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VOLTAMMETRY WITH A MERCURY POOL CATHODE

Thesis submitted in partial fulfillment of requirements
for a Master of Science Degree
Chemistry Department

by

David Peter Stricos MS 1960

Advisor

Professor Jermain D. Porter

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JDP

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TABLE OF CONTENTS

	Page
LIST OF TABLES -----	iv
LIST OF FIGURES -----	v
ACKNOWLEDGMENTS -----	vii
ABSTRACT -----	viii
I INTRODUCTION -----	1
A. Historical Background -----	1
B. Purpose -----	3
II THEORY -----	5
A. General Description of the Process -----	5
B. Mathematical Interpretation -----	8
III EXPERIMENTAL -----	11
A. Equipment -----	11
1. The Polarographic Cell -----	11
2. The Polarographs -----	15
B. Technique -----	16
1. Preparation of Standards -----	16
2. Analysis of Test Solutions -----	17
3. The Use of Desicote -----	18
IV RESULTS -----	21
A. Potassium Nitrate as a Base Electrolyte -----	23
1. Linear Relationship Between Peak Current and Concentration -----	23
2. Precision of the Method -----	28

Gift of Author, January 31, 1963

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TABLE OF CONTENTS

	Page
3. Comparison of Peak Heights Obtained for Various Ions -----	34
4. Behavior of Indium -----	36
5. Other Ions Examined -----	37
B. Potassium Acid Phthalate as a Base Electrolyte -----	38
1. Comparison of Peak Heights Obtained for Various Ions -----	38
2. Other Ions Examined -----	43
C. Ammonia-Ammonium Chloride as a Base Electrolyte -----	43
1. Comparison of Peak Heights Obtained for Various Ions -----	44
2. Other Ions Examined -----	47
D. Results Obtained by Varying the Pool Size -----	47
V DISCUSSION -----	49
A. The Supporting Electrolyte -----	51
B. Analysis of Mixtures -----	52
C. Comparison of Several Approaches to Voltammetry -----	53
D. Anodic Stripping -----	58
E. Analytical Applications -----	60
BIBLIOGRAPHY -----	62

LIST OF TABLES

	Page
I Peak Current as a Function of Concentration for Several Ions in 0.01 Molar Potassium Nitrate -----	25
II Peak Currents Observed for Solutions of 5.00×10^{-5} Molar Cadmium in 0.01 Molar Potassium Nitrate -----	28
III Peak Currents Observed for Solutions of 4.83×10^{-5} Molar Zinc in 0.01 Molar Potassium Nitrate -----	29
IV Peak Currents Observed for Solutions of 3.74×10^{-5} Molar Lead in 0.01 Molar Potassium Nitrate -----	30
V Peak Currents Observed for Solutions of 4.59×10^{-5} Molar Indium in 0.01 Molar Potassium Nitrate -----	31
VI A Comparison of the Peak Heights Cal- culated for 10^{-4} Molar Solutions of Various Ions in 0.01 Molar Potassium Nitrate -----	35
VII Decreasing Peak Height for Indium in 0.01 Molar Potassium Nitrate on Standing -----	37
VIII A Comparison of the Peak Heights Cal- culated for 10^{-4} Molar Solutions of Various Ions in 0.1 Molar Potassium Acid Phthalate -----	39
IX A Comparison of the Peak Heights Cal- culated for 10^{-4} Molar Solutions of Various Ions in 0.1 Molar Ammonia, 0.1 Molar Ammonium Chloride -----	45
X The Peak Current as a Function of Electrode Area -----	48

LIST OF FIGURES

	Page
Figure 1 Mercury-Solution Interface -----	6
Figure 2 The Polarographic Cell -----	13
Figure 3 Diagram of Assembled Apparatus -----	14
Figure 4 Irregular Curves Obtained after Treatment with Desicote -----	20
Figure 5 Conventional Polarogram for Cadmium in <u>0.1M</u> HCl -----	22
Figure 6 Peak Current as a Function of Concentration for Several Ions in <u>0.01M</u> KNO ₃ -----	26
Figure 7 Peak Current as a Function of Concentration for Several Ions in <u>0.01M</u> KNO ₃ -----	27
Figure 8 Peak Obtained for Indium in <u>0.01M</u> KNO ₃ Using the Electrochemograph ----	32
Figure 9 Peak Obtained for Indium in <u>0.01M</u> KNO ₃ Using the Polarotrace -----	33
Figure 10 Peak Obtained for Indium in <u>0.1M</u> Potassium Acid Phthalate Using the Electrochemograph -----	40
Figure 11 Peak Obtained for Copper in <u>0.1M</u> Potassium Acid Phthalate Using the Electrochemograph -----	41
Figure 12 Peak Obtained for Cadmium in <u>0.1M</u> Potassium Acid Phthalate Using the Polarotrace -----	42
Figure 13 Peak Obtained for Nickel in <u>0.1M</u> NH ₃ , <u>0.1M</u> NH ₄ Cl Using Electro- chemograph -----	46

LIST OF FIGURES

	Page
Figure 14 Curve Obtained for a Mixture of Lead, Cadmium and Zinc in <u>0.01M KNO₃</u> Using the Electrochemograph -----	54
Figure 15 Curve Obtained for a Mixture of Bismuth, Lead, Cadmium and Zinc in <u>0.1M Potassium Acid Phthalate</u> Using the Electrochemograph -----	55
Figure 16 Curve Obtained for a Mixture of Copper, Cadmium, Nickel and Zinc in <u>0.1M NH₃</u> , <u>0.1M NH₄Cl</u> Using the Electrochemograph -----	56
Figure 17 Peak Obtained for Cadmium in <u>0.01M KNO₃</u> Using the Electrochemograph ----	57
Figure 18 Peaks Due to Reduction and Anodic Stripping for Cadmium in <u>0.01M KNO₃</u> Using the Electrochemograph ----	59
Figure 19 Peaks Obtained for Cobalt and Zinc in <u>0.1M NH₃</u> , <u>0.1M NH₄Cl</u> Using Electrochemograph -----	61

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ABSTRACT

Voltammetry with a mercury pool cathode has been examined using both slow and rapid scanning techniques. A conventional polarograph was used to interpret the slow scans, and a cathode ray polarograph for the rapid scans. A description of the necessary apparatus is given as well as the experimental details involved.

Three different supporting media were studied: 0.01 molar potassium nitrate, 0.1 molar potassium acid phthalate, and 0.1 molar ammonia-0.1 molar ammonium chloride. Well defined peaks were observed for lead, cadmium, and zinc in potassium nitrate. Indium also gave a peak, but it was not characteristic of a three-electron reduction. Furthermore, indium solutions on standing gave lower peaks, probably owing to hydrolysis. A copper peak was found in this medium, but the start of the peak was ill defined, thus preventing an accurate measurement of the peak current.

In 0.1 molar potassium acid phthalate copper, lead, cadmium, indium, and zinc produced well defined peaks. Bismuth yielded a very sharp peak, but the peak

current was erratic.

Solutions of 0.1 molar ammonium-0.1 molar ammonium chloride proved satisfactory for copper, cadmium, nickel, cobalt, and zinc. The peaks due to cobalt and nickel preceded the zinc reduction by a sufficient voltage to allow their determination in the presence of zinc.

The standard deviation for analyses conducted on different days varied from two to five per cent depending on the ion being studied. The peak currents for the various ions are compared and the half peak potentials listed.

PART I

INTRODUCTION

The polarographic method is comparatively young; the first polarographic measurements were made by Professor Heyrovsky less than forty years ago. However, its range of application is currently growing at a tremendous rate, as evidenced by the ever increasing number of publications concerning its use. In addition, various modifications of the technique have recently been developed. Among these are derivative polarography, polarography and voltammetry with periodically changing potential, and polarography and voltammetry with continuously changing potential. (The use of the term polarography shall be restricted to those methods in which the dropping mercury electrode is employed). This paper deals primarily with voltammetry with continuously changing potential.

A. Historical Background

Conventional polarographic techniques enable the experimenter to analyze solutions containing approximately 10^{-4} molar concentrations of various electroreducible or oxidizable ions. A typical polarogram obtained with the conventional apparatus is shown in figure 5. Since the mercury surface is continuously

renewed by the dropping electrode, and since the rate of voltage scan is fairly slow (0.2 volts/minute) this type of polarogram is effectively a plot of current versus voltage where the current is obtained at a series of fixed potentials. Hence this approach may be referred to as polarography at constant potential. Several excellent texts have been published on this subject (6,8), and its principles are so widely understood as to require no further explanation.

If, on the other hand, a stationary electrode is employed, and the voltage scanning rate is fairly rapid; the curve produced is a peak rather than the usual wave. The analytical usefulness of this phenomenon was first demonstrated by Matheson and Nichols (7), and the fundamentals elucidated by Sevcik and Randles for reversible processes, and by Delahay for irreversible processes. Several studies of voltammetry with continuously changing potential have been carried out by Cooke and his associates (11,15,17) using a mercury pool cathode. These experiments clearly revealed the potentialities of the method. Sevcik and Randles also developed the instrumentation by which this technique could be used with a dropping mercury electrode, the polarogram being presented as a cathode ray trace which is recorded late in the life of

each drop. In this way the dropping electrode behaves as a stationary electrode during the recording of the polarogram. The voltage sweep is synchronized with the drop time in order to obtain reproducible traces. In the present study this instrument will be used in conjunction with a mercury pool cathode. This will supply a reproducible and rapid voltage scan to the pool and also display the reduction peaks. In any event, there is a considerable increase in sensitivity resulting from the peaked nature of the waves. Concentrations of the order of 10^{-6} molar can be determined by this technique. The peak currents are larger than the diffusion currents obtained for the same solution by conventional methods; and, perhaps more important, the distortion produced by the capacity current is not so marked as in conventional polarography.

B. Purpose

Although this method has been shown to offer several unique advantages to the analyst, voltammetry with continuously changing potential is still not very widely used. This may be due in part to a scarcity of information concerning the behavior of various ions in

different supporting media. There appears also to be a need for a description of the experimental details by which useful results can be obtained, in order to further the laboratory application of the method. It is the intent of this report to furnish at least some of this information and, more specifically, to examine voltammetry at the mercury pool using both slow and rapid scanning techniques.

PART II

THEORY

The mathematical derivation of the equations defining the peak currents will not be discussed here. The interested reader is referred to the works of Delahay (2,3), Randles (13), and Sevcik (16) for this information. A general description of the process and the final equations, however, are pertinent to this study and essential to an understanding of the experimental results which follow. They are, therefore, presented at this point.

A. General Description of the Process

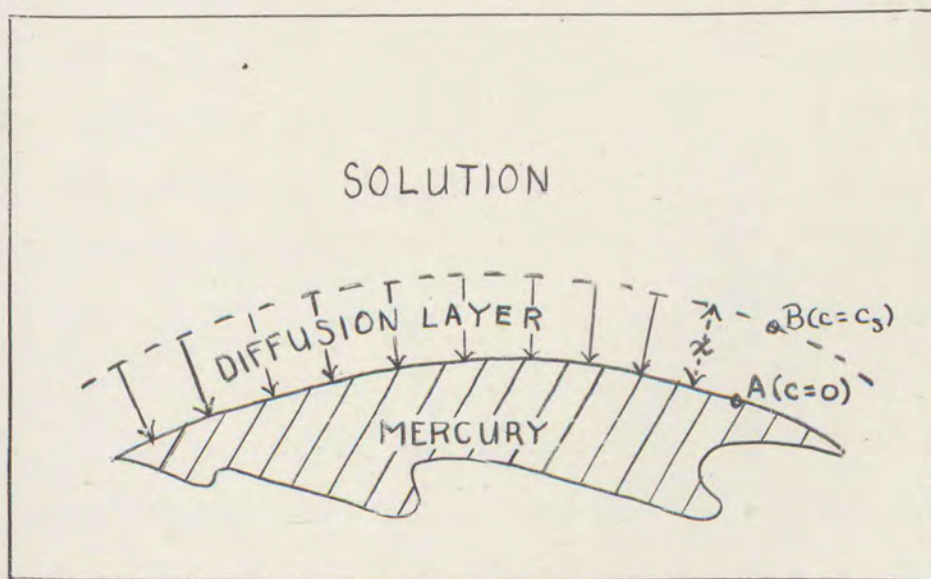
With the present approach, as with conventional polarography, the limiting current is a function of the rate at which the reducible species reaches the mercury surface. In both cases diffusion is the rate determining step. Hence, a qualitative description of this process is extremely worthwhile.

Consider a mercury - solution interface (Figure 1). If the voltage is sufficient to allow the reduction of

the ion in question, a 'diffusion layer' is set up. This narrow (about 0.05 mm) region adjacent to the mercury surface is deficient in the reducible species since that species is rapidly removed by reduction at the mercury surface.

