CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0349510 8

ORNL 1557
Chemistry
4A

STUDIES ON THE ELECTROLYTIC SEPARATION AND DETERMINATION OF TIN, ANTIMONY, AND BISMUTH WITH CONTROLLED CATHODE POTENTIAL

S. A. Reynolds

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION
UCC
POST OFFICE BOX P
OAK RIDGE, TENNESSEE

ORNL 1557

This document consists of 58 pages.
Copy 4 of 271 copies. Series A.

Contract No. W-7405-eng-26

ANALYTICAL CHEMISTRY DIVISION

M. T. Kelley, Director

C. D. Susano, Associate Director

STUDIES ON THE ELECTROLYTIC SEPARATION AND DETERMINATION OF TIN, ANTIMONY, AND BISMUTH WITH CONTROLLED CATHODE POTENTIAL

S. A. Reynolds

DATE ISSUED

JUN 19 1959

OAK RIDGE NATIONAL LABORATORY
Operated by
CARBIDE AND CARBON CHEMICALS COMPANY
A Division of Union Carbide and Carbon Corporation
Post Office Box P
Oak Ridge, Tennessee

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0349510 8

ORNL 1557
Chemistry

INTERNAL DISTRIBUTION

1. C. E. Center
2. Biology Library
3. Health Physics Library
4-5. Central Research Library
6. Reactor Experimental Engineering Library
7-12. Central Files
13. C. E. Larson
14. W. B. Humes (K-25)
15. L. B. Emlet (Y-12)
16. A. M. Weinberg
17. E. H. Taylor
18. E. D. Shipley
19. F. C. VonderLage
20. M. T. Kelley
21. C. P. Keim
22. J. H. Frye, Jr.
23. R. C. Briant
24. J. A. Swartout
25. F. L. Culler
26. S. C. Lind
27. A. H. Snell
28. A. Hollaender
29. G. H. Clewett
30. K. Z. Morgan
31. J. S. Felton
32. A. S. Householder
33. R. S. Livingston
34. D. S. Billington
35. C. E. Winters
36. D. W. Cardwell
37. E. M. King
38. D. D. Cowen
39. S. A. Reynolds
40. M. J. Skinner

EXTERNAL DISTRIBUTION

41. D. B. Benedict, C&CCC, South Charleston
42. R. F. Bacher, California Institute of Technology
43-271. Given distribution as shown in TID-4500 under Chemistry category

DISTRIBUTION PAGE TO BE REMOVED IF REPORT IS GIVEN PUBLIC DISTRIBUTION

PREFACE

This report was prepared as a thesis in partial fulfillment of the requirements for the degree of Master of Science, sought from the University of Tennessee. It was believed by the author that some of the material contained herein might be of use to those engaged in Atomic Energy Commission work, hence its issuance as an Oak Ridge National Laboratory report. The work was not supported directly by the AEC. It was performed in the University of Tennessee laboratories at the Oak Ridge Institute of Nuclear Studies. Grateful acknowledgement is made of the suggestions and criticism of Professors John A. Dean, of the University of Tennessee, L. B. Rogers, of Massachusetts Institute of Technology, and H. H. Willard, of the University of Michigan. The cooperation of Dr. Ralph T. Overman and Mr. Ralph Firminhac of the Institute is appreciated.

S. A. Reynolds

S. A. Reynolds

TABLE OF CONTENTS

CHAPTER PAGE

I. HISTORICAL.....1

A. Controlled-Cathode Electrodeposition.....1

B. Electroanalyses for Bismuth, Antimony, and Tin.....2

C. Proposed Investigation.....6

II. APPARATUS AND REAGENTS.....8

A. Electrodeposition Equipment.....8

B. Auxiliary Apparatus.....10

C. Standards of Bismuth, Antimony, and Tin.....10

D. Radioactive Tracers for Antimony and Tin.....12

III. EXPERIMENTAL.....15

A. Polarographic Determination of Deposition Potentials.....15

B. The General Technique Employed.....17

C. Electrolyte Systems Investigated.....19

1. The Perchlorate System.....19

2. The Simple Sulfate-Chloride System.....22

3. The Nitrate System with Complexing Agents.....25

4. The Sulfate System with Complexing Agents.....26

a. Citrate.....26

b. Citrate-Versene.....34

c. Tartrate.....34

d. Fluoride.....41

IV. DISCUSSION.....42

V. SUMMARY 46

BIBLIOGRAPHY 48

APPENDIX 51

LIST OF TABLES

TABLE		PAGE
I.	Deposition of Copper and Bismuth from Perchloric Acid Solution	21
II.	Depositions from the Sulfuric-Hydrochloric Acid System	24
III.	Deposition from Nitrate Solution	27
IV.	Determinations of Bismuth in Sulfate-Citrate Solution	28
V.	Determinations of Antimony in Sulfate-Citrate Solution	29
VI.	Determination of Tin in Sulfate-Citrate Solution	30
VII.	Analysis of Mixtures of Bismuth and Antimony	35
VIII.	Anomalous Codeposition of Tin with Antimony	36
IX.	Analysis of Tin-Antimony Mixtures	37
X.	Analysis of Mixtures of Bismuth, Antimony, and Tin	38
XI.	Depositions from Citrate-Versene-Sulfate Solution	39
XII.	Depositions from Sulfate-Tartrate Solutions	40

