

CHRONOPOTENTIOMETRIC ANALYSIS OF SOME DILUTE SOLUTIONS IN AQUEOUS MEDIUM

Thesis for the Degree of M. S. MICHIGAN STATE UNIVERSITY Frederick Miller Mong 1957 THES.



•

ł

.

add

MICHIGAN STATE UNIVERSITY

EAST LANSING, MICHIGAN

...

CHRONOPOTENTIOMETRIC ANALYSIS OF SOME DILUTE SOLUTIONS IN AQUEOUS MEDIUM

By

Frederick Miller Mong

A THESIS

Submitted to the College of Science and Arts of Michigan State University of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

4-21-58 G-5164

ACKNOWLEDGMENT

The author wishes to express his sincere gratitude to Dr. Andrew Timnick for his encouragement and direction throughout the course of the investigation and preparation of this thesis.

Name: Frederick Miller Mong

Born: July 25, 1933 in Franklin, Pennsylvania

Academic Career: Franklin High School, 1947-1951

Grove City College, Grove City, Pennsylvania, 1951-1955

Michigan State University East Lansing, Michigan, 1955-1957

Degrees Held: B. S. -- Grove City College, 1955

VITA

CHRONOPOTENTIOMETRIC ANALYSIS OF SOME DILUTE SOLUTIONS IN AQUEOUS MEDIUM

By

Frederick Miller Mong

AN ABSTRACT

Submitted to the College of Science and Arts of Michigan State University of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

Year 1957

Approved (Andrew) Tinnick

ABSTRACT

The instrumentation and analytical application of chronopotentiometry to some dilute aqueous solutions were investigated.

Design and construction of a glass cell, construction of several platinum electrodes and construction and calibration of a constant current supply were carried out. The instrumentation assembly was tested with various concentrations of lead ion in 0.1 M potassium nitrate as the supporting electrolyte. A close check on the geometrically measured area of the platinum electrode and the experimentally obtained area was observed.

The use of a mercury plated platinum electrode in chronopotentiometry was introduced. The presence of plated mercury on a platinum electrode shifted the hydrogen overvoltage 0.3 to 0.4 volts in the negative direction. The shift was sufficient so that several additional ions such as antimony and zinc could be determined with this solid electrode.

Calibration curves were obtained for antimony (III) and bismuth (III) separately, in 1 N nitric acid using a mercury plated platinum electrode. No break could be obtained for arsenic (III) over the range studied or with the various supporting electrolyte tested. A mean

v

deviation of $\pm 1.70\%$ for $\frac{\mathbf{i} \mathbf{T}^{1/2}}{\mathbf{c}}$ was obtained for bismuth (III) over the concentration range of 3×10^{-5} to 1×10^{-3} moles per liter. For antimony (III), $\frac{\mathbf{i} \mathbf{T}^{1/2}}{\mathbf{c}}$ decreased as concentration of this ion decreased from 2×10^{-3} to 6×10^{-4} moles per liter.

Mixtures containing antimony (III) and bismuth (III) were resolved. Arsenic (III) did not interfere in this resolution.

Chronopotentiograms for 0.001 M thallium (I), 0.001 M copper (II) and 0.001 M cadmium (II) each, in 0.1 M potassium chloride as the supporting electrolyte were obtained using a bright platinum electrode.

TABLE OF CONTENTS

Page

-

1. INTRODUCTION	1
II. HISTORICAL AND THEORETICAL BACKGROUND	3
III. EXPERIMENTAL	9
Chemicals and Solutions. Apparatus. Cell. Electrodes. Constant Current Supply. Calibration of Glassware. Arrangement of Apparatus. Procedures. Current Supply Calibration. Preliminary Tests with Lead Solutions. Use of a Mercury-Plated Platinum Electrode. Determination of a Proper Supporting Electrolyte for the Analysis of Antimony (III) and Bismuth (III). Temperature Effect on Transition Time. The Determination of Antimony (III) and Bismuth (III). Analysis of Mixtures of Antimony (III) and Bismuth (III).	9 9 9 11 13 15 15 15 25 29 23 4 37
	بەر 1
IV. DISCUSSION AND CONCLUSIONS	51
LITERATURE CITED	55

.

LIST OF TABLES

age	P	TABLE
16	Summary of Calibration Results for Constant Current Supply.	I.
20	Manual Determination of Lead in 0.1 M Potassium Nitrate at Room Temperature	II.
23	Transition Times for Various Concentrations of Lead (II) in O.1 M Potassium Chloride	III.
	Evaluation of $\frac{i \tau^{1/2}}{c}$ for 0.001 M Lead (II) in 0.1 M	IV.
28	Potassium Chloride Using a Mercury-Coated Platinum Electrode	
29	Effect of Acid Concentration on the Hydrolysis of Antimony (III) and Bismuth (III)	۷.
31	$E_{1/4}$ Values for Bismuth (III) and Antimony (III) in Various Acid Media	VI.
32	Temperature Effect on Transition Time for 6×10^{-4} M Bismuth (III)	VII.
36	Determination of Bismuth (III) in 1 N Nitric Acid	VIII.
40	Determination of Antimony (III) in 1 N Nitric Acid	IX.
44	Some Mixtures of Antimony (III) and Bismuth (III)	Х.

LIST OF FIGURES

IGURE	Page
1. Electrolysis CellActual Size	10
2. Circuit Diagram for Constant Current Supply	12
3. Arrangement of Apparatus	14
4. I-Calibration Plots for Constant Current Supply	17
5. II-Calibration Plots for Constant Current Supply	18
6. Method for the Determination of Transition Time	19
7. Chronopotentiograms of Lead (II) in 0.1 M Potassium Nitrate	21
8. Calibration Plot of $\boldsymbol{\tau}^{1/2}$ vs. Concentration for Lead (II) in 0.1 N Potassium Nitrate	22
9. Calibration Plot of i $\boldsymbol{\tau}^{1/2}$ vs. Concentration for Lead (II) in 0.1 N Potassium Chloride	24
10. Effect of the Mercury Film on the Overvoltage of Hydrogen	27
<pre>11. Effect of the Various Acids as Supporting Electrolytes for Determining Bismuth (III) and Antimony (III)</pre>	30
12. Effect of Temperature on Transition Time for 6 x 10 ⁻⁴ M Bismuth (III) in 1 N Nitric Acid	33
13. Calibration Plots for Bismuth (III)	39
14. Calibration Plots for Antimony (III)	42
15. Calibration Plots for Various Mixtures of Antimony (III) and Bismuth (III)	45
16. Chronopotentiograms of Typical Mixtures of Antimony (III) and Bismuth (III)	46
17. Chronopotentiogram of 0.001 M Thallium (I)	48
18. Chronopotentiogram of 0.001 M Cadmium (II)	49
19. Chronopotentiogram of 0.001 M Copper (II)	50

~

I. INTRODUCTION

Chronopotentiometry is based on the interpretation of the variation of the potential at a working electrode as a function of time when a constant current flows between the working electrode and the auxiliary electrode both of which are immersed in an unstirred solution. The potential of the working electrode is measured against a reference electrode such as the saturated calomel electrode.

