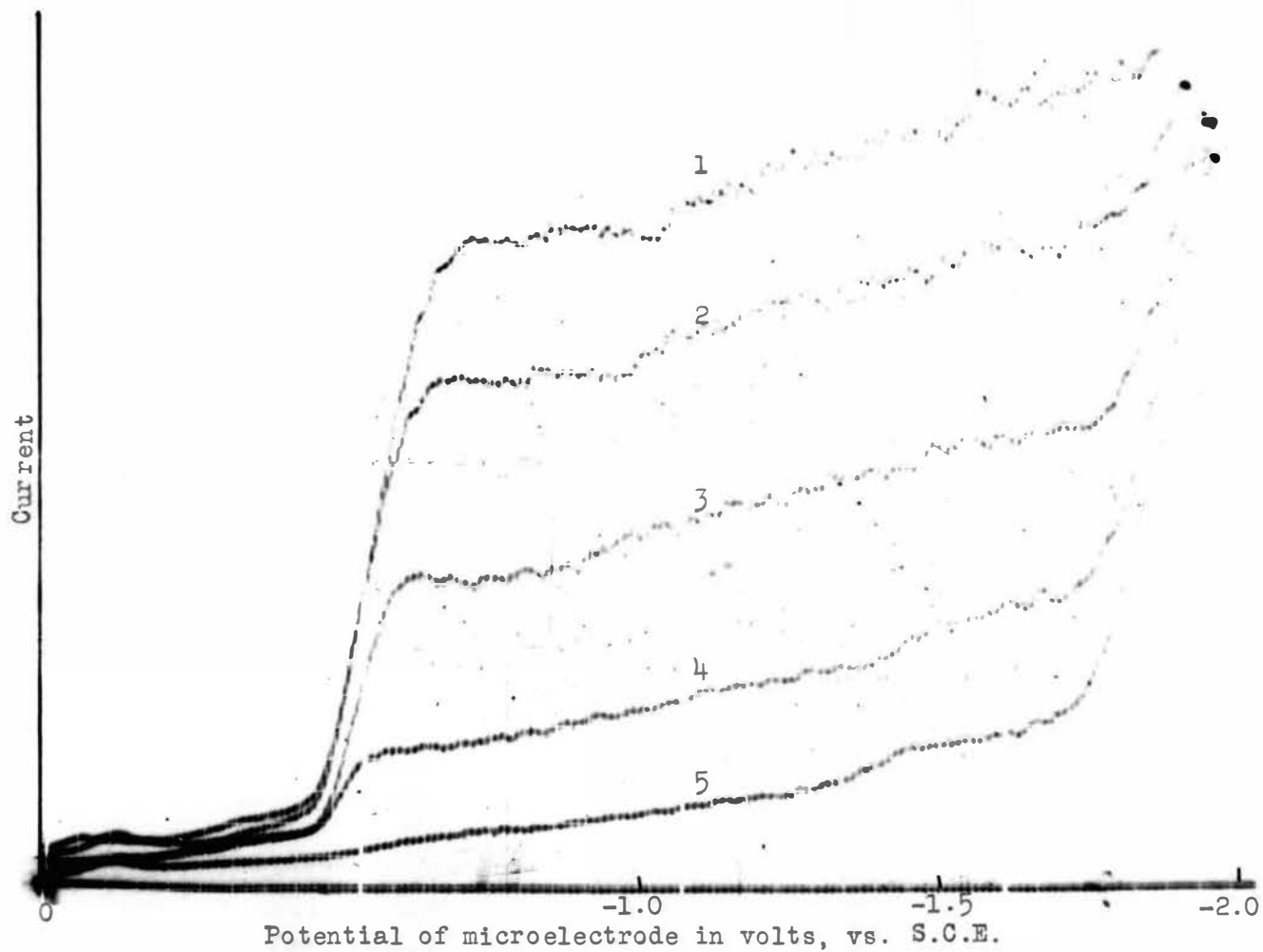


Figure 24 Polarograms of $\text{Cd}(\text{NO}_3)_2$ with the Gold Amalgam Microelectrode

Carrier - 0.1 M KCl
Scanning rate - 3 seconds

1 - 10×10^{-4} M	4 - 1×10^{-4} M
2 - 7×10^{-4} M	5 - Carrier
3 - 4×10^{-4} M	

CONCLUSION

In comparing the performance of the D.M.E. and the rotating micro-electrode, there would seem to be little practical justification for using the latter in general cathodic analysis, except for the elements of time and convenience. However, a microelectrode like the platinum amalgam may be cleaned, plated and the polarogram obtained in about four minutes. A permanent record is easily made, but for routine work may not be needed at all. The photographs may be enlarged as desired, and since the oscillograph grid lines are visible, measurements may be estimated to 0.01 inches (about 1%, for ordinary situations). The instantaneous response and lack of damping with the oscillograph will produce less beautiful, but more accurate, polarograms.

The use of amalgamated microelectrodes practically eliminates a major previous disadvantage of the solid electrode - i.e., that of the low hydrogen overvoltage compared with mercury.