LIST OF FIGURES

FIGURE PAGE

1. Simplified Circuit Diagram of Electrolysis Apparatus.....9

2. Schematic Diagram of Scintillation Counter.....11

3. Typical Deposition Curves for Bismuth.....31

4. Typical Deposition Curve for Antimony.....32

5. Typical Time-Current Curves for Tin.....33

6. Decay Scheme of Antimony-124.....51

7. Decay Scheme of Tin-113.....52

CHAPTER I

HISTORICAL

A. Controlled-Cathode Electrodeposition

The gravimetric determination of a number of metals by electrodeposition has been done for many years. Notable examples of electroanalytical determinations include those for copper, lead, and silver. The conventional "constant current" techniques have been discussed by a number of authors, notably Schleicher[1], and will not be considered in the present work.

Separations by the constant current method depend on the use of "potential buffers," e.g., evolution of hydrogen. If, however, the cathode potential is maintained at a value sufficiently high to deposit quantitatively one metal while remaining too low to deposit a second, separations can be achieved. This technique, known as electroanalysis with "controlled," "graded," or "limited" cathode potential was devised by Sand[2].

The apparatus used may be, in the simplest case, merely the conventional electroanalysis apparatus with the addition of a device, such as a potentiometer or electronic voltmeter, for measuring cathode potential

---

(1) Schleicher, A., "Elektroanalytische Schnellmethoden, Die Chemische Analyse, IV./V. Band" (Boettger, W., ed.), F. Enke, Stuttgart, 1947.

(2) Sand, H.J.S., J. Chem. Soc., 91, 373 (1907), also "Electrochemistry and Electrochemical Analysis," Blackie and Son, Glasgow, 1945, Vol. II.

with respect to a reference electrode. Apparatus, such as that of Diehl[3] and the new Fisher device, for automatically maintaining constant cathode-reference electrode potential have been used successfully.

B. Electroanalysis for Bismuth, Antimony, and Tin

Bismuth has been electrodeposited from perchloric acid[4] and nitrate-fluoride-tartrate[5] systems. With controlled cathode potential techniques, bismuth has been plated from various solution systems: sulfate and nitrate[6], tartrate[7], alkaline cyanide-tartrate[8], and chloride-oxalate[9].

Antimony has been determined by electrodeposition as metal from sulfuric-hydrochloric acid mixture[10], thioantimonite solution (with high results)[11], and by evolution of stibine[12]. It has been determined by

---

(3) Diehl, H., "Electrochemical Analysis with Graded Cathode Potential Control," G. F. Smith Chemical Co., Columbus, O., 1948, pp. 8-20.

(4) Norwitz, G., Analyst, 76, 423 (1950).

(5) Goldberg, C., Metallurgia, 42, 108 (1950).

(6) Kny-Jones, F. G., Analyst, 64, 575 (1939).

(7) Lingane, J. J., and Jones, S. L., Anal. Chem., 23, 1788 (1951).

(8) Kny-Jones, F. G., ibid., 66, 101 (1941).

(9) Kny-Jones, F. G., ibid., 64, 172 (1939).

(10) Norwitz, G., Anal. Chem., 23, 386 (1951).

(11) Willard, H. H., and Diehl, H., "Advanced Quantitative Analysis," D. Van Nostrand Co., New York, N. Y., 1943, p. 348.

(12) Grant, J., Analyst, 53, 626 (1928).

controlled-cathode methods by deposition from hydrochloric acid[13], sulfuric acid[14], and tartrate-sulfate solution[15].

Tin has been determined by the "constant current" method by deposition from hydrochloric acid solution, and oxalic acid-ammonium oxalate mixture[16]. Using the controlled-cathode method, tin has been deposited from hydrochloric acid[17], and hydrochloric acid-tartrate solutions[18].

Separations of bismuth, antimony, and tin should be possible in a simple system, since the standard oxidation potentials are[19]:

$$H_2O + Bi = BiO^+ + 2H^+ + 3e \qquad E^o = -0.32$$

$$H_2O + Sb = SbO^+ + 2H^+ + 3e \qquad E^o = -0.212$$

$$Sn = Sn^{++} + 2e \qquad E^o = 0.136$$

However the bismuth and antimony potentials in 5 molar hydrochloric acid and in hydrochloric-sulfuric acid solution are within 0.02 of each other[20].

---

(13) Schoch, E. P., and Brown, D. J., J. Am. Chem. Soc. 38, 1673 (1916).

(14) Sand, H.J.S., J. Chem. Soc., 93, 1572 (1909).