Even though the fundamentals pertaining to chronopotentiometry were worked out at the beginning of the century, it wasn't until the early 1950's that the potentialities of applying chronopotentiometry in analytical chemistry were realized.

The chronopotentiometric method of analysis offers several advantages that conventional polarography does not possess. No fluctuation in the measured quantity is observed. Mercury or solid electrodes can be used and the performance of both can be treated theoretically. If a solid electrode is used, plated metals may be anodically stripped back into solution and reruns made. The sensitivity of chronopotentiometry is greater so that lower concentrations of reducible or oxidizable ions can be determined. No maximum suppressors need be added to the solutions to be analyzed.

The work which follows was undertaken to extend analytical applications by the use of a platinum electrode for the chronopotentiometric determination of dilute solutions of arsenic (III), antimony (III) and

bismuth (III) separately, or in mixtures. To carry out this work, an electrolytic cell had to be designed and constructed and a constant current source had to be assembled and calibrated.

II. HISTORICAL AND THEORETICAL BACKGROUND

Credit has been given to Weber for initiating the studies on chronopotentiometry in 1879 (33) when he conceived a method for the determination of the diffusion coefficient of zinc sulfate. It was Sand, however, who developed the theoretical aspects of the method and derived the first working equation relating the various factors involved (26).

In his work, Sand studied the variation of ionic concentrations at electrodes in a solution of copper sulfate and sulfuric acid during electrolysis. He devoted special attention to the liberation of hydrogen during electrolysis. He concluded that only after the copper ion concentration had gone to zero at the surface of the electrode, would hydrogen be evolved. The duration of electrolysis for the depletion of the copper ions at the cathode (transition time) was determined experimentally and the following equation was derived to verify this mathematically.

$$\gamma^{1/2} = \frac{\pi^{1/2} \text{ FD}^{1/2} \text{ C N}}{21}$$

in which,

- 1 = current density in amperes/cm.
- T = transition time in seconds.
- **N** = number of electrons involved in the over-all electrode process.
- F =the Faraday, 96,494 coulombs.
- $D = diffusion coefficient in cm^{2}/second.$
- C = concentration in moles/ml.

Sand proposed several conditions which must be met in order that the above equation apply. The solution must be confined in a cylindrical vessel bounded by the electrodes. No convection currents must be allowed to develop. The diffusion of the salt in solution should proceed according to Fick's law and its transport values be constant. He stated that this formula can be made the basis of an approximate method for determining diffusion coefficients.

Cottrell (5) and Karaoglanoff (17) applied the method to the verification of Fick's law of diffusion and to the determination of diffusion coefficients. Karaoglanoff carried out his work on the electrolytic reduction and oxidation of iron alum, ferric sulfate, ferric chloride, ferrous ammonium sulfate, and ferrous sulfate. He verified Sand's formula to the extent that in electrolysis at constant current, potential at an electrode varies as a function of time and that oxidation or reduction processes taking place are diffusion controlled.

Rosebrugh and Miller (25) developed a complete mathematical treatment of changes in concentration which occur at the electrode during electrolysis. Particular attention was given to the changes which occur within the first fraction of a second after the current begins to flow.

Studies in the field up to the middle of this century pertained mainly to reactions occurring on the surface of the working electrode. Hickling, Taylor and Spice (12, 13, 14, 15, 16) studied the anodic behavior of copper, silver, nickel, gold or platinum electrodes in acid, neutral or alkaline media. They identified the various stages in the

polarization of these metals by employing a cathode ray oscillograph.

Wakkad and Emara (30, 31, 32) also studied surface film formation on copper, nickel or platinum electrodes. They employed a direct potentiometric method using a special cell and constant current unit. They confirmed their findings by the oscillographic methods employed by Hickling, et al.

Other work on the anodic passivation of gold has been carried out by Butler and Armstrong (2) and by Shutt and Walton (28).

Stackelberg <u>et al</u>. (29) in 1953 made application of the method of voltammetry at constant current for the determination of diffusion coefficients of Ag(I), Tl(I), Cd(II), Pb(II), Zn(II), Zn(OH), $\overline{,}$, IO₃, Fe(CN)₆ and Fe(CN)₆ in concentrations of 0.001 M in aqueous solutions of sodium chloride, potassium chloride and potassium nitrate up to 3 M in concentration.

Delahay and Berzins (1, 7) in the same year presented rigorous mathematical analysis for three types of electrode processes in electrolysis at constant current in unstirred solutions. These processes were a cathodic process followed by re-oxidation resulting from reversal of the current, reduction of a two-component system and stepwise reduction of a single substance. Rigorous interpretations of potentialtime curves were developed for cases for which only approximate treatments are available in polarography and transitory voltammetry.

Gierst and Juliard (10) carried out a kinetic study of electrode processes occurring by a non-steady state electrolysis under constant current from a study of the relation between the transition time and the constant current. They concluded that the product of i $\mathbf{T}^{1/2}$ is linearly proportional to $D^{1/2}$ and to the concentration only if the electrolysis is exclusively controlled by the diffusion of the depolarizer.

In 1954, Delahay and Mattax (9) verified by experiment that the accuracy of evaluating transition time is primarily determined by three factors. These factors are the degree to which convective transfer interferes with the diffusion process, the precision with which transition time can be determined and finally, the precision on the current density measurement.

Delahay and Mamantov (8) in a review of the theoretical principles of chronopotentiometry presented relationships concerning transition time and potential-time curves for reversible, irreversible, consecutive, stepwise and kinetic processes. For the consecutive process, when two or more ions are present in solution which are reduced at different potentials, the concentration of the ion first reduced may be calculated from its transition time by means of the original Sand equation.

However, for a second ion, since the total electrolysis current now divides between two diffusion currents, the state of concentration polarization with respect to the second ion will be reached less rapidly and the transition time is correspondingly enhanced. The following general equation applies to diffusion-controlled chronopotentiometric systems where more than one reducible ion is present.

$$(\mathbf{T}_{1} + \mathbf{T}_{2} + \cdots + \mathbf{T}_{n})^{1/2} - (\mathbf{T}_{1} + \mathbf{T}_{2} + \cdots + \mathbf{T}_{n-1})^{1/2} = \frac{\pi^{1/2} N_{n} F D_{n}^{1/2} C_{n}}{21}$$

The potential of the working electrode can be calculated from the Nernst equation, and by studying the reaction cathodically can be shown to vary toward more negative values during electrolysis.

$$E = E_0 + \frac{RT}{NF} \ln \frac{fM^+N CM^+N}{fM CM}$$

During electrolysis, the concentration of metal ion decreases at the electrode surface because of the consumption of this ion, while at the same time the concentration of metal increases. As a result, the potential becomes more cathodic as the electrolysis proceeds. Initially, no metal is present so the potential should theoretically be positive infinity. At the end of the electrolysis, the concentration of metal ions should be zero and the potential should theoretically be negative infinity.

It is also shown mathematically (8) that the value of E $\tau/_4$, the potential at one-fourth of the transition time, is equal to the polarographic half-wave potential.

Reilley, Everett and Johns (23) discussed the feasibility of the method for analytical purposes in the cathodic reduction and anodic oxidation of simple ions at platinum and mercury pool electrodes. Several supporting electrolytes were examined and practical apparatus and technique described.