FIGURE 1

MERCURY-SOLUTION INTERFACE



At point A its concentration is nearly zero, and at point B its concentration is equal to that in the bulk of the solution. In other words, a concentration gradient exists across the diffusion layer. Now the flow of the reducible ions as shown by the arrows is, accord-

ing to Fick's Law, directly proportional to this concentration gradient, or...

$$J = -D(\Delta c / \Delta x) \quad (1)$$

where J is the flow of the particular species and D is its diffusion coefficient. From figure 1 it can be seen that $\Delta c = c_s - 0 = c_s$ (the concentration of the reducible ion in the bulk of the solution), and $\Delta x = x$, the width of the diffusion layer. Therefore the rate at which the ions reach the mercury surface, and in turn the limiting current, will be directly proportional to the concentration of that ion in the solution. Note also that the rate of diffusion is inversely proportional to the width of the diffusion layer. This distance (x in figure 1) is actually not constant, but increases with time once the diffusion layer is set up. In conventional polarography this phenomenon manifests itself in the same fashion for each successive drop with the result that average diffusion current at a given potential is constant from drop to drop.

In the present technique, though, the mercury surface is not renewed, and the voltage applied to the mercury pool increases linearly with time. At the start of the scan no reduction occurs and no diffusion layer is set up. When the voltage reaches a value where re-

duction commences, the current increases and the diffusion layer is established (ascending portion of the curve).

As the diffusion layer widens, however, the rate of diffusion decreases causing the current to fall off.

This series of events clearly produces a peak in the current voltage curve. Carrying this reasoning one step further, the shorter the time lapse between the beginning of reduction and the point at which the reaction is diffusion controlled, which corresponds to the beginning of the diffusion current plateau in conventional polarography, the less expansion the diffusion layer will have undergone. Thus, as the voltage scanning rate is increased, the effective width of the diffusion layer is decreased, and greater peak heights are obtained.

B. Mathematical Interpretation

The equation defining the peak current for reversible processes involving soluble substances was derived independently by Randles (13) and Sevcik (16).

The results were of the same form, but with a different numerical constant. Nicholson (10) later confirmed Randles' calculations. The final equation is;

$$i_p = K n A D^{1/2} C^0 v^{1/2} \quad (2)$$

where, i_p = peak current (amperes)

K = constant

n = number of electrons involved in the reduction

A = area of the electrode (cm^2)

C^0 = bulk concentration of the reducible ion (mole cm^{-3})

D = diffusion coefficient of the ion reduced ($\text{cm}^2 \text{ sec}^{-1}$)

v = voltage scanning rate (volts sec^{-1})

The value of K calculated by Sevcik was 2.17×10^5 , while the value found by Randles was 2.72×10^5 .

For the reversible deposition of an insoluble substance Berzins and Delahay (2) obtained the same general formula with a K of 3.67×10^5 . Delahay (3) has also derived the equation defining the peak current for totally irreversible processes; the equation is,

$$i_p = 3.01 \times 10^5 n (\alpha n_a)^{1/2} A D^{1/2} C^0 v^{1/2} \quad (3)$$

where, α = transfer coefficient

n_a = number of electrons involved in the rate determining step

Since α is less than one, and n_a is generally less than n : the equation predicts that peak currents for irreversible processes would be smaller than one would predict for a reversible process.

An excellent summary of the mathematics associated with the method was published by Delahay (4)

along with a qualitative description of the electrode process. This reference would be a good starting point for those desiring to familiarize themselves with the method.

The peak currents measured in this study were found to be less than the values predicted using either the Sevcik or the Randles constant. However, of greater importance analytically, the peak current was found to be directly proportional to the concentration of the reducible ion. It is also evident from the data given that the peak current is a function of the area of the electrode and the scanning rate, although in establishing a calibration curve these factors would be held constant.

PART III

EXPERIMENTAL

A. Equipment1. The Polarographic Cell

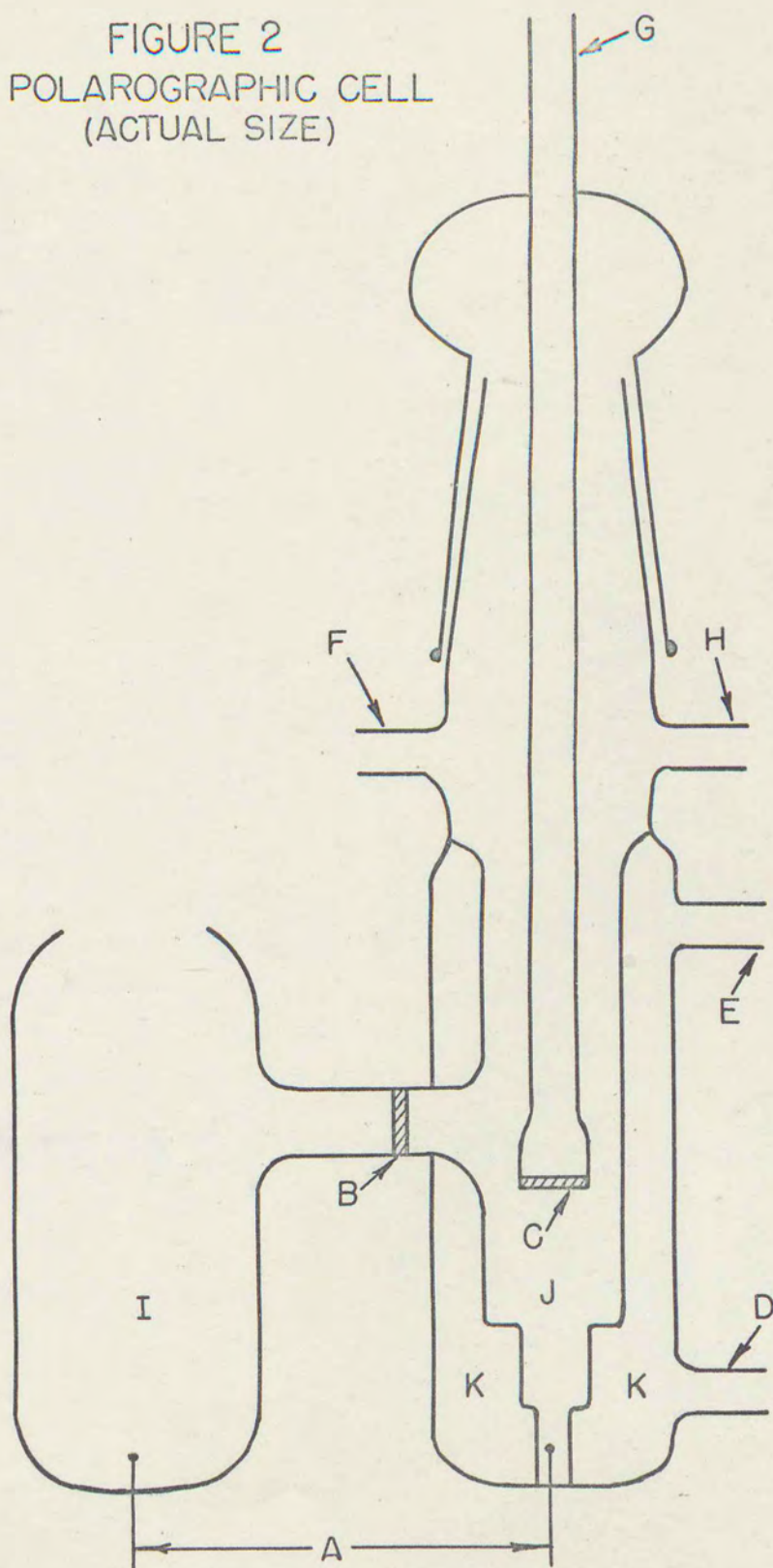
An H-type polarographic cell (figure 2) was used throughout this study. It was virtually the same as that described by Streuli and Cooke (17) except that three pool sizes were available. By placing different quantities of mercury in the cell, pools of 0.5, 1.0, and 2.0 centimeters diameter could be obtained. The temperature of the test solutions was maintained by passing water from a constant temperature bath ($25.0 \pm 0.1^{\circ} \text{C}$) through a jacket surrounding the solution compartment. The saturated calomel reference electrode was isolated from the test solutions by a potassium chloride - agar salt bridge.

Solutions were purged by passing nitrogen through the coarse porosity disc with the top in place. By means of a two-way stopcock the nitrogen could be directed over the solution and thence to a bubbler to prevent back diffusion of air into the cell. This

FIGURE 2: THE POLAROGRAPHIC CELL

- A. Platinum Wire
- B. Medium Porosity Sintered Glass Disc
- C. Coarse Porosity Sintered Glass Disc
- D. Inlet for Constant Temperature Water
- E. Outlet for Constant Temperature Water
- F. Nitrogen Inlet to Blanket Test Solution
- G. Nitrogen Inlet to Purge Test Solution
- H. Nitrogen Outlet
- I. Reference Electrode Compartment
- J. Solution Compartment
- K. Water Jacket

FIGURE 2
THE POLAROGRAPHIC CELL
(ACTUAL SIZE)



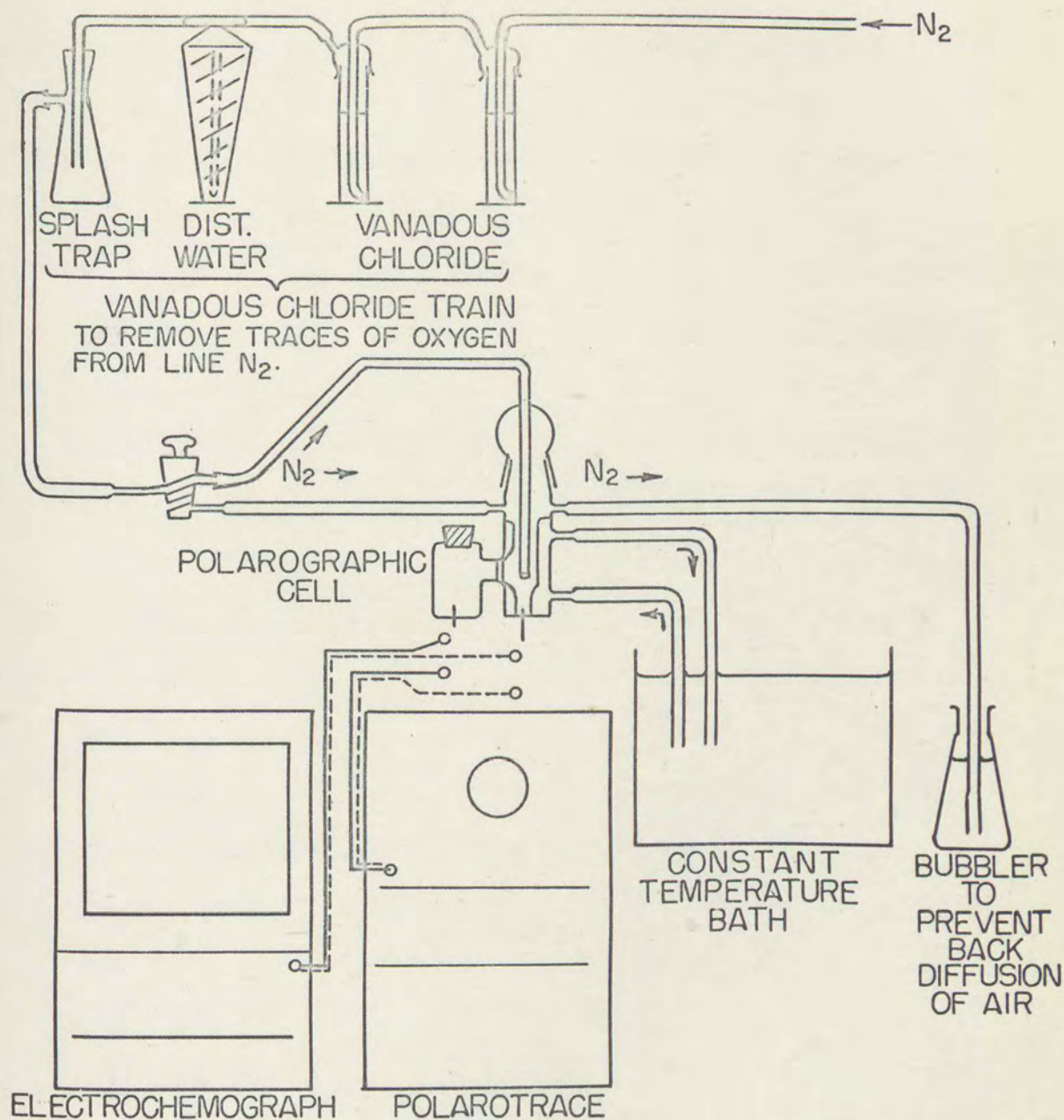


FIGURE 3
DIAGRAM OF ASSEMBLED APPARATUS

served to effectively blanket the solutions during the recording of the current voltage curves. A vanadous chloride train (9) was employed to remove traces of oxygen from the line nitrogen.

Mercury for the pool was stored in a grease-free burette for at least twenty-four hours prior to its use. This technique has been recommended (17) to eliminate irregularities in the current voltage curves resulting from the presence of small amounts of oil in the mercury.

The constant temperature bath and the stand for the polarographic cell were placed on a foam rubber pad to minimize vibration.

2. The Polarographs

For the slow scans a Leeds and Northrup Electro-chemograph Type E was used. This instrument furnished a scanning rate of 0.2 volts per minute and produced pen and ink recordings of the current voltage curves on a strip chart recorder.