(15) Lee, D., and Cook, G. B., British Atomic Energy Report AERE-C/R-430 (1950).

(16) Willard, H. H., and Diehl, H., "Advanced Quantitative Analysis," D. Van Nostrand Co., New York, N. Y., 1943, p. 326.

(17) Diehl, H., "Electrochemical Analysis with Graded Cathode Potential Control," G. F. Smith Chemical Co., Columbus, O., 1948, pp. 47-49.

(18) Lingane, J. J., and Jones, S. L., Anal. Chem., 23, 1798 (1951).

(19) Latimer, W. M., "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1952, pp. 118, 122, 149.

(20) Lingane, J. J., and Auerbach, C., Anal. Chem., 23, 986 (1951).

Bismuth has been determined in the presence of antimony in tartrate solution at appropriate pH values[21,22]. Determination of bismuth and antimony in mixtures has been done by plating both together, then dissolving the plate, oxidizing the antimony, and replating the bismuth[22]. Separations of tin from either antimony or bismuth have been made[23,24].

Since antimony and tin each have two well-defined oxidation states in aqueous solution, the ease of reduction of the upper state to the lower, or to metal, must be considered. A general oxidation-reduction equation may be written

$$\text{Red} \longrightarrow \text{Ox} + ne,$$

where Red refers to the reduced form of the material; Ox refers to the oxidized form, and n is the number of electrons transferred in the reaction. The oxidation potential of a mixture of the two oxidation states is given by the equation[25]

$$E = E^{o} - \frac{0.0591}{n} \log \frac{(\text{Ox})}{(\text{Red})}, \text{ (at } 25^{o})$$

where (Ox) and (Red) refer to concentrations, E is the potential of the system, and E^{o} is its standard potential, i.e., when (Ox) is equal to (Red) and both are in standard states.

---

(21) Lingane, J. J., and Jones, S. L., Anal. Chem., 23, 1798 (1951).

(22) Schoch, E. P., and Brown, D. J., J. Am. Chem. Soc., 38, 1660 (1916).

(23) Willard, H. H., and Diehl, H., "Advanced Quantitative Analysis," D. Van Nostrand Co., New York, N. Y., 1943, p. 57.

(24) Schoch, E. P., and Brown, D. J., J. Am. Chem. Soc., 38, 1673(1916).

(25) Willard, H. H., Merritt, L. L., and Dean, J. A., "Instrumental Methods of Analysis," Van Nostrand Co., New York, N. Y., 1951, p. 207.

For quantitative reduction, it may be assumed that (Ox) must be made 0.1 mg. per 100 ml., i.e., 10^{-5} M., if the molecular weight is taken as 100. If the initial concentration of oxidized substance was 0.1 M., the final ratio, (Ox)/(Red) is 10^{-4}. The previous equation becomes (approximately)

$$E = E^{o} - \frac{0.06}{n} \log 10^{-4},$$

and, since n is two for both antimony and tin, the equation further reduces to

$$E = E^{o} + 0.12.$$

It is necessary, therefore, to attain or exceed this value of E to reduce tin or antimony at the cathode or by reducing agents. The oxidation potential of the antimonous-antimonic system is approximately -0.6 volt, and that of the stannous-stannic system is -0.15 volt[26]. Hydroxylamine and hydrazine are satisfactory, therefore, to reduce tin and antimony, since their potentials are higher than the above values by more than 0.12 volt[27,28].

Anodic oxidation of antimony and tin may be prevented by the use of suitable depolarizers, i.e., substances which will be oxidized in preference to antimonous or stannous ions. Hydrazine or hydroxylamine are

---

(26) Latimer, W. M., "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1952, pp. 119, 148.

(27) Latimer, op. cit., p. 99

(28) Willard, H. H., Merritt, L. L., and Dean, J. A., "Instrumental Methods of Analysis," Van Nostrand Co., New York, N. Y., 1951, p. 328.

known to be suitable for this purpose[29,30].

Antimonic ion forms very stable complexes with such anions as fluoride and tartrate[31]. The potential required to reduce the antimonic complex may be very high. It appears that a reduction of antimony before deposition is desirable, if it is thought that any antimonic ion is present. This may be done by heating with hydrazine in concentrated sulfuric acid[32].

C. Proposed Investigation

It was proposed to investigate the separation and determination of bismuth, antimony, and tin by electrodeposition with controlled cathode potential. Quantitative recovery of the pure metals was to be studied, and separations tested by preparation and analysis of known mixtures. A further test of separations would be furnished by use of radioactive tracers for antimony and bismuth.

---

(29) Norwitz, G., Anal. Chem., 23, 386 (1951).

(30) Lingane, J. J., and Jones, S. L., Anal. Chem., 23, 1788 (1951).

(31) Diehl, H., "Electrochemical Analysis with Graded Cathode Potential Control," G. F. Smith Chemical Co., Columbus, O., 1948, p. 40.

(32) Hillebrand, W. F., Lundell, G.E.F., Bright, H. A., and Hoffman, J. I., "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 70.