Nicholson and Karchmer (21) made application of the method to the determination of lead ion in nitric acid solution. Their results confirm the analytical usefulness of the method.

Reilley and Scribner (24) described a new method of end-point detection in a volumetric method which they called chronopotentiometric titrations. The relationship between chronopotentiometry and poteniometric titrimetry, the possible types of titration curves and the factors which govern the sensitivity of the method were discussed. The method has the advantages of the amperometric method but is applicable to the titration of small volumes or concentrations and in situations where stirring is undesirable.

Nikelly and Cooke (22) analyzed for very dilute solutions of metals by anodically removing them under controlled conditions.

Recently, Laitinen and Ferguson (19) found that salts dissolved in high temperature molten systems may be studied by chronopotentiometry. Using platinum electrodes, measurements made on the chlorides of Bismuth (III), cadmium (II), silver (I) and copper (I) in a lithium chloride-potassium chloride eutectic mixture at 450° showed the theoretical relationships among applied current density, concentration and transition time. The accuracy of the method was $\pm 2.6\%$.

For the most complete work on theory and experimental evaluation of chronopotentiometry, Chapter 8 in the book by Delahay (6) is an excellent review.

III. EXPERIMENTAL

Chemicals and Solutions

Reagent grade chemicals were used to prepare individual 0.1 M stock solutions of lead nitrate in distilled water, antimony trichloride in 4 N hydrochloric acid and bismuth nitrate in 4 N hydrochloric acid. These stock solutions were analyzed by precipitating lead as lead chromate (3) and bismuth as the oxy-chloride (34). Antimony was determined by a permanganate titration (34). A 0.1 M arsenic stock solution was prepared by dissolving primary standard grade arsenious oxide in 1 N potassium hydroxide, neutralizing the base, then making the final solution 1 N in hydrochloric acid. Primary standard grade silver nitrate was used in the current supply calibration. Also prepared were individual 0.001 M solutions of reagent grade thallous nitrate, cadmium chloride, cupric nitrate and zinc nitrate. One normal nitric acid, 0.1 N potassium chloride or 0.1 N potassium nitrate was used as the supporting electrolyte throughout the work, although other common supporting electrolytes were tried for comparison. Matheson oilpumped nitrogen was bubbled through each solution prior to electrolysis to remove any oxygen present.

Apparatus

Cell

The electrolysis cell shown in Figure 1 was designed for simplicity and convenience in its use. Actual construction was carried out by Mr. Gene Hood in the laboratory glassblowing shop. The cell consists of an



ACTUAL SIZE

anode compartment and a cathode compartment separated by a sintered glass disk to prevent free mixing of anolyte and catholyte. Stopcocks at the bottom of both compartments were attached for easy draining. The cathode compartment is surrounded by a jacket through which constant temperature water can be circulated. The cell was supported by means of a heavy duty clamp bolted rigidly to a heavy steel stand. Several mats were then placed under the steel stand. Vibrations to the cell were thus kept to a minimum.

Electrodes

Various sized platinum electrodes were prepared by heat-soldering 0.018 mm. thick platinum foils onto platinum wires sealed into the end of six mm. diameter soft glass tubes. Approximately one cm. from the sealed end inside the glass tube, the platinum wire was silver soldered to a copper wire of similar thickness which extended out of the end of the glass tube and to the current supply connection.

Constant Current Supply

A simple constant current unit shown schematically in Figure 2 was constructed to supply any current from approximately 4-2500 microamperes. The circuit is arranged so that the current can be directed through the cell or by-passed around it. The current can also be made to flow in either direction.

CURRENT SUPPLY CIRCUIT DIAGRAM CODE (For Figure 2)

R₁. 1000 ohms, 2-watt resistor^a

- R₂. 4000 ohms, 2-watt resistor^a
- R₃. 32 megohms, 1-watt resistor^a
- R₄. 16 megohms, 1-watt resistor^a
- R₅. 8 megohms, 1-watt resistor^a
- R₆. 4 megohms, 1-watt resistor^a
- R₇. 2 megohms, 1-watt resistor^b
- R_a. l megohms, l-watt resistor^b
- R_a. 500,000 ohms, 1-watt resistor^b
- R₁₀. 200,000 ohms, 1-watt resistor^b
- R₁₁. 100,000 ohms, 1-watt resistor^b
- R₁₂. 50,000 ohms, 2-watt resistor^b
- R₁₃. 20,000 ohms, 10-turn Helipot
- R₁₄. 20,000 ohms, 2-watt resistor^a
- T₁. Thordarson T-22R32 Transformer, 350-0-350 V, 110 ma., 5V.-2A.; 6.3 V. CT-3A; 6.3V. CT-3A.

S1,S2. SPST switch

- S₃. SPDT 3-position switch
- S4. DPDT 2-position switch
- S₅. ll-position switch
- C1, C2. 8 mfd., electrolytic condenser, 450 volts.

^aWire Wound Type ^bCarbon type



FIGURE 2. CIRCUIT DIAGRAM FOR CONSTANT CURRENT SUPPLY.

Calibration of Glassware

All volumetric flasks, pipets and burets were calibrated by standard techniques. Corrections were then applied when necessary. The dilute solutions used in this work were prepared from the analyzed stock solutions using this calibrated equipment.

Arrangement of the Apparatus

The arrangement of the apparatus is shown in Figure 3. A saturated calomel electrode. a working electrode. and glass tubes for nitrogen inlet and outlet are uniformly arranged into the catholyte compartment and supported by means of a rubber stopper. The two-way nitrogen system may be adjusted for initial sweeping of the solution. or alternately for passing nitrogen above the solution during electrolysis. A fritted glass disk at the bottom of the bubbler increases the dispersion of the nitrogen. The length of the saturated calomel electrode was extended thirty-two mm. by molding an epon-type plastic resin onto the top. This allows the tip to dip several cm. into the solution. The anode was supported at the level of the solution bridge by means of a rubber stopper. All glass tubing was of five or six mm. diameter and extended at least one inch above the rubber stopper. While the current passes between the two electrodes, the voltage change between the working electrode and the saturated calomel electrode is observed on a model 9600 Beckman Zeromatic pH meter and recorded automatically as a function of time by a Honeywell-Brown Electronik recorder, model



ARRANGEMENT OF APPARATUS. FIGURE 3.

number SY153x12(VA)-W7-6.^a A fifty-ohm precision resistor was installed across the recorder terminals of the Zeromatic so that the recorder would operate in the desired range. A Precision Scientific Company constant temperature water bath regulates the temperature around the catholyte compartment to $25.00 \pm 0.05^{\circ}$ C.

Procedures

Current Supply Calibration

The constant current supply was calibrated by means of a silver coulometer. Accurate weighing of silver deposited on a small platinum gauze electrode from a 2M silver nitrate solution containing 0.01% gelatin enabled calculation of the average current passed during an accurately timed interval. A silver wire served as the anode. By varying the instrument settings, a calibration curve for each position was thus obtained. Calibration results are listed in Table I and shown graphically in Figures 4 and 5.

The current supply polarity was established by observing the color change of phenolphthalein at the cathode. This color change is caused by the excess of hydroxyl ions at this electrode during electrolysis.