A cathode ray polarograph, the Polarotrace, manufactured by Southern Instruments Computer Division of England, was used for the more rapid scans. The circuitry of the instrument is rather involved, but it has been described in the literature (1,12,14). The nominal scanning rate in this case was eighteen volts per minute. The Polarotrace incorporates a cathode ray

screen on which the curve is traced once every seven seconds. A grid on the screen makes possible a direct reading of the peak height. The scan itself covers 0.6 volts in two seconds. This is followed by a five-second delay period during which time the voltage applied to the pool is held constant at the starting potential. The curves were generally found to be reproducible from one trace to the next, since an ion reduced during the scan is anodically stripped from the mercury during the delay period. A permanent record is ordinarily kept by means of a camera attachment which fits over the cathode ray screen. Unfortunately it was not available when this study was carried out, however, a record was made when desired by noting the current at several potentials and plotting the curve on graph paper.

B. Technique

1. Preparation of Standards

Standard solutions were prepared from the pure metals with the exception of chromium which was prepared from Bureau of Standards potassium dichromate. Each was dissolved in a minimum of acid and diluted to one liter. Aliquots of these stock solutions were taken and further diluted as required. All water used for solution preparation and rinsing was deionized and distilled. All

glassware was rinsed with a fifty per cent nitric acid solution followed by three or four rinses with distilled water.

2. Analysis of Test Solutions

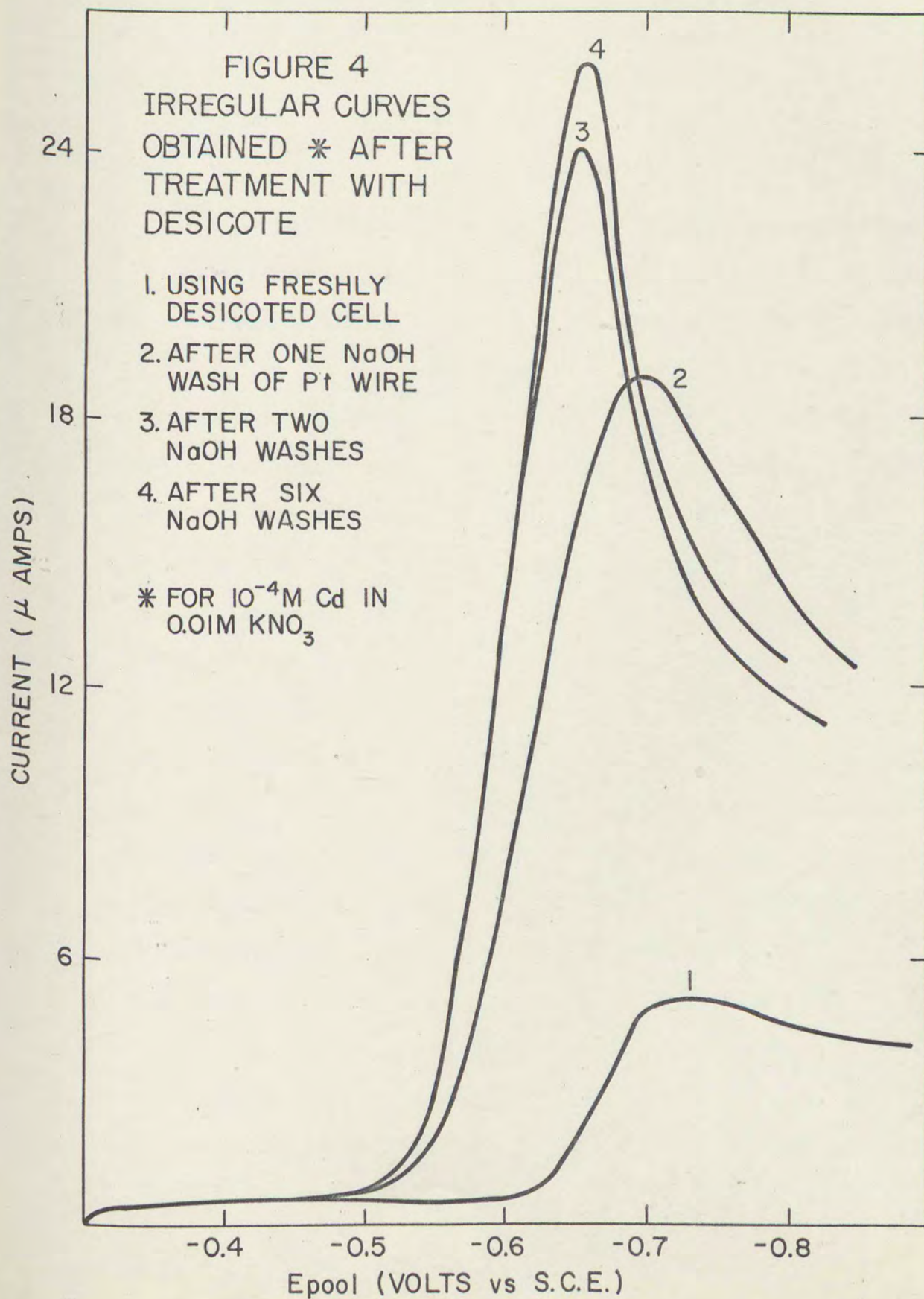
Contamination from previously analyzed solutions caused some difficulty in the early part of this work. The procedure finally adopted was to rinse the cell four times with distilled water and then two times with the solution to be analyzed. The cell cover was replaced with each filling of the cell, and the solution purged for a few seconds so that the nitrogen purge line was thoroughly rinsed. The cell was then filled to a level just above the side arm to the reference electrode. The cover with the nitrogen purge line was inserted and the solution deaerated for fifteen minutes. Mercury from the burette was then added to form the pool. The cover was replaced and the solution deaerated for an additional two or three minutes. This final purge was found to be necessary to give a horizontal base line to the current voltage curves; since, in the short time required to add the mercury, enough oxygen was picked up to distort the curves. The two-way stopcock in the nitrogen line was then adjusted to pass nitrogen over the surface of the solution.

The leads from the Polarotrace were connected to the platinum wires extending from the reference and pool electrodes. The starting potential was set at about 0.2 volts more positive than the half peak potential. The scale factor was adjusted to give a convenient peak height which was read directly from the grid. In some cases spurious peaks appeared in the first few scans, hence the peak height was only determined after several scans had been completed. Next, the leads were replaced by those from the Electrochemograph. The current voltage curve was recorded and the peak height measured by extrapolation of the base line preceding the peak. If a repeat scan is to be run on the same solution, it is wise to hold the potential at the starting point for several minutes to allow the anodic stripping to go to completion. This will preclude a sloping base line due to the steadily decreasing anodic current.

3. The Use of Desicote

Unless the cell wall is treated in some way, the test solutions tend to creep around the mercury pool. In so doing the effective area of the pool is increased, and variable results are obtained. Beckman Desicote was found to correct this situation, but it seemed to produce an additional problem. Immediately after applying Desicote

to the cell wall the current voltage curves were seen to be seriously affected (figure 4). The half peak potentials were shifted to more negative values, and the peak heights were greatly reduced. It was found, however, that the curves could be restored to their original form by rinsing the platinum wire in the bottom of the cell with concentrated sodium hydroxide. This was done by fashioning a medicine dropper from an eight inch length of glass tubing, and carefully placing a few drops of the solution in the cell to just cover the wire. The cell was thoroughly rinsed and a new solution analyzed. After about five such washes, the current voltage curve was unchanged and no further difficulty of this type was experienced.

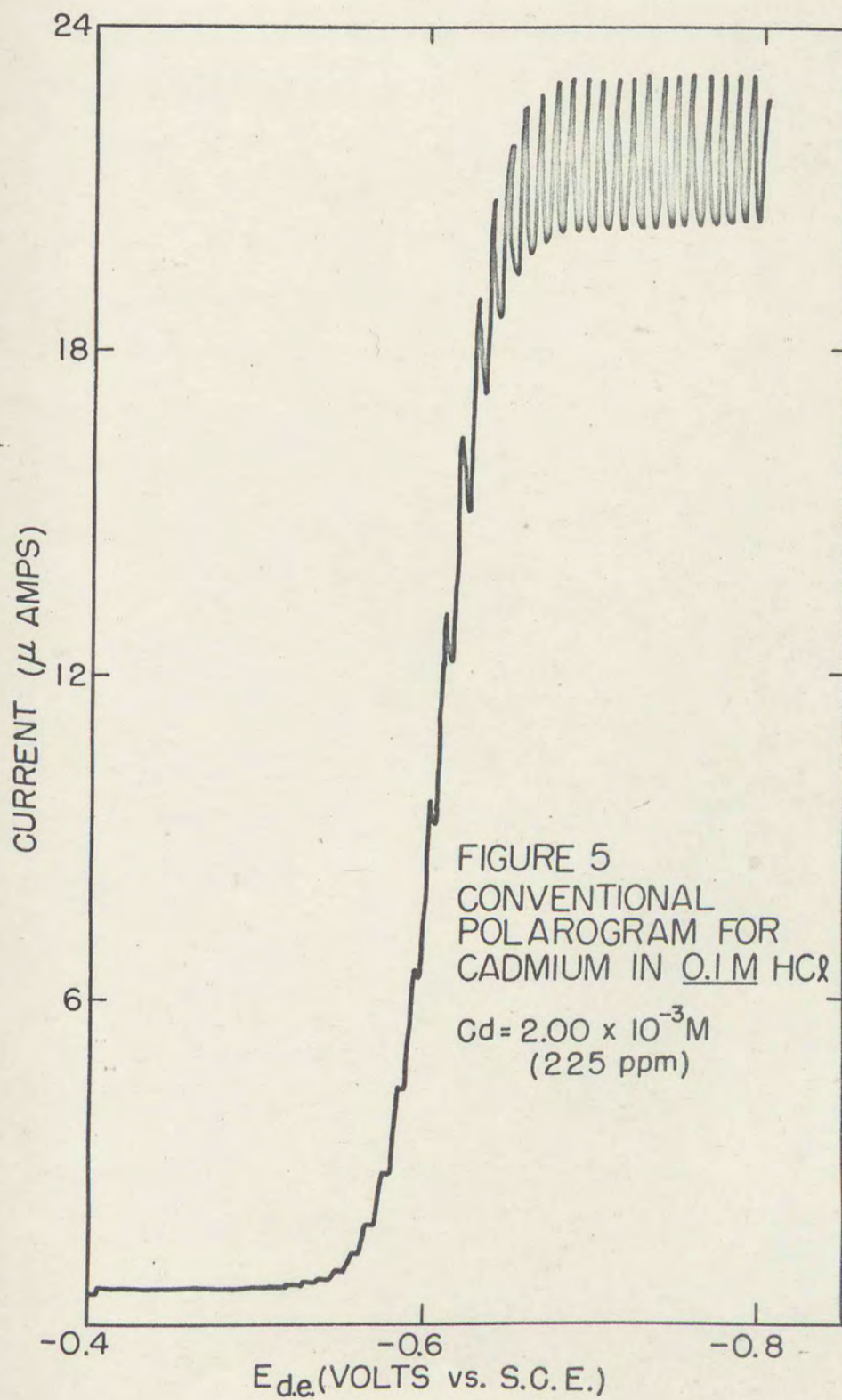


PART IV

RESULTS

A considerable amount of time was consumed early in this study in an attempt to obtain consistent data; the reproducibility was very poor. Several factors were found to be responsible for the varying results. The most serious variations were those following the application of Desicote to the cell wall. Contamination from previously analyzed solutions also proved troublesome when very dilute solutions were being examined. For this reason, exploratory work should be done using reasonably concentrated solutions, say 10^{-4} molar. Another source of error, especially with the cathode ray polarograph, was the variation of the slope of the base line preceding the peak. Purging the solutions for several minutes after the mercury was added to the cell resulted in a horizontal base line, hence this practice was followed throughout. Once these problems were corrected the reproducibility became very satisfactory.

Before presenting any extensive data obtained by voltammetry with continuously changing potential, one conventional polarogram is given (figure 5). Though this



type of curve is quite familiar, it allows a visual comparison of the kinds of curves produced by the two techniques.

A. Potassium Nitrate as a Base Electrolyte

Streuli and Cooke (17) studied the behavior of several ions in 0.01 molar potassium nitrate. The results found here were not in complete agreement with their values, but this is not unexpected in view of the variables involved. The area of the pool, for example, can be only approximated. Furthermore those workers prepared their standards from salts of the respective metals, while the standards in this case were prepared by dissolution of the metal in an appropriate acid. Although very small amounts of acid were introduced in this way, the effect, notably for indium, may have been considerable.

Recrystallized potassium nitrate was used in the preparation of this supporting electrolyte. A curve run in the absence of any deliberately added ions revealed no impurities except for a small amount of zinc (less than 0.1 part per million).

1. Linear Relationship Between Peak Current and Concentration

The following data, illustrating the linear

relationship between the peak current and the concentration were obtained with various concentrations of a number of ions in 0.01 molar potassium nitrate. These data are shown graphically in figures six and seven.