Investigation was to include methods of dissolution of pure metals, mixtures, and alloys, effects on electrodeposition caused by anions such as chloride, sulfate, and nitrate, complexing agents, pH, temperature, and deposition potentials. The ultimate aim of the research was establishment of a satisfactory electroanalytical procedure for determination of bismuth, antimony and tin.

CHAPTER II

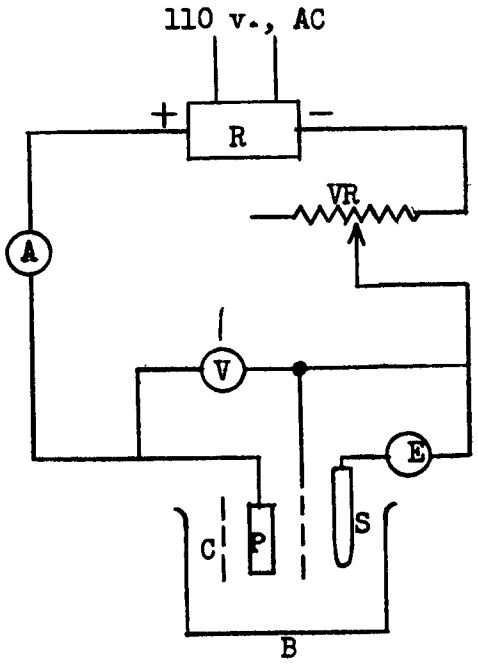
APPARATUS AND REAGENTS

A. Electrodeposition Equipment

Two electroplating devices were used. The first, which was used until the second became available, was the Controlled Cathode Apparatus, Model SP-10538, manufactured by Special Instruments Laboratory, Knoxville, Tennessee. This device consists essentially of a rectifier, a heliopot for control of the applied voltage, a voltmeter, and an ammeter with shunts enabling the reading of full-scale currents of 10, 1, and 0.1 ampere. Magnetic stirring was used.

The second device employed was the Sargent-Slomin Electrolytic Analyzer, manufactured by E. H. Sargent Company. This instrument has the same features as the first one, expect that it has a rheostat-controlled heating surface for the electrolysis beaker, and employs a rotor with a clamp for the anode, and has a clamp also for the cathode. It is considerably easier to use than the first device. 150-milliliter beakers were used in almost all determinations. The electrodes were of conventional gauze type.

For measuring the cathode potentials a Beckman pH meter, Model H2, was employed, with a small calomel electrode (S.C.E.).



LEGEND

R - rectifier
A - ammeter
VR - variable resistance
V - voltmeter
S - reference electrode
E - electronic voltmeter (Beckman pH meter)
P - anode
C - cathode
B - beaker containing electrolyte

Figure 1. - Simplified Circuit Diagram of Electrolysis Apparatus

B. Auxiliary Apparatus

A second Beckman pH meter, with standard glass and calomel electrodes, was used for all pH measurements. A Sargent Polarograph, Model XXI, was employed, with platinum micro wire and disc electrodes.

For tracer studies a scintillation gamma counter (Figure 2) was employed. Samples were placed in cup-type planchets supported over the crystal by means of a slide with a well into which the planchets were fitted.

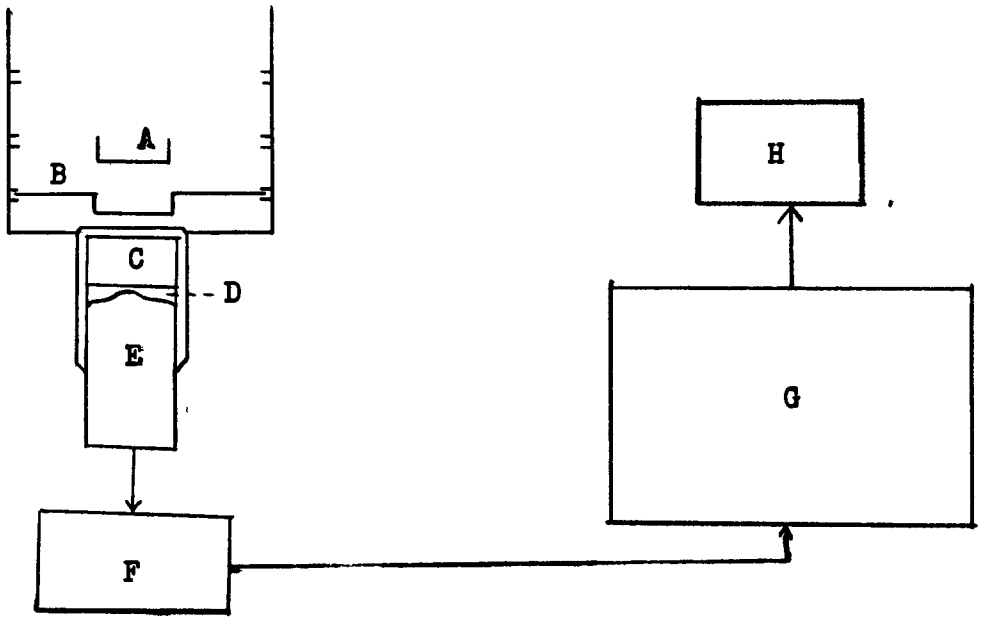
C. Standards of Bismuth, Antimony and Tin

1. Bismuth. Bismuth metal, labeled 99.8 per cent, was weighed in preparing samples for experiments. The assay of the manufacturer, General Chemical Company, was accepted. The concentration of antimony was said to be less than 0.01 per cent.