Preliminary Tests with Lead Solutions

To test the apparatus, preliminary runs employing a platinum electrode were carried out with lead solutions of various concentration in 0.1 M potassium nitrate without regard to temperature change. The

^aThe speed of the chart was accurately measured to be 1.18 sec. per cm. with a stopwatch. This speed was used throughout the entire work which follows.

SUMMARY OF CALIBRATION RESULTS FOR CONSTANT CURRENT SUPPLY

Current S elector Position	Time (Seconds)	Grams Silver Deposited	Micro -a mperes (Calculated)
9-800	600	0.001789 ^ª	2670
9-300	600	0.001237 ^b	1850
9 -0	900	0.001407 ^b	1400
8-800	900	0.001358 ^b	1350
8-300	1,000	0.001087	9 75
8-0	1,000	0.000823	737
7 - 800	1,200	0.000750	560
7-300	2,410	0.001074	400
7 - 0	3,600	0.001233	307
6-800	3,600	0.001115	278
6-500	4,800	0.001243	232
6-100	6,000	0.001131	169
5-800	7,200	0.001099	136.5
5-100	12,000	0.001148	85.7
4-800	16 ,0 00	0.001211	67.9
4-100	22,000	0.001015	41.4
3-800	27,000	0.001046	34.7
3-100	36,000	0.000856	21.3
2 -800	54,000	0.001049	17.4
1-800	72,000	0.000690	8.58

^aAverage of three results.

^bAverage of two results.



17

SUPPLY.



GURRENT FIGURE 5. II-CALIBRATION PLOTS FOR CONSTANT SUPPLY. surface area of the platinum electrode used was both geometrically and experimentally measured for comparison. The voltage changes were followed manually on the Beckman Zeromatic pH meter while time was followed with a stopwatch. The corresponding potentials and times were then plotted manually.

All transition times were measured graphically according to the suggestion of Delahay (8). In Figure 6, segment BE is constructed so that AB and FE are one-fourth the distance of AC and FD, respectively. OP, which then represents the transition time at $E_{1/4}$, is drawn parallel to AC and DF. All measurements were made using a pair of dividers.



Figure 6. Method for the Determination of Transition Time.

Table II shows the results of manually determining transition times at room temperature for 0.0005 to 0.0015 M lead (II). These chronopotentiograms are shown in Figure 7. In Figure 8, the relationship between $\tau^{1/2}$ and concentration is shown. The dotted line shows the calculated $\tau^{1/2}$ values assuming the diffusion coefficient of lead to be 0.98 x 10⁻⁵ cm² per second (18) and the area of the electrode to be 2.10 cm² as determined by geometric measurement. The solid line represents the experimentally evaluated $\tau^{1/2}$ values.

TABLE II

MANUAL DETERMINATION OF LEAD IN O.1 M POTASSIUM NITRATE AT ROOM TEMPERATURE

Pb(II) conc. (moles/liter)	Current Selector Position	7 (Sec.)	7 ^{1/2}	A, cm. ² (Calc.)	$\frac{1}{c} \frac{\mathbf{r}^{1/2}}{c}$
0.0005	6-300	6.0	2.46	1.83	1.00
0.0008	6-300	19.0	4.48	2.08	1,12
0.0010	6-300	32.0	5.66	2.10	1.13
0.00 15	6-300	89.0	9.43	2.32	1.25

Average Electrode Area = 2.08 cm². Measured Electrode Area = 2.10 cm².

Chronopotentiograms obtained after the above described preliminary work were automatically recorded by the Brown Electronik recorder. Table III lists the values of i $T^{1/2}$ for 0.01 to 0.00005 M lead (II) in 0.1 M potassium chloride while Figure 9 shows these results graphically. The temperature of the cell was maintained at 25.00 ± 0.05° C.



FIGURE 7. CHRONOPOTENTIOGRAMS OF LEAD II IN O.IM POTASSIUM NITRATE.



	TABLE

TRANSITION TIMES FOR VARIOUS CONCENTRATIONS OF LEAD (II) IN 0.1 M POTASSIUM CHLORIDE

Pb(II) conc. (Mole/liter)	log conc.	Current Selector Position	Current (ua)	$\mathcal{I}^{(Sec.)}$	مر 1/2	1 م ¹ /ء	log 1 7 ^{1/2}
0.01	-2.00	9 -800	2670	6.L4	6.42	17,120	4. 23
10.0	-2.00	9-800	2670	42.5	6.51	17,380	4.40
0.005	-2.30	8-500	1125	54.4	7.37	8,300	3.92
0.005	-2.30	8-500	1125	56.7	7.52	8,460	3.93
100.0	-3.00	6-500	232	41.3	6.42	1,490	3.17
100.0	-3.00	6-500	232	41.3	6.42	1,490	3.17
0.0005	-3.30	5-500	ΊΙζ	62.6 ^a	7.90	908	2.96
0.0005	- 3.30	5-500	115	62.6 ^a	7.90	908	2.96
1000°0	-4.00	4–100	η.τή	62.6	7.90	327	2.51
1000.0	-4.00	h–100	4. T.4	62.6	7.90	327	2.51
1000°0	-14.00	3-800	34.7	74.4	8.62	299	2.48
1000°0	-4.00	3-800	34.7	76.7	8.75	303	2.48
0.00005	-4.30	2-800	17.4	12 0	0.11	192	2.28
0.00005	-4.30	2-800	17.4	130	η.ιι	198	2.30

^aSeparated into two waves with the total **height** taken as \mathcal{T} .


Use of a Mercury-Plated Platinum Electrode

The relatively low overvoltage (11) for hydrogen discharge at a platinum electrode limits the working range of this type electrode in chronopotentiometry, especially in acid solution. The working range, however, can be extended as much as 0.3-0.4 volts in the negative direction by employing a mercury-coated platinum electrode. This shift is brought about by the much higher overvoltage for hydrogen discharge on mercury than platinum. Although the shift with a mercury-coated electrode is not as pronounced as with pure mercury, it is sufficient to obtain good chronopotentiograms for many additional ions.

Many attempts in the past were made to prepare suitable and reproducible mercury surfaces on clean platinum. Reilley and Scribner (24) obtained a mercury-copper surface on a platinum foil electrode for use in chronopotentiometry by first plating a thin film of copper onto the platinum surface and then immersing in mercury. The method by which Marple and Rogers (20) electrolytically plated mercury onto a platinum micro-electrode for use in polarography (4) was employed in this work with considerable success. The method was rapid and gave reproducible mercury films on the platinum surface. Various plating times were tried with four minutes being the time chosen. The following procedure was used for preparing this mercury film on the platinum surface.

The electrode to be mercury-plated was first cleaned by immersing in hot concentrated nitric acid, rinsed with distilled water, allowed to soak at least two minutes in saturated potassium chloride and again rinsed with distilled water. It was then supported in approximately

twenty-five ml. of saturated mercuric nitrate at a distance of two cm. from a small coiled platinum wire which served as the anode. The current from two 1.5 volt dry cells, connected in series, was allowed to flow for four minutes. The electrode was then removed, rinsed with distilled water and stored in saturated potassium chloride until ready for use. It must not be allowed to stand in open air for more than a few minutes and any water clinging to it, when ready for use, must be shaken off.