TABLE I
PEAK CURRENT AS A FUNCTION OF CONCENTRATION FOR
SEVERAL IONS IN 0.01 MOLAR POTASSIUM NITRATE

Element	Molarity x 10 ⁵	ppm	Peak Current (μ amps.)	
			Electrochemo.	Polarotrace
Cadmium	0.50	0.56	1.4	9.0
	1.00	1.12	2.6	16.6
	1.50	1.69	4.1	25.4
	2.00	2.25	5.2	32.8
Zinc	0.69	0.45	2.4	14.3
	1.04	0.68	3.2	20.2
	1.74	1.14	4.6	28.8
	3.47	2.27	8.7	56.0
Lead	0.57	1.17	1.8	10.8
	0.94	1.94	3.0	17.4
	1.31	2.72	4.2	24.6
Indium	1.84	2.11	6.0	35.0
	2.75	3.16	9.6	58.5
	3.07	4.22	13.2	81.2

FIGURE 6

PEAK CURRENT AS A FUNCTION OF
CONCENTRATION FOR SEVERAL IONS
IN 0.01 M KNO_3

(DATA OBTAINED WITH ELECTROCHEMOGRAPH,
SCANNING RATE = 0.2 VOLTS/MIN.)

PEAK CURRENT (μ AMPS)

12
10
8
6
4
2
0

CONCENTRATION (ppm)

Zn^{++}

In^{+++}

Cd^{++}

Pb^{++}

0

1

2

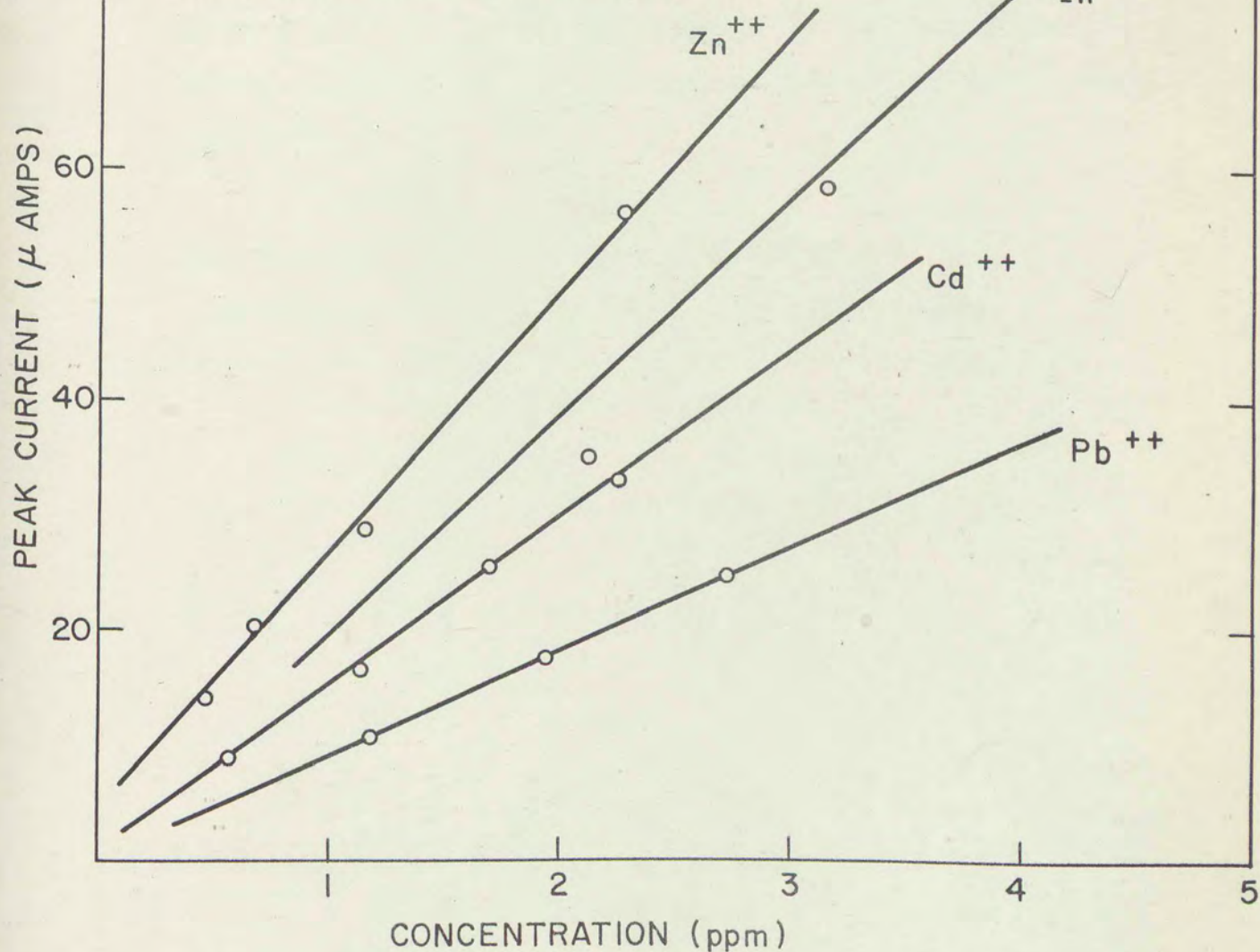
3

4

FIGURE 7

PEAK CURRENT AS A FUNCTION OF
CONCENTRATION FOR SEVERAL IONS
IN 0.01 M KNO_3

(DATA OBTAINED WITH POLAROTRACE,
SCANNING RATE = 18 VOLTS/MIN.)



2. Precision of the Method

In order to compare the peak heights and estimate the precision for various ions, more concentrated solutions were used. Solutions containing about 5×10^{-5} molar concentrations of the ions being studied were found to yield convenient peak heights on both polarographs. These, then, were prepared and analyzed with the following results:

TABLE II

PEAK CURRENTS OBSERVED FOR SOLUTIONS OF 5.00×10^{-5}
MOLAR CADMIUM IN 0.01 MOLAR POTASSIUM NITRATE

Peak Current (μ amps.)	
Electrochemograph	Polarotrace
12.96	81.00
13.12	82.00
12.86	80.80
12.70	78.75
12.58	79.25
12.86	79.00
12.36	73.95
<u>12.62</u>	<u>80.00</u>
Avg.=12.76	Avg.=79.34

A statistical analysis of these data gave a standard deviation of $\pm 0.24 \mu$ amps. or $\pm 1.9\%$ relative using the Electrochemograph.

Similarly, the standard deviation for the Polarotrace was $\pm 2.58 \mu$ amps. or $\pm 3.3\%$ relative.

TABLE III

PEAK CURRENTS OBSERVED FOR SOLUTIONS OF
 4.83×10^{-5} MOLAR ZINC IN 0.01 MOLAR POTASSIUM NITRATE

Peak Current (μ amps.)	
Electrochemograph	Polarotrace
12.04	71.50
12.12	70.50
11.14	70.50
10.73	74.00
<u>11.85</u>	<u>72.00</u>
Avg.=11.58	Avg.=71.70

The standard deviation found for the Electrochemograph was $\pm 0.61 \mu$ amps. or 5.3% relative. For the Polarotrace the standard deviation was $\pm 1.41 \mu$ amps. or 2.0% relative.

TABLE IV
PEAK CURRENTS OBSERVED FOR SOLUTIONS OF
 3.74×10^{-5} MOLAR LEAD IN 0.01 MOLAR POTASSIUM NITRATE

Peak Current (μ amps.)	
Electrochemograph	Polarotrace
11.58	58.20
11.53	67.60
11.88	68.85
<u>11.20</u>	<u>66.00</u>
Avg.=11.55	Avg.=65.16

The standard deviation for the Electrochemograph was found to be $\pm 0.28 \mu$ amps. or 2.4% relative. The standard deviation for the Polarotrace was found to be $\pm 4.79 \mu$ amps. or 7.4% relative.

TABLE V
PEAK CURRENTS OBSERVED FOR SOLUTIONS OF
 4.59×10^{-5} MOLAR INDIUM IN 0.01 MOLAR POTASSIUM NITRATE

Peak Current (μ amps.)	
Electrochemograph	Polarotrace
16.62	92.50
15.69	102.25
16.26	102.00
<u>16.96</u>	<u>100.25</u>
Avg.=16.38	Avg.= 99.25

The standard deviation for the Electrochemograph was found to be $\pm 0.54 \mu$ amps. or 3.3% relative. For the Polarotrace the value found was $\pm 4.59 \mu$ amps. or 4.6% relative.

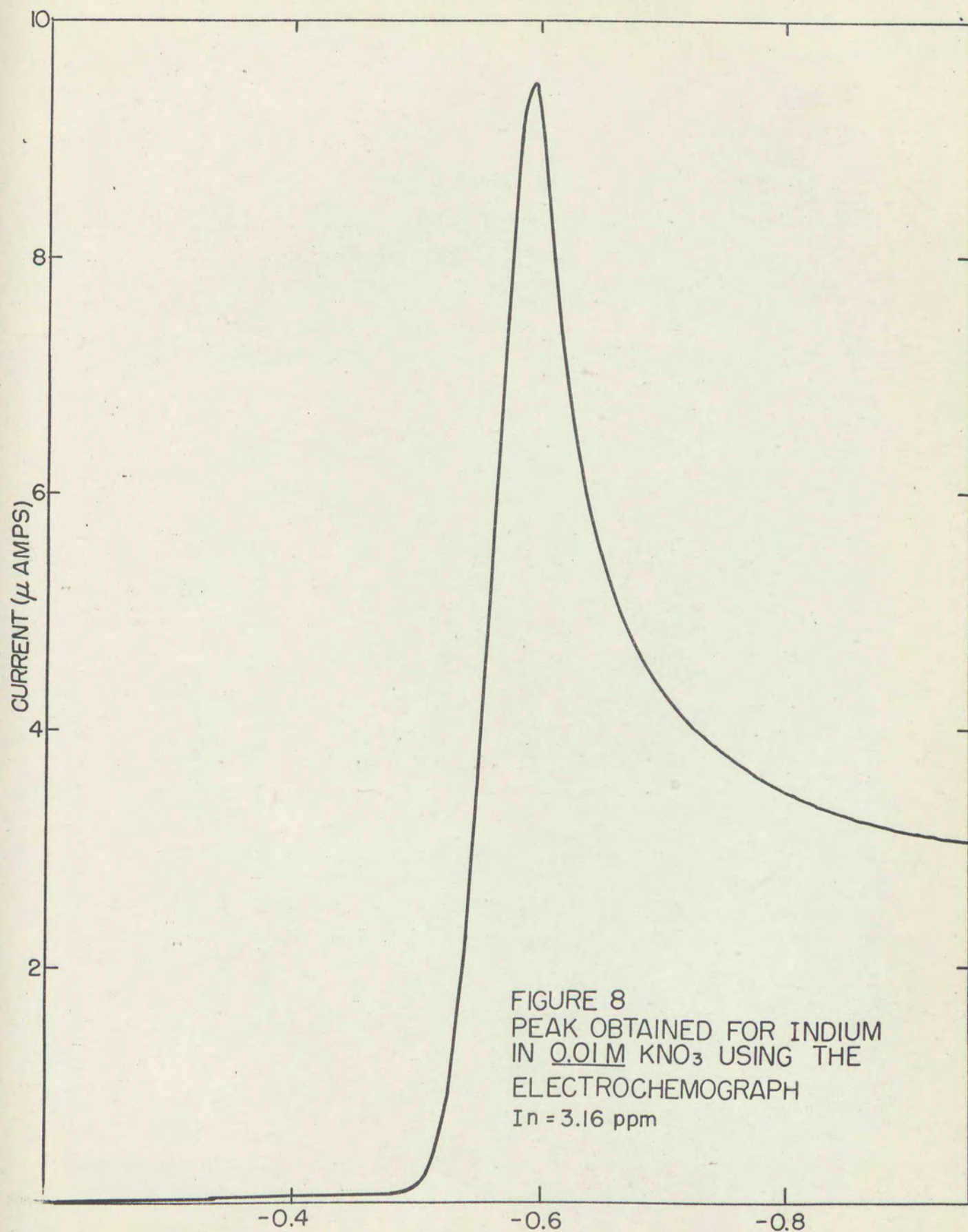
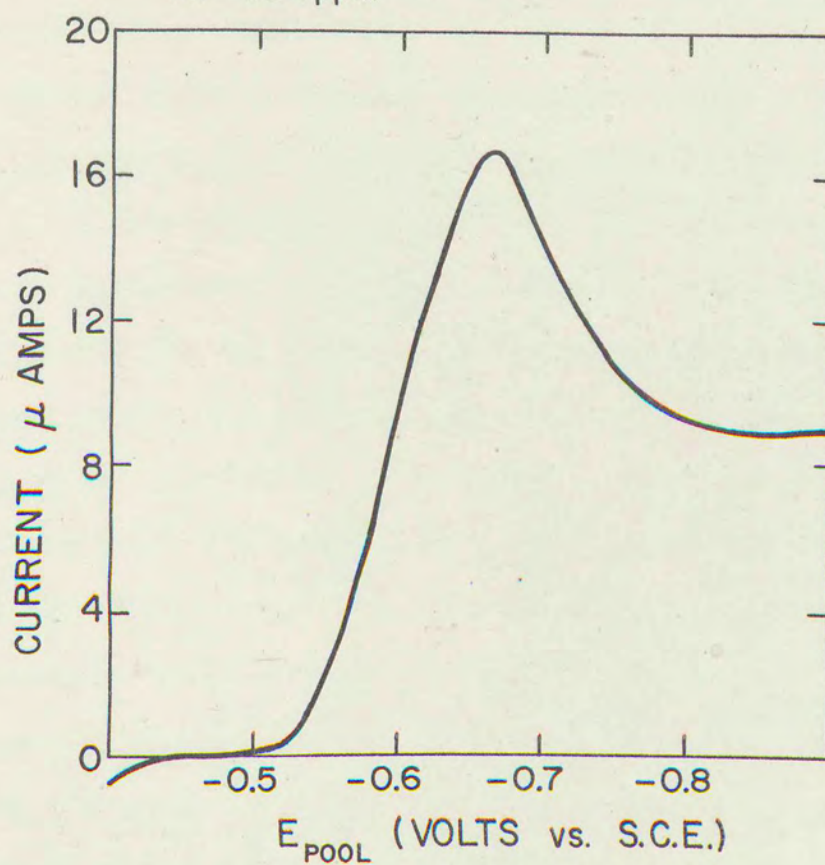


FIGURE 9
PEAK OBTAINED FOR
INDIUM IN 0.01 M KNO_3
USING THE POLAROTRACE
 $\text{In} = 1.05 \text{ ppm}$



The peak currents listed for each element on the preceding pages were obtained on different days. The precision therefore represents the day to day variation of the results. Repeat scans on the same solution would exhibit somewhat better precision. It should also be pointed out that each peak current listed is not the result of one scan, but is the average of several scans on a single day.