There seems no reason to believe that the amalgamated microelectrode will give half-wave potentials approaching those of the D.M.E. as the scanning speed is increased. In his postulation, Cooke overlooked the fact that although higher scanning rates and/or lower concentrations yield less metal product to dissolve in the mercury, the rate of dissolution and of diffusion of the deposited metal into the mercury may not keep up with the electrode process. Under the most ideal conditions, therefore, it is probable that the surface amalgam is far more concentrated than would have been expected. With the D.M.E., new surface is constantly forming, during the growth of the drop as well as by means of its replacement by fresh drops of mercury. That some such occurrence

took place is obvious from the results obtained in this research.

It would seem from this study, therefore, that new sets of values for half-wave potentials must be determined for use with these rotating amalgam electrodes. Once this is done, however, the greater speed with which determinations can be made employing such electrodes should make this a very useful technique in polarographic analysis.

BIBLIOGRAPHY

- (1) Airey, L., *Analyst*, 72, 304 (1947).
- (2) Cooke, W. D., *Anal. Chem.*, 25, 215 (1953).
- (3) Delahay, P., *J. Phys. & Colloid Chem.*, 53, 1279 (1949).
- (4) Delahay, P., *J. Phys. & Colloid Chem.*, 54, 402 (1950).
- (5) Delahay, P., *J. Phys. & Colloid Chem.*, 54, 630 (1950).
- (6) Heyrovsky, J., *Chem. Listy.*, 16, 256 (1922).
- (7) Heyrovsky, J. and S. Berezicky, *Coll. Czech. Chem. Commun.*, 1, 19 (1929).
- (8) Heyrovsky, J. and P. Forejt, *Z. Physik. Chem.*, 193, 77 (1943).
- (9) Heyrovsky, J. and D. Ilkovic, *Coll. Czech. Chem. Commun.*, 7, 198 (1935).
- (10) Heyrovsky, J. and M. Shikata, *rec. trav. chim.*, 44, 496 (1925).
- (11) Kolthoff, I. and J. Lingane, *Polarography*, p. 159, Interscience Publishers, N.Y., 1952.
- (12) Kucera, G., *Ann. Physik.*, 11, 529 (1903).
- (13) Laitinen, H. and I. Kolthoff, *J. Phys. Chem.*, 45, 1079 (1941).
- (14) Maness, R. F., *Investigation of Polarographic Electrodes*, Unpublished M.S. Thesis, Oklahoma A. and M. College, 1949.
- (15) Matheson, L. and M. Nichols, *Trans. Electrochem. Soc.*, 73, 169 (1938).
- (16) Nernst, W. and E. Merriam, *Z. Physik. Chem.*, 52, 235 (1905).
- (17) O'Kelley, G. and H. Wilcox, *J. Alabama Acad. Sci.*, 19, 10 (1947).
- (18) Prytz, M. and Y. Østerud, *Tids. Kjemi Bergvesen Met.*, 1, 27 (1941).
- (19) Randles, J., *Analyst*, 72, 301 (1947).
- (20) Randles, J., *Trans. Faraday Soc.*, 44, 322 (1948).
- (21) Rogers, L., H. Miller, R. Goodrich and A. Stehney, *Anal. Chem.*, 21, 777 (1949).

- (22) Rosenthal, R., A. Lorch and P. Hammett, J. Am. Chem. Soc., 59, 1795 (1937).
- (23) Salomon, E., Z. physik. Chem., 24, 55 (1897).
- (24) Sevcik, A., Coll. Czech. Chem. Commun., 13, 349 (1948).
- (25) Skobets, E., P. Turov and V. Ryabokon, Zavodskaya Lab., 15, 912 (1949).

VITA

Phillip Albert Lewis
candidate for the degree of
Master of Science

Thesis: Scanning Rates and the Rotating Microelectrode in Polarography

Major: Analytical Chemistry

Biographical:

Born: February 21, 1921, at Indianapolis, Indiana.

Education: Aurora College, 1938-1942; B. S. degree, 1942.
Illinois Institute of Technology, 1947-1949; graduate study.
Oklahoma A. and M. College, 1951-1954; graduate study.

Employment: Duluth Junior College, 1946; instructor, chemistry
and mathematics.
Aurora College, 1946-1947, 1949-1951; assistant professor,
chemistry.
Illinois Institute of Technology, 1947-1949; graduate assist-
ant, teaching.
Oklahoma A. and M. College, 1951-1953; teaching assistant.
Oklahoma A. and M. College, 1953-1954; research assistant.

Military: Signal Corps Reserve, Sixth Service Command, 1942-1943;
pre-radar, electronics, ultra-high frequency and radar repair
schools.
A.S.T.P., Polytechnic Institute of Brooklyn, 1943-1944; terms
IV and V, advanced electrical engineering.
Signal Corps, Army of U.S., 1943-1946; radio operator, radio
repair, transmitter attendant and clerk-typist specialist
numbers.

Professional: Member of the American Chemical Society, member of Phi
Lambda Upsilon, and associate member of The Society of Sigma Xi.

Date of Final Examination: January, 1954.

Thesis Title: Scanning Rates and the Rotating Microelectrode in
Polarography

Author: Phillip Albert Lewis

Thesis Adviser: Dr. Paul Arthur

The content and form have been checked and approved by the author and thesis adviser. The Graduate School Office assumes no responsibility for errors either in form or content. The copies are sent to the bindery just as they are approved by the author and faculty adviser.

Typist: JoAnne S. Lewis