Evidence for the importance of the mercury film is shown in Figure 10. Part B of Figure 10 shows that a mercury film deposited on the platinum electrode in four minutes is sufficient to shift the hydrogen discharge so that a well-defined chronopotentiogram for antimony (III) in 1 N nitric acid medium is obtained. Part A of Figure 10 shows that the four minute mercury deposit is not sufficient for zinc (II) in 0.1 N potassium chloride. An additional two minute plating time was necessary.

To check performance and working area of a new mercury coated platinum electrode, a series of runs was made using several current selector settings for 0.001 M lead (II) in 0.1 M potassium chloride. A mean deviation of $\pm 1.54\%$ for $\frac{i \tau^{1/2}}{c}$ was obtained. The mean calculated electrode area was 2.77 cm² as compared to the geometrical measurement of 2.69 cm². These results can be seen in Table IV.



ON THE OVERVOLTAGE OF HYDROGEN.

TABLE IV

EVALUATION OF $\frac{1}{c} \frac{\tau^{1/2}}{c}$ FOR 0.001 M LEAD (11) IN 0.1 M POTASSIUM CHLORIDE USING A MERCURY-COATED PLATINUM ELECTRODE

Current	ß		Ru	n L	-		Ru	n 2	
Selector Position	^E 1/4 (vs S.C.E.)	${\cal H}^{(Sec.)}$	۲ ^{1/2}	$\frac{1 r^{1/2}}{c}$	Area ^a (Calc.)	(Sec.)	T ^{1/2}	$\frac{i \tau^1/z}{c}$	Area ^a (Calc.)
0-1	48	23.4	4.83	1.48	2.74	22.0	l ı. 68	1 •Lili	2.67
6-700	- <u>1</u> ,18	31.9	5.65	1.48	2.74	31.9	5.65	1.48	2.74
6-400	48	50.1	7.07	1.52	2.81	50.1	7.07	1.52	2.81
0-2	48	23.1	4.80	1.47	2.72	23.6	4.84	1.49	2.75
002-9	48	34.2	5.84	1.53	2.83	33.1	5.75	1.51	2.79
6-400	48	51.3	7.16	1.54	2.85	48.0	6.92	1.49	2.75
aArea	$r, cm^2 = \frac{21}{c N}$	τ''/2 1000 F τ' ¹ /2 ^{D¹/}	210 ⁶						

Determination of a Proper Supporting Electrolyte for the Analysis of Antimony (III) and Bismuth (III)

Solutions of 0.001 M antimony (III) and 0.001 M bismuth (III) each, were prepared in acid solution for the prevention of hydrolysis. Table V shows the effect of varying the acid concentration for several acids.

TABLE V

			-			
Acid	HN	03	HO	21	Hz	S04
Normality	Bi(III)	Sb(III)	Bi(III)	Sb(III)	Bi(III)	Sb(III)
1.5	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
1.0	Soluble	Soluble	Soluble	Soluble	Hydrolyzes	s Soluble
0.5	Hydrolyze	s Soluble	Soluble	Soluble		Soluble
0.2		Slight Hydrolysis	Slight Hydrolysi	Slight is Hydroly	sis	Slight Hydrolysis

Effect of Acid Concentration on the Hydrolysis of Antimony (III) and Bismuth (III)

For comparison, solutions of antimony (III) and of bismuth (III) were made up in 1 N nitric acid, in 1 N hydrochloric acid, in 0.5 N hydrochloric acid and in 1.5 N sulfuric acid. Figure 11 shows the chronopotentiograms obtained with the various solutions and different current positions. With 1 N nitric acid the least shift and greatest spread in the $E_{1/4}$ values of antimony (III) and bismuth (III) are observed. For these reasons, 1 N nitric acid was chosen as the supporting electrolyte for subsequent work on antimony (III) and bismuth (III). A summary of these results appears in Table VI.



TABLE VI

$E_{1/}$	VALUES	FOR	BISMUTH	(III)) AND	ANTIMONY	(III)
-/4		IN	VARIOUS	ACID	MEDIA	L	

Ion Determined (0.001 M Conc.)	Curve ^a Number	Supporting Electrolyte	Current Selector Position	E _{1/4} (vs S.C.E.)	T (Sec.)
- Bi (III)	1	1 N HNO3	7-0	050	37.6
Bi (III)	2	1 N HNO3	7 - 500	050	13.6
Bi (III)	5	l N HCl	7 - 0	100	53.8
Bi (III)	6	I N HCl	7 - 500	125	16.7
Bi (III)	9	0.5 N HCl	7 - 0	050	51.4
Bi (III)	10	0.5 N HCl	7 - 500	085	14.8
Bi (III)	13	1.5 N H ₂ SO4	7 - 0	015	30.1
Bi (III)	14	1.5 N H ₂ SO ₄	7 - 500	045	15.6
Sb (III)	3	1 N HNO3	7 - 0	180	45.4
Sb (III)	4	1 N HNO3	7 - 500	170	13.0
Sb (III)	7	1 N HCl	7 - 0	160	32.8
Sb (III)	8	l N HCl	7 - 500	170	22.2
Sb (III)	11	0.5 N HCl	7 - 0	120	44.5
Sb (III)	12	0.5 N HC1	7 - 500	180	21.3
Sb (III)	15	1.5 N H ₂ SO ₄ .	7-0	140	29.5
Sb (III)	16	1.5 N H ₂ SO ₄	. 7 - 500	180	14.8

^aThe curve number refers to the numbered curves in Figure 11.

Table VII shows the effect of temperature on transition time for 6×10^{-4} molar bismuth (III) in 1 N nitric acid. This is also demonstrated graphically in Figure 12. By increasing the temperature from 20.0° to 40.0° C., the transition time varied by a factor of 2.2.

|--|

TEMPERATURE EFFECT ON TRANSITION TIME FOR 6×10^{-4} M BISMUTH (III)

Temp. C.	1 (Sec.)	T ^{1/2}	E _{1/4} (vs. S.C.E.)	$\frac{\mathbf{i} \mathbf{T}^{1/2}}{c}^{\mathbf{a}}$
20.0	21.5	4.64	04	1.79
20.0	21.5	4.64	04	1.79
22.0	25.4	5.04	 05	1.95
22.0	26.0	5.09	05	1.97
24.0	27.4	5.23	05	2.02
24.0	28.3	5.32	 05	2.06
25.0	27.2	5.20	 05	2.01
25.0	28.6	5.34	 05	2.07
26.0	27.2	5.20	05	2.01
26.0	30.7	5.53	 05	2.14
28.0	30.5	5.52	 05	2.13
28.0	32.8	5.72	 05	2.21
30.0	32.6	5.70	04	2.21
30.0	35.4	5.94	04	2.30
35.0	40.7	6.36	04	2.46
35.0	40.7	6.36	04	2.46
40.0	46.6	6.82	04	2.64
40.0	46.6	6.82	04	2.64

^aCurrent selector position was 6-500 for these results.



The Determination of Antimony (III) and Bismuth (III)

Individual solutions containing only one of the metallic ions ranging in concentration from 3×10^{-5} to 1×10^{-3} moles per liter of bismuth (III), and 6×10^{-4} to 2×10^{-3} moles per liter of antimony (III) in 1 N nitric acid were prepared from the analyzed stock solutions and chronopotentiograms recorded. A mercury-coated platinum electrode was employed, although it is not necessary for the determination of bismuth.