3. Comparison of Peak Heights Obtained for Various Ions

The foregoing data afford a comparison of the peak heights obtained with different ions if the current for each ion is calculated for a given concentration. The current for each ion at a concentration of 10^{-4} molar was therefore calculated. These results together with the half peak potentials found are summarized below. The half peak potentials were evaluated visually from the curves. The limits of error given are the 95% confidence limits (5), which take into account the standard deviation and the number of times the particular sample was analyzed.

TABLE VI

A COMPARISON OF THE PEAK HEIGHTS
 CALCULATED FOR 10^{-4} MOLAR SOLUTIONS OF VARIOUS IONS
 IN 0.01 MOLAR POTASSIUM NITRATE

Element	Electrochemograph		Polarotrace	
	Peak Current	Half Peak Potential	Peak Current	Half Peak Potential
	(μ amps.)	(Volts vs. S.C.E.)	(μ amps.)	(Volts vs. S.C.E.)
Cadmium	25.5 ± 0.4	-0.60	159 ± 4	-0.62
Zirc	24.0 ± 1.6	-1.04	148 ± 4	-1.13
Lead	30.9 ± 1.2	-0.39	174 ± 20	-0.40
Indium	35.7 ± 1.4	-0.57	216 ± 16	-0.59

4. Behavior of Indium

Streuli and Cooke (17) reported that indium gave a small wave flattened at the top. The indium peaks observed in this study confirmed this result in that the indium peak was much smaller and broader than one would predict for a three-electron reduction (figure 8). On the other hand, the results were fairly reproducible when the solutions were analyzed immediately after their preparation. Analysis of these same solutions on standing, however, showed that the peak heights decreased with time, perhaps due to hydrolysis of the indium. The fact that the indium standard was prepared by dissolution of the metal in nitric acid may have retarded the hydrolysis to a measureable rate. The data below illustrate the results found for solutions on standing.

TABLE VII
DECREASING PEAK HEIGHT FOR INDIUM
IN 0.01 MOLAR POTASSIUM NITRATE ON STANDING

Indium Concentration = 2.11 parts per million

Time Elapsed Since Preparation (Hours)	Peak Current (μ amps.)	
	Electro- chemograph	Polarotrace
0	6.3	38.0
24	4.5	26.3
84	2.5	14.7
192	2.4	14.6

5. Other Ions Examined

Besides the elements already discussed, several others were examined. Solutions of iron, chromium, nickel, and cobalt in 0.01 molar potassium nitrate did not produce peaks over the voltage range available. Hence, these elements are not determinable in this medium; or, more optimistically, these elements should not normally interfere with the determination of lead, cadmium, indium, and zinc.

A copper peak was observed at about zero volts, but the start of the wave was partially masked by the wave common to all solutions, which occurs at slightly more positive potentials. As a result the peak height could not be accurately measured.

Bismuth apparently hydrolyzes very rapidly in this medium, for solutions of that ion gave rise to extremely small peaks of unpredictable height.

B. Potassium Acid Phthalate as a Base Electrolyte

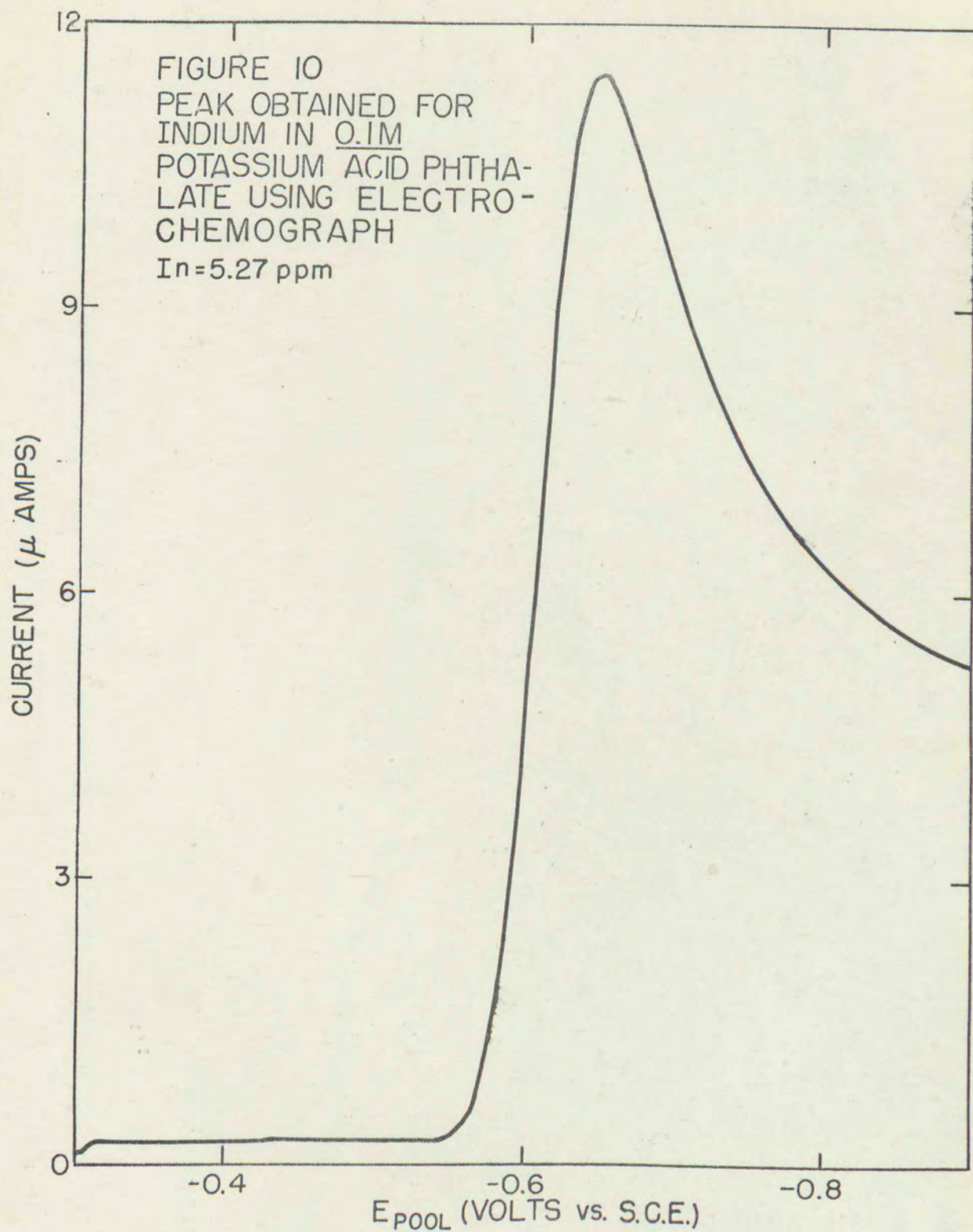
Reagent grade potassium acid phthalate was used without pretreatment for this study. A small amount of zinc was present as an impurity but did not contribute significantly to the results.

1. Comparison of Peak Heights Obtained for Various Ions

Solutions of a number of ions in 0.1 molar potassium acid phthalate were prepared and analyzed. From these data the peak heights for 10^{-4} molar solutions were calculated. The final results are listed below along with the half peak potentials. The limits of error quoted are again the 95% confidence limits.

TABLE VIII
A COMPARISON OF THE PEAK HEIGHTS
CALCULATED FOR 10^{-4} MOLAR SOLUTIONS OF VARIOUS IONS
IN 0.1 MOLAR POTASSIUM ACID PHTHALATE

Element	Electrochemograph		Polarotrace	
	Peak Current (μ amps.)	Half Peak Potential (Volts vs. S.C.E.)	Peak Current (μ amps.)	Half Peak Potential (Volts vs. S.C.E.)
Cadmium	26.8 ± 1.8	-0.60	191 ± 6	-0.61
Zinc	25.7 ± 1.3	-1.02	196 ± 11	-1.08
Lead	28.0 ± 1.3	-0.42	212 ± 4	-0.42
Indium	24.8 ± 0.9	-0.60	148 ± 6	-0.61
Copper	24.7 ± 1.4	-0.01	126 ± 17	-0.02



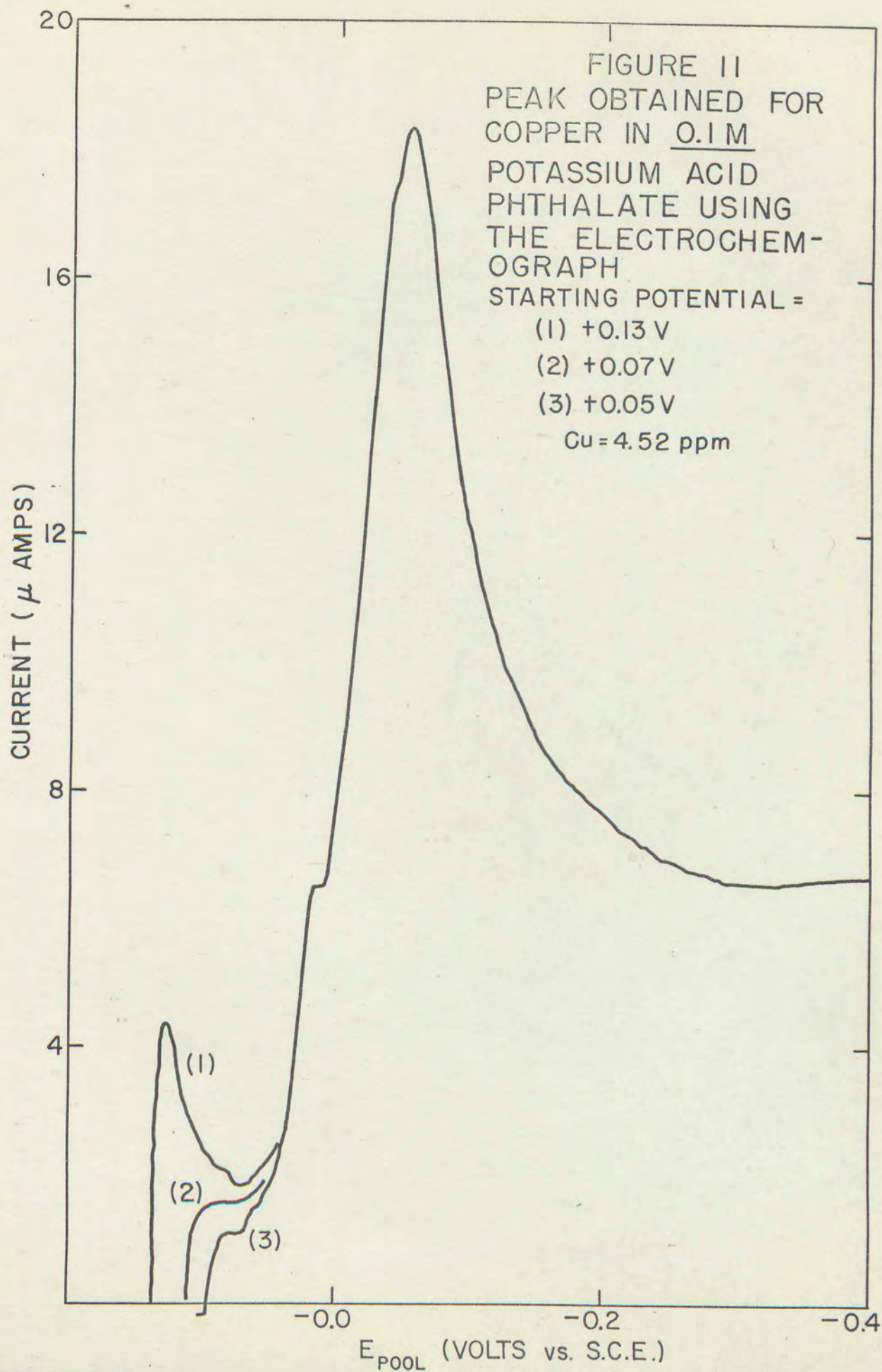
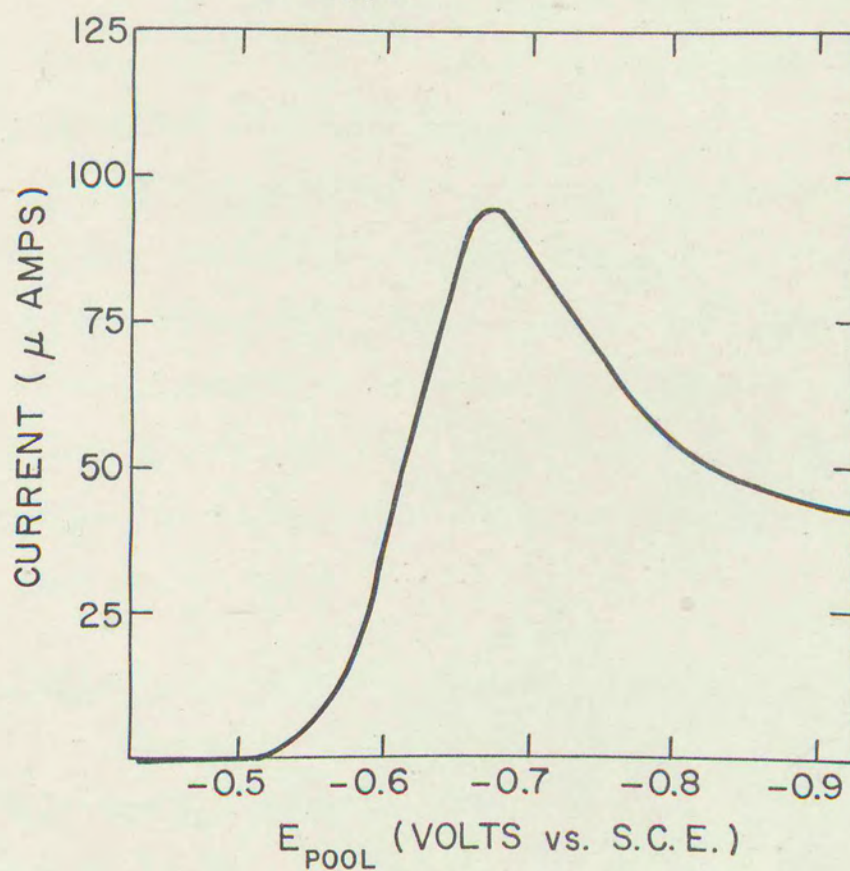