2. Antimony. The antimony standard was antimony metal, C. P., produced by Fisher Chemical Company. It was assayed by dissolution in sulfuric acid and titration with standard potassium permanganate[33]. Triplicate assay results yielded an average of 99.64 per cent, with a mean deviation of 0.08 per cent. The metal was taken to be 99.6 per cent antimony for experimental purposes. Lead appeared a reasonable impurity, hence it was

---

(33) Willard, H. H., and Diehl, H., "Advanced Quantitative Analysis," D. Van Nostrand Co., New York, N. Y., 1943, p. 96.



A - Sample Planchet
B - Slide
C - Anthracene Crystal
D - "Light-pipe"
E - Photomultiplier Tube
F - Pre-amplifier
G - Amplifier-Scaler Unit
H - Recorder

Figure 2. - Schematic Diagram of Scintillation Counter

determined approximately. Results by electrodeposition[34] and polarography[35] yielded a value of 0.3 per cent.

3. Tin. The C. P. tin metal was assayed by the method reported by Diehl[36]. Results were 99.24 (mechanical loss noted), 100.3, and 100.1 per cent. The latter two were within experimental error of 100 per cent, hence it was concluded that the tin was pure.

D. Radioactive Tracers for Antimony and Tin

The antimony radioisotope employed in tracer studies was antimony-124, of which the decay scheme[37] is given in the Appendix (Figure 6). The tin radioisotope used was tin-113, with its indium-113 daughter. The decay scheme[38] appears in the Appendix (Figure 7). Slight contamination of tin tracer with radioantimony, and of antimony tracer with radiotin, has been noted[39]. For this reason it was necessary to purify the tracers before use.

---

(34) Lingane, J. J., and Jones, S. L., Anal. Chem., 23, 1798 (1951).

(35) Kolthoff, I. M., and Lingane, J. J., "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, p. 268.

(36) Diehl, H., "Electrochemical Analysis with Graded Cathode Potential Control," G. F. Smith Chemical Co., Columbus, O., 1948, p. 55.

(37) Way, K., Fano, L., Scott, M. R., Thew, K., "Nuclear Data," Circular of the National Bureau of Standards 499, U. S. Government Printing Office, 1950, p. 139.

(38) Way, K., et al., op. cit., p. 133.

(39) Reynolds, S. A., Unpublished radioanalytical results obtained at Oak Ridge National Laboratory.

About 0.1 millicurie of each tracer was available. (One millicurie is equivalent to 2.22×10^9 disintegrations per minute.) For each experiment, about 2×10^7 disintegrations per minute of tracer was employed. This corresponded to approximately 5×10^5 counts per minute, since the efficiency of the counter was about 2.5 per cent.

Antimony-124 tracer was purified by mixing it (small volume of hydrochloric acid solution) with 10 ml. of concentrated sulfuric acid, adding C. P. antimony metal (as "carrier"), bismuth and tin, heating to dissolve, and plating bismuth, then antimony by a technique given in Chapter III, Section C.4.a. The prior plating of bismuth served to remove any possible noble-metal contaminant from the solution, and the limited cathode potential prevented the plating of tin, cadmium, or other impurity less noble than antimony. After drying and weighing, the antimony was dissolved from the electrode in the system to be used for tracer study, e.g., hot concentrated sulfuric acid or nitric acid-citrate mixture. The weight of inactive antimony included in the tracer was added to the weights dissolved in the experiments employing tracer.

Tin tracer was purified in a similar way. The small volume of concentrated tin-113 tracer in hydrochloric acid was mixed with concentrated sulfuric acid, antimony and tin metal were added and dissolved by heating. Antimony was deposited, then, on a fresh electrode, tin was deposited. The technique is described in Chapter III, Section C.4.a.

It was necessary to wait sixteen or more hours after separation of tin for the indium daughter activity to re-establish equilibrium[40]. In neither case was quantitative recovery of tracer attempted, but yields were reasonable (90-98%).

---

(40) Friedlander, G., and Kennedy, J. W., "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 109-114.

CHAPTER III

EXPERIMENTAL

A. Polarographic Determination of Deposition Potentials

Lingane and Jones[41] determined deposition potentials of copper and bismuch in tartrate-nitrate solution at various pH values polarographically. The partial polarogram of a solution of the desired composition was taken, and the essentially straight, steeply rising line representing deposition of the metal present was extrapolated to its intersection with the residual-current line. The intersection was taken as the deposition potential under the conditions of the experiment.