The following procedure was developed for best results from the preliminary work on lead. The cell is rinsed several times with portions of the sample solution and then both compartments are filled to approximately one cm. above the solution bridge. Constant temperature water at 25.00 \pm 0.05[°] C. is circulated through the cell jacket. Air is removed from the solution by bubbling with nitrogen for at least ten minutes. The platinum working electrode which had been soaking in saturated potassium chloride during this bubbling period is then quickly inserted and the volume above the solution purged for a few minutes with nitrogen. Great care must be taken not to touch the electrode when inserting it to prevent deactivation. The water bath is then turned off during the electrolysis and recording to reduce vibrations. The recorder and pH meter are connected and adjusted. These instruments should be allowed a fifteen minute warm-up period prior to electrolysis. The current supply switch is turned to the forward position and the chronopotentiogram recorded.

Calibration curves obtained for bismuth and antimony are listed in Tables VIII and IX and are shown graphically in Figures 13 and 14,

respectively. The deviation of the mean for the constant $\frac{i r^{1/2}}{c}$ obtained for bismuth (III) was $\pm 1.70\%$ over the range 3×10^{-5} to 1×10^{-3} moles per liter. However, from 1×10^{-4} to 9×10^{-4} moles per liter, this deviation was $\pm 1.17\%$ and from 3×10^{-5} to 9×10^{-5} moles per liter was $\pm 2.41\%$. The deviation of $\frac{i r^{1/2}}{c}$ for antimony could not be obtained because the constant decreased as the concentration decreased. Even though this calibration plot for antimony is not linear over the entire range studied, it can still be employed for the determination of antimony (III). This abnormal behavior has been encountered by others (8, 10) and is usually explained by assuming that some chemical reaction occurs before the actual electron transfer process. These kinetic effects which can be detected by chronopotentiometry do not necessarily appear in polarography.

DETERMINATION OF BISMUTH (IJI) IN 1 N NITRIC ACID

Conc. (Moles/Liter)	Current Selector Position	^E 1/4 (vs. S.C.E.)	T (Sec.)	T ^{1/2}	$\frac{\mathbf{i} \mathbf{T}^{1/2}}{c}$
0.001	7-0	07	44.8	6.68	2.03
0.001	7 - 0	07	53.2	7.28	2.23
0.001	6 - 500	07	87.4	9.34	2.17
0.001	6-500	07	94.5	9.70	2. 25
0.0009	7 -0	04	34.3	5.85	2.00
0.0009	7-0	04	36.6	6.04	2.06
0.0009	6-500	04	63.7	7.97	2.05
0.0009	6-500	04	64.3	8.02	2.07
0.0008	7-0	04	28.3	5.31	2.04
0.0008	7 - 0	04	28.3	5.31	2.04
0.0008	6 - 500	04	54.8	7.40	2.14
8000.0	6 - 500	04	49.6	7.04	2.04
0.0007	7 - 0	04	22.5	4.74	2.07
0.0007	7 - 0	04	23.0	4.78	2.09
0.0007	6 - 500	04	39.4	6.26	2.07
0.0007	6- 500	04	39.4	6.26	2.07
0.0006	7 - 0	04	15.3	3.90	1.99
0.0006	7 - 0	04	16.1	4.01	2.05
0.0006	6 - 500	04	27.2	5.22	2.02
0.0006	6 - 500	04	27.7	5.26	2.03
0.0005	7-0	04	11.2	3.34	2.05
0.0005	7 -0	04	11.3	3.36	2.06
0.0005	6 - 500	04	18.9	4.34	2.01
0.0005	6 - 500	04	19.8	4.44	2.06
0.0004	7-0	04	6.85	2.61	2.00
0.0004	7 - 0	04	6.49	2.54	1.95
0.0004	6-500	04	12.7	3.56	2.06

Continued

Conc. (Moles/Liter)	Current Selector Position	^E 1/4 (vs. S.C.E.)	1 (Sec.)	T ^{1/2}	$\frac{\mathrm{i} \mathbf{\tau}^{1/2}}{\mathrm{c}}$
0.0004	6-500	04	13.0	3.60	2.09
0.0002	6-0	04	7.32	2.70	2.08
0.0002	6 - 0	04	7.08	2.68	2.06
0.0002	6 - 500	04	2.60	1.61	1.87
0.0002	6 - 500	04	2.60	1.61	1.87
0.0001	4-0	03	27.8	5.28	1.96
0.0001	4-0	03	29.5	5.43	2.01
0.0001	3 - 500	01	49.8	7.05	2.03
0.0001	3 - 500	01	50.3	7.08	2.04
0.00009	4-0	0.0	26.0	5.10	2.09
0.00009	4-0	0.0	26.5	5.14	2.11
0.00009	3 - 500	0.0	40.2	6.34	2.03
0.00009	3 - 500	0.0	40.8	6.38	2.04
80000.0	4-0	0.0	18.9	4.34	2.01
0.00008	4-0	0.0	19.8	4.44	2.05
80000.0	3-500	0.0	34.2	5.84	2.10
80000.0	3 - 500	0.0	34.2	5.84	2.10
0.00006	4-0	0.0	10.6	3.25	2.01
0.00006	4-0	0.0	11.1	3.43	2.11
0.00006	3 - 500	0.0	17.7	4.20	2.01
0.00006	3-500	0.0	18.4	4.28	2.05
0.00005	4-0	0.0	8.03	2.83	2.09
0.00005	4-0	0.0	7.55	2.74	2.03
0.00005	3-500	0.0	14.1	3.75	2.16
0.00005	3 - 500	0.0	14.1	3.75	2.16
0.00004	4-0	0.0	4.72	2.17	2.01
0.00004	4-0	0.0	4.72	2.17	2.01
0,00004	3 - 500	0.0	8.50	2.91	2.10
0.00004	3 - 500	0.0	8.85	2.97	2.15

TABLE VIII - Continued

Continued

TABLE VIII - Continued

Conc. (Moles/Liter)	Current Selector Position	^E 1/4 (vs. S.C.E.)	T (Sec.)	T ^{1/2}	$\frac{\mathbf{i} \mathbf{r}^{1/2}}{c}$
0.00003	ц - 0	0.0	2.60	1.61	1.99
0.00003	4-0	0.0	2.60	1.61	1.99
0.00003	3-500	0.0	5.08	2.25	2.16
0.00003	3-500	0.0	5.43	2.33	2.24

Average =
$$2.06$$

For
$$\frac{i \mathbf{\tau}^{1/2}}{c}$$
;