FIGURE 12
PEAK OBTAINED
FOR CADMIUM IN 0.1 M
POTASSIUM ACID PHTHALATE
USING THE POLAROTRACE
Cd = 5.62 ppm



2. Other Ions Examined

A very well defined peak was obtained for bismuth, but the peak height was not reproducible. Though undesirable from an analytical viewpoint, the peak found (figure 15) did serve to illustrate the type of curve obtainable for a three-electron reduction.

Iron, chromium, and nickel again produced no peaks. The reduction peak for the latter probably coincides with the hydrogen wave.

The copper peak found with the electrochemograph contained a slight distortion on the ascending branch (figure 11). With the polarotrace the curve appeared to be a combination of two peaks with almost the same half peak potential. Unfortunately, time did not permit a thorough study of this phenomenon.

C. Ammonia-Ammonium Chloride as a Base Electrolyte

Solutions for this study were prepared by taking appropriate quantities of reagent grade ammonium chloride and ammonium hydroxide to give a supporting electrolyte of 0.1 molar ammonia, 0.1 molar ammonium chloride. A significant amount of zinc was contributed by these reagents. In the

final solutions a peak current of 1.12μ amps. was observed for zinc with the Electrochemograph which corresponds to 0.24 ppm. This correction was applied in computing the peak height for zinc in Table IX.

1. Comparison of Peak Heights Obtained for Various Ions

Solutions containing about 5×10^{-5} molar concentrations of a number of ions were examined as was done for the other supporting media. The peak currents for 10^{-4} molar solutions were similarly calculated and are listed below.

The peak currents for cobalt and nickel with the polarotrace are not given, since both ions gave erratic results. The cobalt peak varied in an unpredictable fashion, while the peak for nickel decreased on successive scans. The reason for this is discussed in part V.

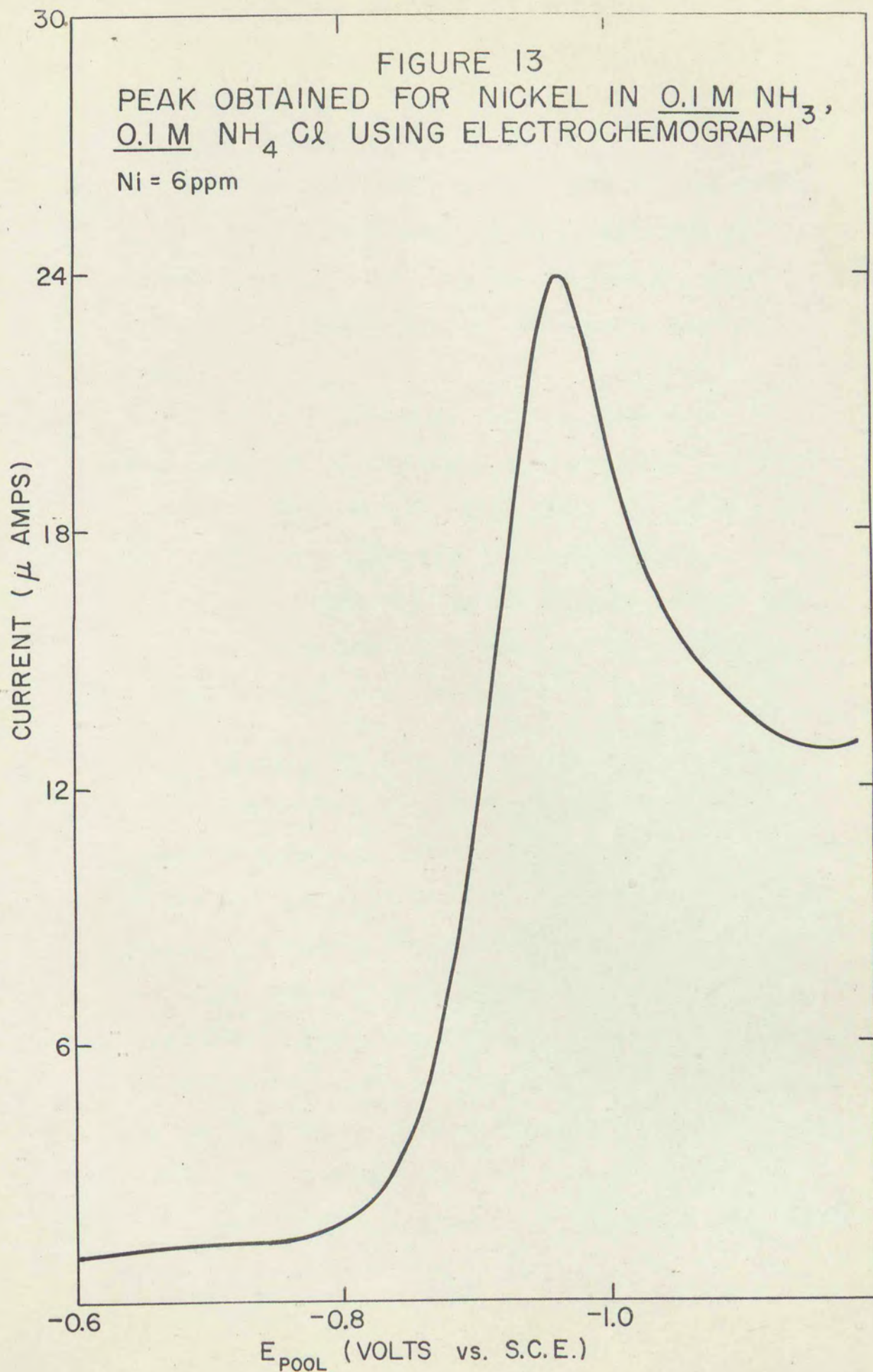
TABLE IX
A COMPARISON OF THE PEAK HEIGHTS
CALCULATED FOR 10^{-4} MOLAR SOLUTIONS OF VARIOUS IONS
IN 0.1 MOLAR AMMONIA, 0.1 MOLAR AMMONIUM CHLORIDE

Element	Electrochemograph		Polarotrace	
	Peak Current	Half Peak Potential	Peak Current	Half Peak Potential
	(μ amps.)	(Volts vs. S.C.E.)	(μ amps.)	(Volts vs. S.C.E.)
Cadmium	32.6 ± 1.1	-0.68	258 ± 11	-0.68
Zinc	31.0 ± 2.5	-1.18	240 ± 11	-1.26
Cobalt	22.6 ± 0.3	-1.04	-	-
Copper	11.5 ± 0.5	-0.35	91.4 ± 11.0	-0.33
Nickel	22.7 ± 0.5	-0.92	-	-

FIGURE 13

PEAK OBTAINED FOR NICKEL IN 0.1 M NH_3 ,
0.1 M NH_4Cl USING ELECTROCHEMOGRAPH

Ni = 6ppm



2. Other Ions Examined

A peak for lead was obtained in this medium, but the peak height was extremely small and the results irregular. This was not surprising, since hydrolysis of lead would be expected in such a solution.

Uranium solutions were also examined. A small peak, which appeared to represent a one-electron reduction, was found at -0.64 volts vs. S.C.E. However, the peak height was not reproducible.

An attempt was made to obtain a cobalt peak in 2.0 molar ammonia, 2.0 molar ammonium chloride. In this case, though, no wave was found.

D. Results Obtained by Varying the Pool Size

Although a pool diameter of two centimeters proved satisfactory for all measurements, variation of the pool size can be readily accomplished, if desired, by adding different amounts of mercury to the cell. The 0.5 centimeter pool, however, was not very useful, since the cell wall could not be desiccated. The solutions tended to creep around the mercury with the result that the peak current increased with time. Nevertheless a solution of 5×10^{-5} molar cadmium in 0.01 molar potassium nitrate was examined using three pool sizes. The results demonstrate that the peak

current is directly proportional to the electrode area, although in view of the uncertainty in estimating the area of the pool the agreement is perhaps in part fortuitous.

TABLE X

THE PEAK CURRENT AS A FUNCTION OF ELECTRODE AREA
Solution = 5×10^{-5} molar cadmium in 0.01 molar KNO_3

Diameter of pool (cm)	Estimated area of pool (cm^2)	Peak current (μ amps.)	<u>Peak current</u> <u>Area</u>
2.0	4.4	160	36
1.0	1.4	48	34
0.5	0.47	16	34

PART V

DISCUSSION

At the outset of this work several questions concerning the use of the cathode ray polarograph with a mercury pool had to be settled. One of these was the possibility that the curves produced would not be the same from one trace to the next. This difficulty was only encountered in the case of nickel. The peak produced by the first scan was quite large, but successive scans yielded steadily decreasing peaks. This was probably because the nickel reduced during the scan was not anodically stripped during the delay period. Such an occurrence would cause a gradual depletion of the nickel from the solution around the electrode accompanied by a corresponding decrease in the peak height. A rapid calculation shows that the decreasing current for nickel was not due to a gross depletion of the ion from the bulk of the solution. For a sample containing three parts per million of nickel the initial peak was about eighty μ amps. The total area under the curve is equal to the number of

coulombs involved in one scan, and was estimated graphically to be 4.6×10^{-5} coulombs. This represents the reduction of 4.8×10^{-10} gram equivalents of nickel or 1.4×10^{-2} μ grams. Assuming a volume of five milliliters, the total nickel content of the sample was fifteen μ grams. Therefore, 0.1% of the nickel in the sample was reduced during the first scan, and lesser amounts during the following scans. The actual decrease in the peak height between the first and second scans was greater than 10%. Clearly then, gross depletion of the nickel does not account for the decrease. Instead, the nickel is merely depleted from that portion of the solution adjacent to the mercury, causing the peak height for the following scan to be much smaller. For the other ions studied the anodic stripping apparently approaches completion during the delay period, since the peak height was fairly constant for many scans.

Another question was the pool size to be used. The polarographic cell was designed so that this could be varied, if necessary, but the two-centimeter pool proved satisfactory for both polarographs and was used throughout this work.

A. The Supporting Electrolyte

The selection of the supporting electrolyte will, as in conventional polarography, depend upon the ion being determined and the other ions present. A few generalizations can be made, however, which should be helpful in making the choice.

To begin with, it is apparent from the figures given that with basic solutions the available voltage range is extended to more negative potentials. Ions such as zinc or nickel then would most likely give better results in slightly basic solutions, since there would be little contribution to the peak height from the hydrogen wave.

Everything else being equal, the supporting electrolyte from which the largest peak current is obtained would be selected. However, the form of the peak should also be taken into account, since a small sharp peak is likely to be more useful than a taller, broader one. For example, cadmium and lead gave about the same peak height in 0.01 molar potassium nitrate and 0.1 molar potassium acid phthalate. For both ions however, the peaks were narrower in potassium acid phthalate. In other words the peaks cover narrower ranges of potentials. For that reason there is less

likelihood of interference from ions reduced at nearby potentials, and conversely, less likelihood of interference from cadmium or lead in the determination of a different ion.