The above technique was tried for evaluation of deposition potentials of copper, bismuth, antimony, and tin in the present research. It proved to be rather unreliable for bismuth and antimony, because of the irreversible nature of the plating, which lead to the formation of thin layers of these metals on the platinum microelectrodes. These films were removed only by drastic treatment with nitric-hydrochloric acid mixture or hot sulfuric acid. Copper showed reversible deposition, giving rise to a dissolution current when the potential of the cathode was reduced below the level at which it deposited. Bismuth and antimony showed no such effect.

---

(41) Lingane, J. J., and Jones, S. L., Anal. Chem., 23, 1798 (1951).

A limited amount of experimental work was done by the method described above. All polarograms were recorded on a Sargent Model XXI Polarograph. Reference electrodes were of two types: (1) mercurous sulfate-saturated potassium sulfate (abbreviated hereafter S.K.S.), and (2) saturated calomel (S.C.E.). The platinum microelectrodes were either in the form of a disc about one mm. in diameter, or a wire. The potential of the microelectrode was varied automatically by the instrument, and the current was recorded.

In the course of the present work the potential of the S.K.S. was determined to be 0.41 ± 0.02 volt with respect to the S.C.E. Since the oxidation potential of the S.C.E. at 25° is -0.246[42] with respect to the normal hydrogen electrode (N.H.E.), the oxidation potential of the S.K.S. is -0.656 ± 0.02, in agreement with the value given by Kolthoff and Lingane, -0.65[43].

The deposition potential of copper at a concentration of 0.5 mg. per ml. in dilute perchloric acid was found to be -0.56 volt with respect to the S.K.S. This corresponds to -0.10 volt versus the N.H.E. Since the oxidation potential of copper is -0.337[44], considerable overvoltage[45]

---

(42) Willard, H. H., Merritt, L. L., and Dean, J. A., "Instrumental Methods of Analysis," D. Van Nostrand Co., 1951, p. 193.

(43) Kolthoff, I. M., and Lingane, J. J., "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, p. 480.

(44) Latimer, W. M., "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1952, p. 185.

(45) Walton, H. F., "Principles and Methods of Chemical Analysis," Prentice-Hall, New York, N. Y., 1952, pp. 65-71.

must be involved. The deposition potential of bismuth under similar conditions was -0.58 volt with respect to the S.K.S., or -0.08 versus the N.H.E. The oxidation potential of bismuth is -0.32 (Chapter I, Section B). It is apparent that copper and bismuth could not be separated by deposition from simple acid solution.

Potentials of antimony by the polarographic method were erratic, preventing any significant values from being obtained. In one N. perchloric acid tin did not deposit before the evolution of hydrogen, as expected from its oxidation potential, 0.136. In one N. sodium perchlorate at pH 11, deposition appeared to begin at -1.5 volts versus the S.K.S.

B. The General Technique Employed

Weighed samples of metals under study were dissolved in the appropriate acid, using the same beaker which was to serve for electrolysis. The acid was diluted somewhat, then the other materials such as complexing agents and depolarizers[46] were added, and final dilution to the desired volume was made. This volume was usually 120-140 ml. The solution was heated by means of a resistance tape while the "Spinlab" apparatus was in use, and later by means of the heating unit of the Sargent apparatus.

---

(46) Walton, H. F., "Principles and Methods of Chemical Analysis," Prentice-Hall, New York, N. Y., 1952, pp. 63-65.

If the proper cathode potential was not known beforehand for a given system, an approximate value was determined by decreasing the cathode potential until the ammeter showed a small current flowing and plating was noticeable on the cathode. (Unless otherwise specified, cathode-reference cell potentials are given herein with their actual signs, i.e., in a reduction sense.) The potential of the metal-coated cathode was then determined by opening the plating circuit and noting the cathode-reference cell potential. During deposition, the cathode potential was maintained 0.1-0.2 volt more negative than the initial value of the potential of the metal-coated cathode.

After completion of the plating, the cathode was removed from the solution, washed with distilled water as it was withdrawn. It was then washed twice in separate beakers of water (since the solutions were usually high in salt concentration), and finally in acetone. The cathode was dried either by suspending it over a hot plate, or in a gentle stream of filtered air at room temperature. The latter procedure avoided any danger from air oxidation[47] at elevated temperature.

When a tracer was used, it was added at the beginning of the dissolution process to make sure that interchange (intimate mixing of radioactive and inactive species) took place. Although the radioelement

---

(47) Walton, H. F., "Principles and Methods of Chemical Analysis," Prentice-Hall, New York, N. Y., 1952, p. 74.

had already been incorporated into some of the inactive species in purification of the tracer, nevertheless the precautionary step above was necessary. Some operation in dissolution or filution could result in a chemical state of the bulk element which might not be characteristic of the tracer unless it was present at the time.