Average deviation = 0.035

Percent deviation from average = \pm 1.70



TABLE IX

DETERMINATION OF ANTIMONY (III) IN 1 N NITRIC ACID

Conc. (Mole s/ Liter)	Current Selector Po s ition	^E 1/4 (vs. S.C.E.)	1 (Sec.)	1 ^{1/2}	$\frac{\mathrm{i} \mathbf{r}^{1/2}}{\mathrm{c}}$
0.00200	7 - 500	16	72.0	8.48	1.97
0.00200	7 - 500	16	75.5	8.68	2.02
0.00180	7-500	16	65.8	8.10	1.97
0.00180	7 - 500	16	64.0	8.00	2.06
0.00150	7-500	16	42.5	6. 52	2.01
0.00150	7 - 500	16	41.3	6.42	1.98
0.00120	7 - 500	16	29.8	5.45	2.11
0.00100	7 - 500	16	17.7	4.20	1 .9 5
0.00100	7-500	16	17.7	4.20	1.95
0.00100	7-100	18	31.9	5.64	1.91
0.00100	7-100	18	32.6	5.70	1.93
0.00100	6 900	18	47.2	6.86	2.02
0.00100	6 - 900	18	47.2	6.86	2.02
0.00090	7-100	17	19.5	4.42	1.66
0.00090	7-100	17	19.8	4.44	1.67
0.00090	6-900	17	30.7	5.54	1.81
0.00090	6-900	17	30.7	5.54	1.81
0.00085	7-100	17	13.0	3.60	1.43
0.00085	7-100	17	13.0	3.60	1.43
0.00085	6 .9 00	17	21.3	4.62	1.60
0.00085	6-900	17	21.5	4.63	1.60
0.00080	7-100	16	8.50	2.93	1.24
0.00080	7-100	16	8.85	2.97	1.26
0.00080	6-900	16	14.9	3.85	1.41
0.00080	6-900	16	14.9	3.85	1.41
0.00075	7-100	16	6.14	2.48	1.12
0.00075	7-100	16	6.14	2.48	1.12

Conc. (Moles/Liter)	Current Selector Position	^E 1/4 (vs. S.C.E.)	T (Sec.)	T ^{1/2}	$\frac{\mathrm{i} \mathbf{T}^{1/2}}{\mathrm{c}}$
0.00075	6-900	16	9.92	3.15	1.23
0.00075	6-900	16	10.4	3.22	1.26
0.00070	7-100	16	4.96	2.23	1.07
0.00070	7-100	16	4.96	2.23	1.07
0.00070	6-900	16	8.50	2.91	1.22
0.00070	6-900	16	8.50	2.91	1.22
0.00060	7-100	16	2.36	1.53	0.688
0.00060	7 - 100	16	2.36	1.53	0.688
0.00060	6 - 900	16	3.78	1.94	0.952
0.00060	6-900	16	3.78	1.94	0.952

-

TABLE IX - Continued



Analysis of Mixtures of Antimony (III) and Bismuth (III)

Various mixtures of bismuth (III) and arsenic (III), antimony (III) and arsenic (III), antimony (III) and bismuth (III), and one mixture containing all three ions in 1 N nitric acid were prepared from the stock solutions and chronopotentiograms recorded. Some typical chronopotentiograms are shown in Figure 16. The results are listed in Table X and calibration plots for bismuth (III) and antimony (III) present together in a mixture (solutions 4-8 in Table X) are shown in Figure 15.

loln.	Mixture	Current Selector Position	E _{1/4} (vs. S.C.E.)	\mathbf{r}_{1}	$\tau_{11}^{1/2}$ Bi(III) (r_{z}	τ ^{1/2} [(SbIII)	$(\mathcal{T}_{1}^{+}\mathcal{T}_{2}^{-})^{1/2}\mathcal{T}_{1}^{1/1}$	2] 1 T ^{1/2} : (for Bill!)	$ \underset{(\text{for SbIII})}{\text{ll}(\boldsymbol{\tau}_1 + \boldsymbol{\tau}_2)^{1/2} - \boldsymbol{\tau}_1^{1/2}} $
	0.001 M Bi(III) ^a	0-7	05	39.5	6.28		:	;	1928	;
Ч	0.001 M Bi(III) ^a	9-2	05	37.8	6.15	ł	ł	:	1890	;
2	0.001 M Bi(III) ^a	7-500	05	17.5	4.18	:	;	ł	1890	;
2	0.001 M Bi(III) ^a	7-500	- .05	17.5	4.18	1	;	ł	1890	1
ς	0.001 M Sb(III) ^a	7-100	15	31.9	5.64	ł	;	;	1910	;
Ś	0.001 M Sb(III) ^a	001-2	 15	31.9	5.64	:	;	!	1910	;
ţ	0.0002 M Bi(III) 0.0005 M SB(III)	6-500	04 12	11.8 	3.43 	34.2	5.85	 3.34	796 	
м	0.0008 M Bi(III) 0.0005 M Sb(III)	7-500	03 08	ין. ועד 	3.80 	21.3		2.18	1760 	
9	0.0005 M Bi(III) 0.0008 M Sb(III)	6-800	04 09	24.8 	4.98 	 12 1	 11.0	7.02	1388 	 1950
2	0.0008 M B4(III) 0.0008 M Sb(III)	7-500	02 09	15.4 	3.92	1.9.4	7.02	 4.13	1820 	 1930
ω	0.001 M Bi(III) ^a 0.001 M SB(III)	7-500	06 11	22.4	4.73		<u></u> 8.76	5.23	2180 	 2430

SOME MIXTURES OF ANTIMONY (III) AND BISMUTH (III) TABLE X

^a0.001 Moles per liter As(III) added. ^bi is in micro-amperes.





Other Chronopotentiograms

Some other chronopotentiograms were obtained for thallium (I), cadmium (II) and copper (II) in 0.001 N concentration using a bright platinum electrode. The supporting electrolyte employed was 0.1 M potassium chloride. These results are shown in Figures 17, 18 and 19.











IV. DISCUSSION AND CONCLUSIONS

The instrumentation necessary for a study of chronopotentiometry was assembled and gave satisfactory results.

The use of bright platinum as a working electrode in chronopotentiometry is convenient as it is easy to clean, chemically inert and the geometrically measured area checked very closely with that obtained by calculation. A linear relationship between i $\tau^{1/2}$ and concentration was obtained for a concentration range determined with one current density. A curve was obtained when log i $\tau^{1/2}$ was plotted against log of the lead (II) concentration for the whole concentration range studied, 0.00005 to 0.01 mole per liter of lead (II). Several current densities were necessary. High concentrations required higher current densities and lower concentrations required lower current densities.

The use of a platinum electrode on which a thin film of mercury has been plated combines the advantages of using a bright platinum electrode and a mercury pool electrode. The method of directly plating mercury onto the platinum surface for use in chronopotentiometry was not previously reported, although amalgams have been used (24). The working range of the mercury plated platinum electrode is extended 0.3 to 0.4 volts in the negative direction. This is still not as great a working range as would be obtained using a pure mercury pool. The renewal of the mercury surface was necessary when it began to darken after repeated use. The electrode darkens more readily when used in solutions of higher concentration. For the determination of antimony (III) and bismuth (III), separately or in mixtures, 1 N nitric acid as the supporting electrolyte prevented hydrolysis and gave favorable results. Hydrochloric and sulfuric acids in varying concentration of each, were tried for comparison but were not as satisfactory.

Temperature change greatly affected transition time. By increasing the temperature from 20.0 to 40.0° C., the transition time for 6 x 10^{-4} M bismuth (III) varied by a factor of 2.2.