It is interesting to note also that an ion may be determined in a medium in which it is normally considered insoluble. As long as the solubility product is not exceeded, such a possibility should not be ignored.

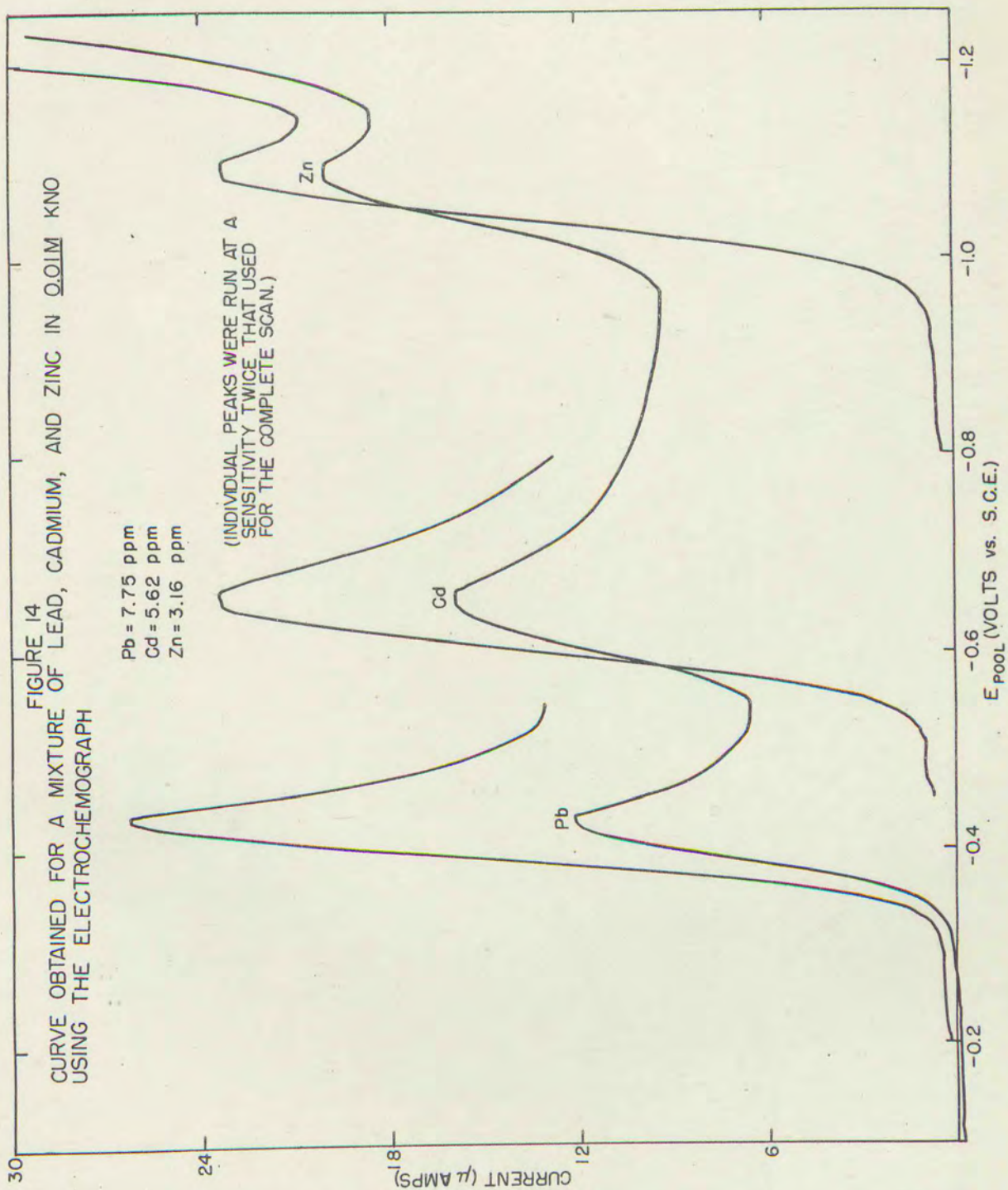
B. Analysis of Mixtures

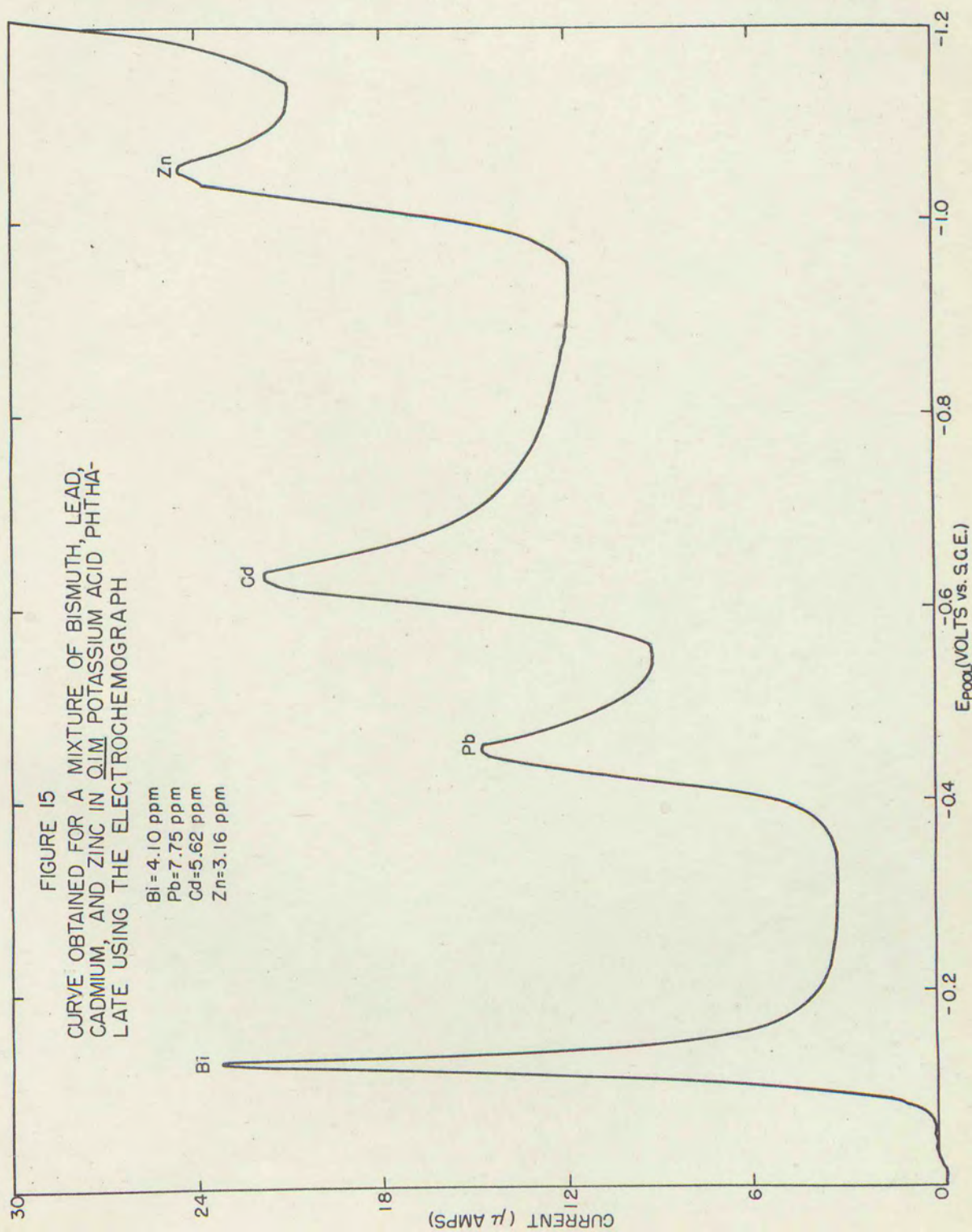
When several ions are to be determined in the same solution, the peak current for the ion reduced at the lowest potential is read first. Then the potential applied to the pool is set at a voltage greater than that at which the peak for the first reduction occurred. The current is allowed to decay to a steady value, and the peak for the second ion is recorded. The process is repeated for each succeeding ion. Figure 14 shows the curve resulting from an uninterrupted voltage scan superimposed on the individual peaks obtained in the above manner. Similar continuous curves are given in figures 15 and 16.

C. Comparison of Several Approaches to Voltammetry

The two techniques employed in this study, namely the use of a mercury pool electrode with a conventional polarograph (slow scan) and a cathode ray polarograph (rapid scan), offer increased sensitivity and resolution as compared to conventional polarography. The rapid scanning technique is five to ten times more sensitive, although a demand for its greatest sensitivity may be rare. The use of the cathode ray polarograph also makes for a more rapid analysis since less time is taken to record and interpret the curves. The conventional polarograph, however is less expensive and more readily available. Furthermore, the sensitivity using such an instrument is certainly adequate for most applications. Figure 17, for example, shows the peak current found for a solution of 10^{-6} molar cadmium. A better picture of the relative sensitivity of each approach is given by the currents found for a solution of 10^{-4} molar cadmium. By conventional polarography with a dropping electrode the current was 1.0μ amps.; with the pool and a conventional polarograph, 26μ amps.; with the pool and a cathode ray polarograph, 159μ amps.

This discussion would be lacking indeed if no mention were made of the use of a cathode ray polaro-





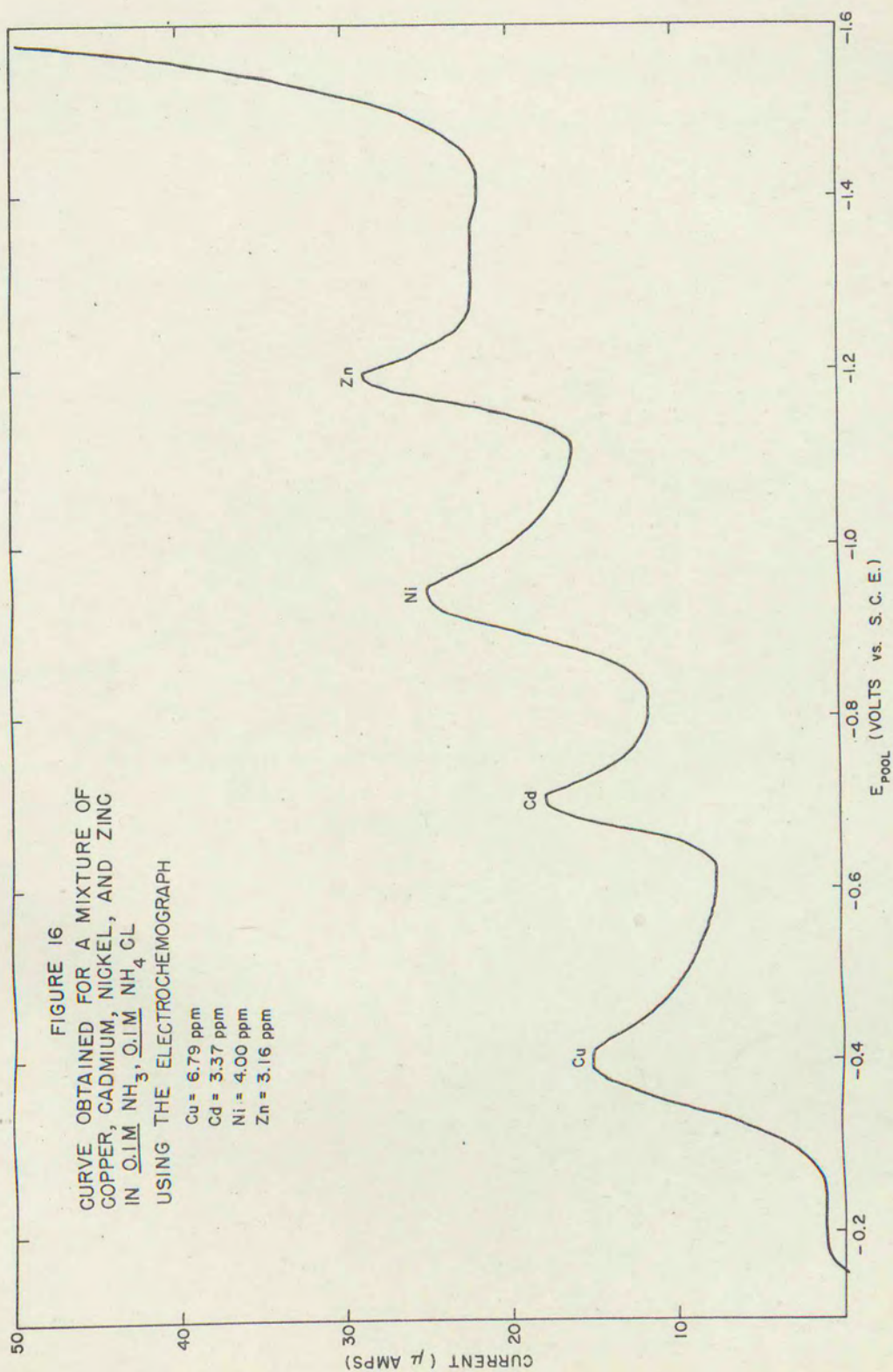
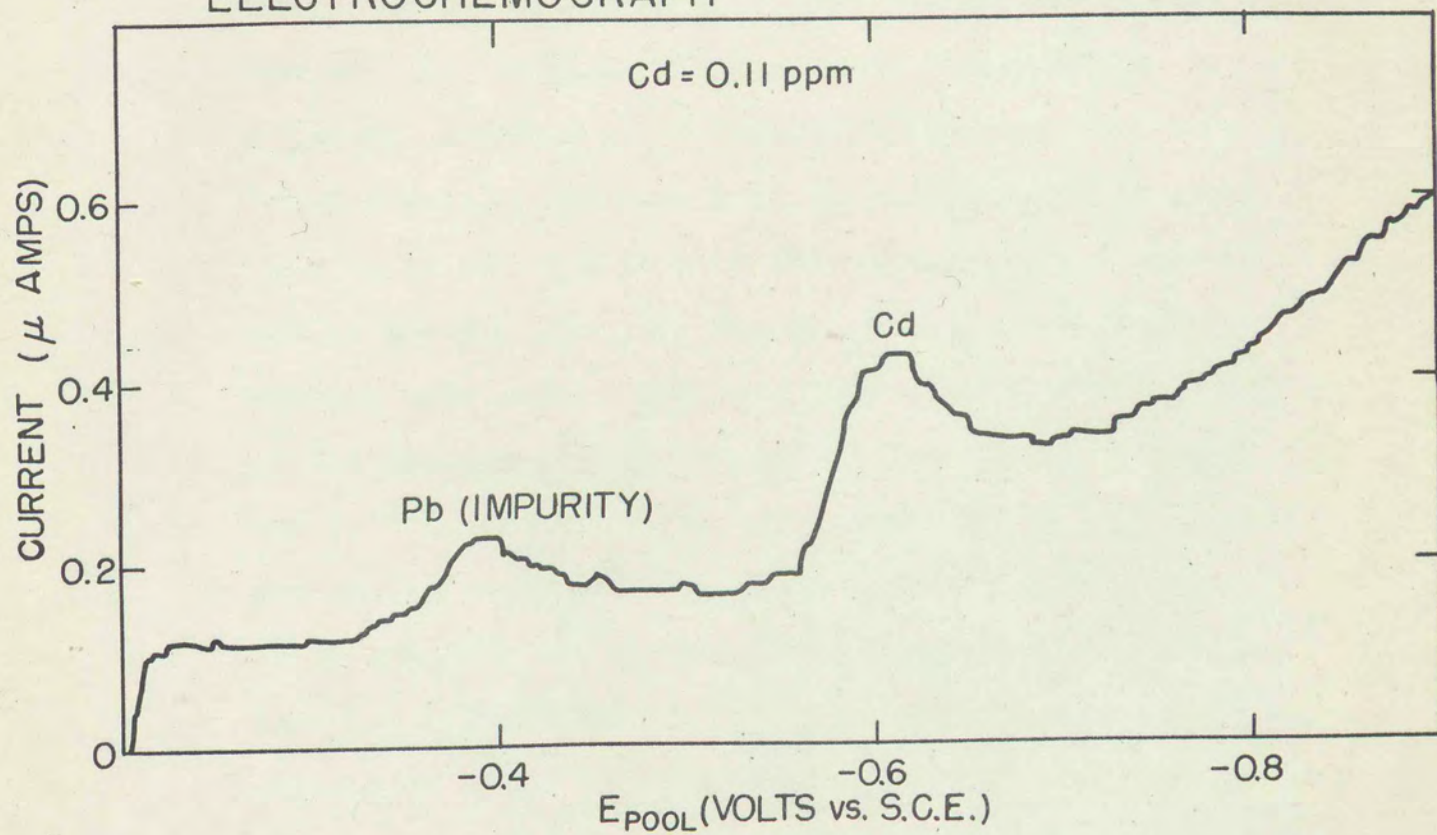