In making radioactivity measurements, 2-ml. samples were placed in cup-type steel planchets, which were supported in the well of the slide over the crystal of the scintillation counter (Figure 2). Metallic deposits were dissolved, diluted to known volume, and aliquots taken for measurement. Gamma photons were counted, thus avoiding self-absorption difficulties characteristic of measurement of beta radiation[48] and enabling sensitive measurement in solution form.

C. Electrolyte Systems Investigated

1. The Perchlorate System

The perchlorate system was investigated briefly because metals in perchloric acid solutions exist essentially as simple aquo ions[49], and because bismuth (and presumably antimony) perchlorate should hydrolize less readily than other salts[50]. Norwitz had plated

---

(48) Schweitzer, G. K., and Whitney, I. B., "Radioactive Tracer Techniques," D. Van Nostrand Co., New York, N. Y., 1949, pp. 112-113.

(49) Meyer, R. J., "Gmelins Handbuch der Anorganischen Chemie," S-N 5, Verlag Chemie G.M.B.H., Leipzig-Berlin, 1926, p. 401.

(50) Willard, H. H., personal communication, October, 1951.

bismuth from perchloric acid[51].

Some polarographic determinations of deposition potentials were attempted, but no plating of antimony or tin was done in the perchlorate system. Although nitric-hydrochloric acid mixture could be used to dissolve these metals, precipitation occurred on evaporation with perchloric acid to drive off the other, volatile acids. The compounds precipitated were presumably antimony tetroxide, Sb_2O_4, and metastannic acid, H_2SnO_3[52]. It was not desirable to heat the metals in concentrated perchloric acid because of potential explosion hazard[53].

Bismuth metal dissolved readily in perchloric acid, with the addition of a small amount of nitric acid. Results on plating copper and bismuth are given in Table I. Polarographic determination of unplated bismuth, using a tartrate supporting electrolyte[54], showed less than one mg. remaining in solution.

It is noted in Table I that the observed potential for the copper-coated electrode was -0.38 volt at a copper concentration of 1.7 mg. per ml. (~0.03 M.) and -0.43 volt at 0.7 mg. per ml. (~0.01 M.). The corresponding oxidation potentials with respect to the N.H.E. are -0.27 and

---

(51) Norwitz, G., Analyst, 75, 473 (1950).

(52) Treadwell, F. P., and Hall, W. T., "Analytical Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1937, pp. 161, 167.

(53) Hillebrand, W. F., Lundell, G.E.F., Bright, H. A., and Hoffman, J. I., "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 40.

(54) Kolthoff, I. M., and Lingane, J. J., "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, p. 263.

TABLE I

DEPOSITION OF COPPER AND BISMUTH FROM PERCHLORIC ACID SOLUTION

Acid Normality	Metal Potential[a]	Cathode Potential[b]	Metal	Amounts, mg. Taken	Found	Difference
0.19	-0.38	-0.55	Cu	243.4	243.1	-0.3
0.5	-0.43	-0.55	Cu	97.4	97.5	+0.1
0.5	-0.42	-0.60	Bi	100.0	100.9	+0.9
0.5	-----	-0.50	Cu	97.5	191.8	+94.3[c]
	-----	-0.65	Bi	100.0	198.3	+0.8[d]

[a]With respect to S.K.S.
[b]Used during deposition.
[c]In excess of weight of Cu.
[d]In excess of weight of Cu + Bi.

-0.22. Applying the Nernst equation,

$$E = E^{o} - \frac{0.0591}{n} \log C,$$

with concentration instead of activity, one obtains the values for the formal potential[55] -0.32 (0.2 N. $HClO_4$) and -0.28 (0.5 N. $HClO_4$). The first is in approximate agreement with the standard oxidation potential of copper, -0.337 volt. Similarly, the bismuth potential, -0.42 (S.K.S.) at 0.7 mg. per ml. (~0.003 M.) corresponds to a formal potential of -0.28, somewhat higher than the standard value, -0.32.

It is obvious that copper and bismuth cannot be separated electrolytically in the simple perchloric acid system.

2. The Simple Sulfate-Chloride System

Norwitz[56] plated antimony from sulfuric-hydrochloric acid mixture which was approximately 3 N. in sulfuric and 0.5 N. in hydrochloric acid. Because of his success with this system it was tried in the present work. The saturated calomel reference electrode was used in this and all subsequent investigations. The advantage of this system is that antimony is not precipitated from chloride solution at a pH at which it would be precipitated from perchloric acid, because of the formation of a chloride complex, presumably $SbCl_4^-$. Bismuth also forms a chloride complex, $BiCl_4^-$[57].

Solutions were prepared by dissolving the metals in concentrated

---

(55) Walton, H. F., "Principles and Methods of Chemical Analysis," Prentice-Hall, New York, N. Y., 1952, pp. 60, 196-197.

(56) Norwitz, G., Anal. Chem., 23, 386 (1951).