Calibration plots for bismuth (III) were obtained over the concentration range of 3×10^{-5} to 1×10^{-3} moles per liter with a mean deviation for $\frac{1}{c} \frac{\tau^{1/2}}{c}$ of $\pm 1.70\%$. Over the range of 1×10^{-4} to 9×10^{-4} moles per liter, this deviation amounted to $\pm 1.17\%$ while from 3×10^{-5} to 9×10^{-5} moles per liter it amounted to $\pm 2.41\%$. This indicates that as the concentration of bismuth (III) decreases, precision decreases. Calibration plots for antimony (III) were obtained but were not linear over the entire range studied. The values obtained for $\frac{1}{c} \frac{\tau^{1/2}}{c}$ decreased as the concentration decreased from 2.06 at 2×10^{-3} moles per liter to 0.688 at 6×10^{-4} moles per liter. This anomaly has been observed by others (8, 10). It is presumably caused by reactions occurring on the surface of the electrode prior to actual reduction. The value of $\frac{1}{c} \frac{\tau^{1/2}}{c}$ is thus constant only when electrolysis is exclusively controlled by the diffusion of the depolarizer with no kinetic effects during the reduction process.

Separations of bismuth, antimony and arsenic must often be made since they are all in group two of the qualitative analysis scheme.

Determination of small amounts of these mixtures is often required in the analysis of ores, alloys and residues (27). Resolution and determination of small amounts of these elements can be made chronopotentiometrically in the presence of most of the common interferences providing their $E_{1/4}$ values differ by at least 0.10 to 0.15 volts from the $E_{1/4}$ values of the other substances presence. It was not possible in this investigation to obtain a break for the reduction of arsenic (III) over the range studied and with the supporting electrolytes tested. For that reason, there is no interference from arsenic in the determination of bismuth and antimony. The $E_{1/4}$ values of bismuth and antimony are far enough separated to effect their separation chronopotentiometrically. This has been demonstrated experimentally. Calibration plots were made for various mixtures of antimony (III) and bismuth (III). A straight line plot was obtained for bismuth (III) over the concentration range of 2×10^{-4} to 1×10^{-3} moles per liter with various concentrations of antimony present. The values of the constant $\frac{1}{c}$ obtained for bismuth (III) in the presence of antimony (III) are slightly higher than those obtained with no antimony present. A curved calibration plot was obtained for antimony (III) in the presence of bismuth (III). This curve differs from that obtained when only antimony (III) is present but the constant, which is $\frac{i[(\boldsymbol{T}_1 + \boldsymbol{T}_2)^{1/2} - \boldsymbol{T}_1^{1/2}]}{2}$ in this case, still decreases as concentration decreases. Therefore, to successfully analyze for mixtures of bismuth (III) and antimony (III), reference should be made to calibration plots for these mixtures (See Figure 15).

The study of chronopotentiometry is by no means limited to an inorganic study in aqueous medium but can be extended to organic analysis in aqueous or non-aqueous media. In a non-aqueous medium, interference from hydrogen discharge could be avoided.

LITERATURE CITED

- 1) Berzins, T. and Delahay, P., J. Am. Chem. Soc., <u>75</u>, 4205 (1953).
- 2) Butler, J. A. V. and Armstrong, G., Trans. Faraday Soc., <u>30</u>, 1173 (1934).
- 3) Clowes and Coleman, "Quantitative Chemical Analysis," J. and A. Churchhill Ltd., London (1944).
- 4) Cooke, W. D., Anal. Chem., <u>25</u>, 215 (1953).
- 5) Cottrell, F. G., Z. physik. Chem., <u>42</u>, 385 (1903).
- 6) Delahay, P., "New Instrumental Methods in Electrochemistry," Interscience, New York (1954).
- 7) Delahay, P. and Berzing, T., J. Am. Chem. Soc., <u>75</u>, 2486 (1953).
- 8) Delahay, P. and Mamantov, G., Anal. Chem., <u>27</u>, 478 (1955).
- 9) Delahay, P. and Mattax, C. C., J. Am. Chem. Soc., <u>76</u>, 874 (1954).
- 10) Gierst, L. and Juliard, A. L., J. Phys. Chem., <u>57</u>, 701 (1953).
- 11) Heyrovsky, J., Rec. trav. chim., 499 (1925).
- 12) Hickling, A., Trans. Faraday Soc., <u>41</u>, 333 (1945).
- 13) Hickling, A., <u>Ibid</u>., 42, 518 (1946).
- 14) Hickling, A. and Spice, J. E., <u>Ibid</u>., 43, 762 (1947).
- 15) Hickling, A. and Taylor, D., Faraday Soc. Discussion, <u>1</u>, 277 (1947).
- 16) Hickling, A. and Taylor, D., Trans. Faraday Soc., <u>44</u>, 262 (1948).
- 17) Karaoglanoff, Z., Z. Electrochem., <u>12</u>, 5 (1906).
- 18) Kolthoff, I. M. and Lingane, J. J., "Polarography," 2nd Ed., Interscience, New York (1952).
- 19) Laitinen, H. A. and Ferguson, W. S., Anal. Chem., <u>29</u>, 4 (1957).
- 20) Marple, T. L. and Rogers, L. B., <u>Ibid.</u>, 25, 1351 (1953).
- 21) Nicholson, M. M. and Karchmer, J. H., <u>Ibid</u>., 27, 1095 (1955).

- 22) Nikelly, J. G. and Cooke, W. D., <u>Ibid</u>., 29, 933 (1957).
- 23) Reilley, C. N., Everett, G. W. and Johns, R. H., <u>Ibid.</u>, <u>27</u>, 483 (1955).
- 24) Reilley, C. N. and Scribner, W. G., <u>Ibid.</u>, <u>27</u>, 1210 (1955).
- 25) Rosebrugh, T. R. and Miller, W. L., J. Phys. Chem., <u>14</u>, 816 (1910).
- 26) Sand, H. J. S., Phil Mag., <u>1</u>, 45 (1901).
- Scott, W. W., "Standard Methods of Chemical Analysis," Vol. I,
 D. Van Nostrand Company, New York (1927).
- 28) Shutt, W. J. and Walton, A., Trans. Faraday Soc., 28, 740 (1932).
- 29) Stackelberg, M. von, Pilgram, M. and Toome, V., Z. Electrochem., 57, 342 (1953).
- 30) Wakkad, S. E. S. El and Emara, S. H., J. Chem. Soc., 461 (1952).
- 31) Wakkad, S. E. S. El and Emara, S. H., Ibid., 3504 (1953).
- 32) Wakkad, S. E. S. El and Emara, S. H., Ibid., 3508 (1953).
- 33) Weber, H. F., Wied. Ann., 7, 536 (1879). (Via Reference 32).
- 34) Willard, H. H. and Diehl, H., "Advanced Quantitative Analysis," D. Van Nostrand Co., New York (1952).

CHEMISTRY LIBRARY Date Due			
PR 1 7 '81			
	·		
Damac 90.9			
Demeo-799			

MICHIGAN STATE UNIVERSITY OF AGRICULTURE AND APPLIED SCIENCE DEPARTMENT OF CHEMISTRY EAST LANSING, MICHIGAN

CHEMISTRY LIBRARY

Thesis c.2 Mong, Chronopotentiometric analysis of some dilute solutions in aqueous medium.