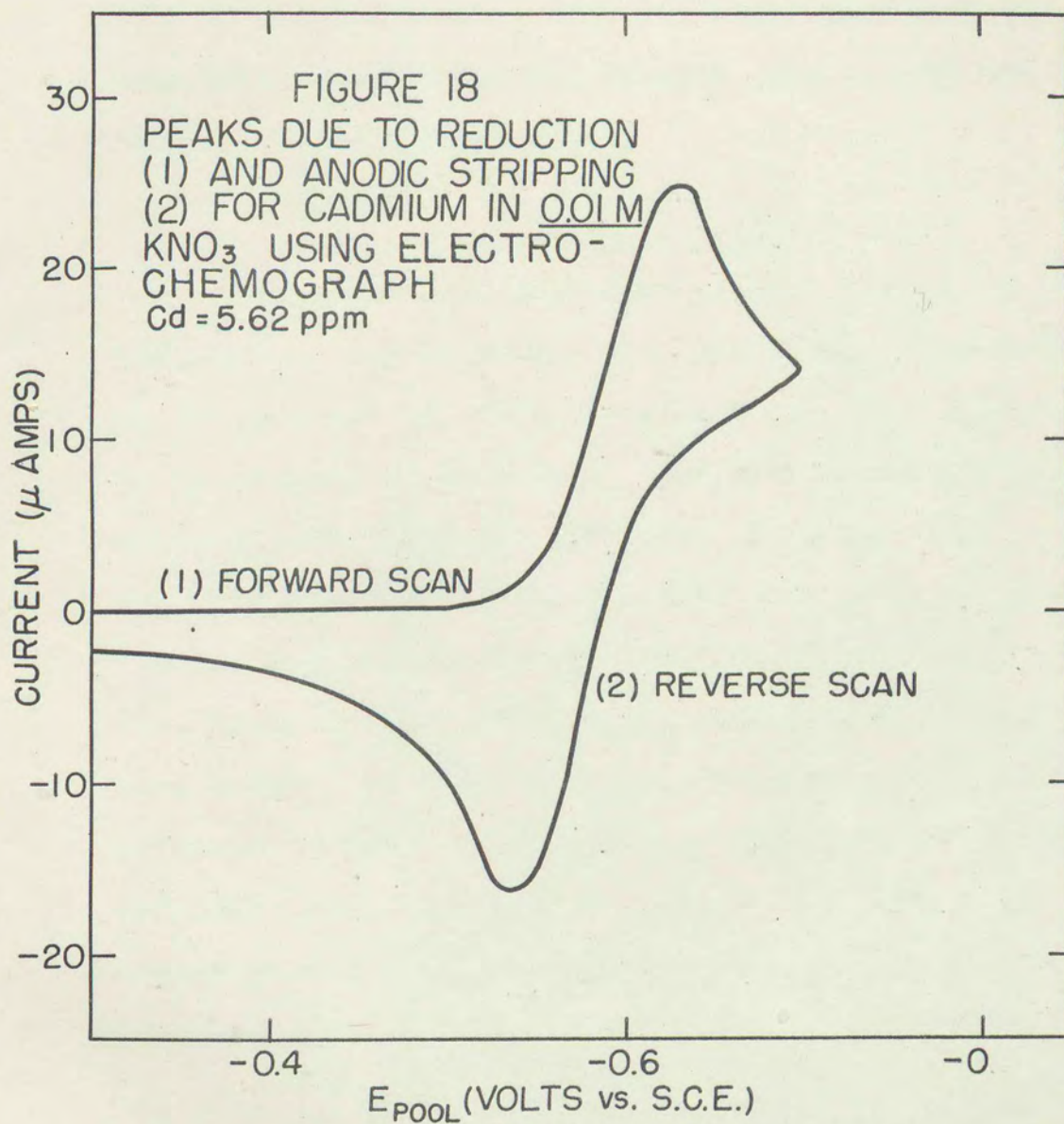
FIGURE 17
PEAK OBTAINED FOR CADMIUM IN 0.01M KNO_3 USING
ELECTROCHEMOGRAPH



graph with a dropping mercury electrode. This approach is much more versatile than any employing a stationary electrode, since the hydrogen overvoltage is greater with a dropping electrode. This means simply that the wave for hydrogen is displaced towards more negative potentials. For example, the hydrogen wave for 0.1 molar potassium acid phthalate began at about -1.1 volts vs. S.C.E. with the mercury pool electrode and at about -1.5 volts vs. S.C.E. with the dropping mercury electrode. The peak currents are less because of the smaller electrode area (value found, $7.0\mu\text{amps.}$ for 10^{-4} molar cadmium), but the method is still an extremely sensitive one. This approach appears to offer slightly better reproducibility than the techniques studied here. The results are about as precise as those obtained by conventional polarography.

D. Anodic Stripping

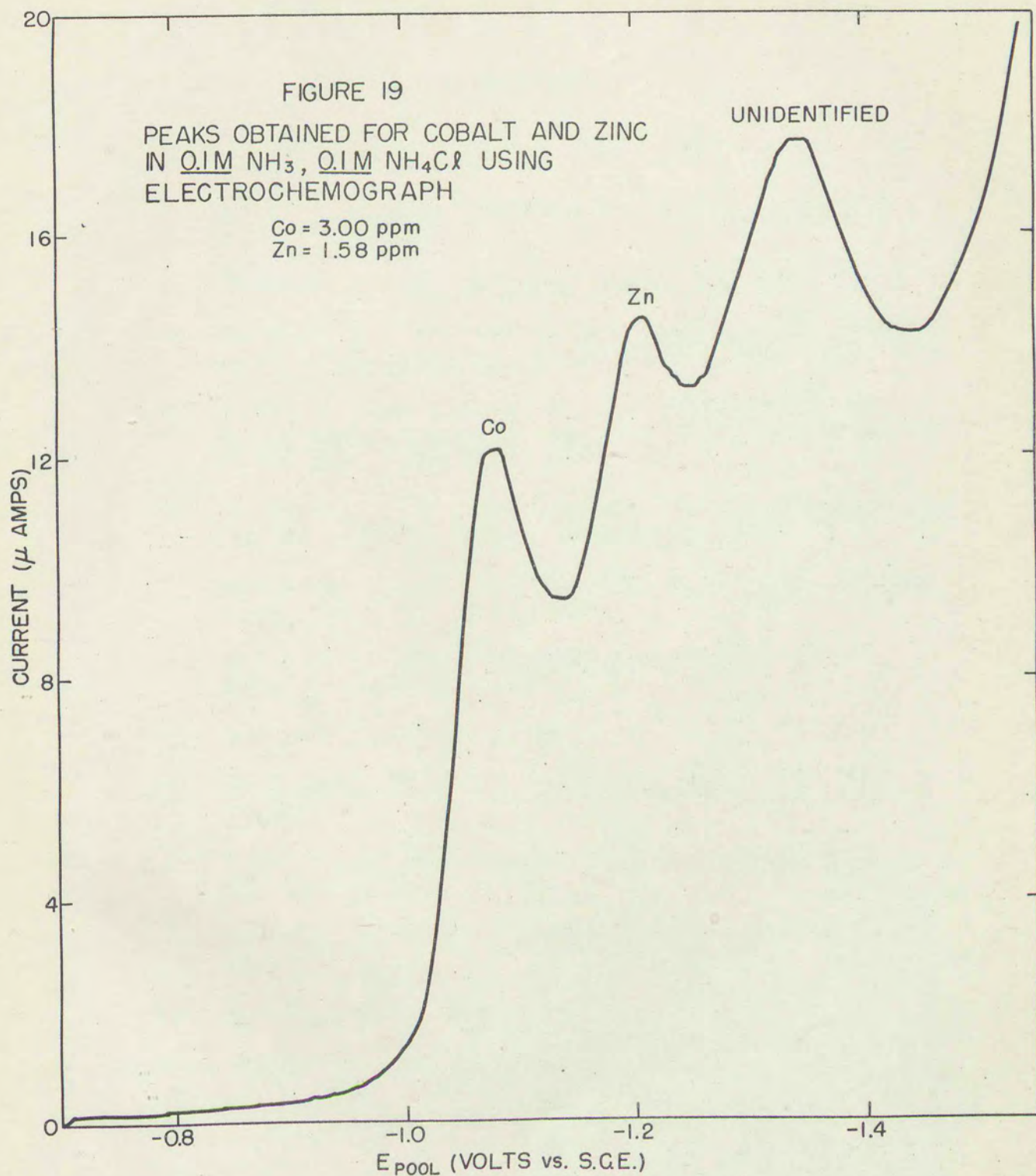
Reversal of the scan, that is scanning towards more positive potentials, is yet another approach that may be used (11). A peak, or more properly, a valley in the current-voltage curve results from the anodic dissolution of an ion from the mercury. By properly regulating conditions, this method can be even more sensitive than methods involving a forward



scan. The type of curve produced is illustrated in figure 18. The reverse scan was replotted along the same voltages used for the forward scan so that the two curves could be compared.

E. Analytical Applications

From the data presented several analytical applications can be seen. Zinc should be determinable in the presence of nickel in either potassium nitrate or potassium acid phthalate. But with ammonia-ammonium chloride the nickel peak precedes the zinc. The analysis of nickel in the presence of zinc should therefore be possible in that medium. The same medium should also serve for the analysis of cobalt in the presence of zinc (figure 19). Cadmium and lead can be determined in potassium nitrate or potassium acid phthalate. The determination of indium could best be carried out in potassium acid phthalate, since hydrolysis occurs in the other media examined.



PART VI
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