(57) Diehl, H., "Electrochemical Analysis with Graded Cathode Potential Control," G. F. Smith Chemical Co., Columbus, O., 1948, p. 42.

sulfuric acid, diluting, adding the required amount of hydrochloric acid and one gram of hydroxylamine hydrochloride as anodic depolarizer. Electrolysis was done at room temperature, and was continued until the current had fallen to a small, constant value, almost always less than 10 mamp. for bismuth and antimony. Bismuth, antimony, and tin reacted readily in hot concentrated sulfuric acid, however the sulfates (or perhaps the pyrosulfates) of bismuth and antimony precipitated if the amounts of bismuth or antimony exceeded 60 mg. or 200 mg. respectively, When bismuth and antimony were both present the precipitation was more noticeable, and inhibited the dissolution of antimony. Long heating periods were necessary, and in some experiments the antimony never dissolved completely. Tin dissolved very readily, forming sulfur dioxide and some free sulfur.

The observed electrode potential for bismuth at 0.7 mg. per ml. in the sulfuric-hydrochloric acid system was -0.11 with respect to the S.C.E., or -0.14 versus the N.H.E. The formal potential was then -0.19. Diehl reported -0.16 for a chloride solution[58]. The potential of an antimony-coated electrode in an antimony solution containing 0.3 mg. per ml. was -0.09 (S.C.E.). This corresponds to -0.16 (N.H.E.) The formal potential was therefore -0.21, in agreement with the standard oxidation potential, -0.212. The observed deposition potentials were approximately -0.13 for bismuth and -0.2 for antimony (S.C.E.).

From Table II it may be concluded that deposition of bismuth from sulfuric-hydrochloric acid mixture might be made satisfactory, but bismuth-

---

(58) Diehl, H., "Electrochemical Analysis with Graded Cathode Potential Control," G. F. Smith Chemical Co., Columbus, O., 1948, p. 42.

TABLE II

DEPOSITIONS FROM THE SULFURIC-HYDROCHLORIC ACID SYSTEM

Cathode Potential (S.C.E.)	Amounts of Metals, mg. Bismuth			Antimony		
	Taken	Found	Diff.	Taken	Found	Diff.
-0.2	130.9	131.1	+0.2	0	---	---
-0.25	105.4	104.6	-0.8	0	---	---
-0.25	130.5	125.0	-5.5[a]	0	---	---
-0.22	100.1	99.4	-0.7	0	---	---
-0.25	120.4	147.4[b]	+27.4	104.8	---	---
-0.22	124.9	216.7[b]	+91.8	106.2	228.4[c]	-2.7[d]

[a]Poor adherence.
[b]Sb codeposited.
[c]Further plating at -0.4 volt.
[d]Compared to sum of Sb + Bi weights.

antimony separation was not feasible. The method was therefore abandoned.

3. The Nitrate System with Complexing Agents

Lingane and Jones deposited copper, bismuth, lead, and tin from nitrate-tartrate solution[59]. They showed that antimony did not deposit under their conditions of tartrate concentration, pH, and potential employed for bismuth and copper. Its behavior under the conditions of lower pH and higher potential used for tin was not discussed. It therefore appeared worthwhile to investigate the similar nitrate-citrate system.

The general technique employed involved dissolution in a mixture of one part of nitric acid with two parts of 1 M. sodium citrate. One ml. of hydrochloric acid was added to dissolve tin. Nitrous acid and oxides of nitrogen were destroyed by addition of a gram of urea[60]. The desired amounts of complexing agent and depolarizer were then added, the pH and volume were adjusted, and plating of bismuth carried out. The depolarizers employed were hydroxylamine hydrochloride (HAH) and hydrazine hydrochloride (HYH). In most experiments, before plating antimony or tin, concentrated hydrochloric acid was added to bring the pH well below one. This released much of the elements from their complexes[61], allowing deposition to proceed at reasonable potentials.

---

(59) Lingane, J. J., and Jones, S. L., Anal. Chem., 23, 1798 (1951)

(60) Willard, H. H., and Furman, N. H., "Elementary Quantitative Analysis," D. Van Nostrand Co., New York, N. Y., 1940, p. 431.

(61) Lingane, J. J., and Jones, S. L., ibid., p. 1803.

Table III summarizes the results. It may be concluded that nitric acid-citrate mixture oxidizes antimony to the pentavalent state, to a slight extent. This presumably forms a stable complex with citrate. The addition of hydrochloric acid in dissolution oxidizes much more of the antimony. Bismuth and tin give fair results in this system.

4. The Sulfate System with Complexing Agents

Most of the investigation was concerned with this system. The advantages of sulfuric acid attack include the ease of dissolution of small amounts of bismuth, antimony, and tin, plus the fact of slight oxidation of antimony. The investigation was concerned with the effects of amounts of metals, nature and concentration of complexing agents, temperature of deposition, and cathode potential. These were examined with respect to completeness of separations and quantitative recovery.

a. Citrate. The technique employed has been described in earlier sections of this chapter.

During deposition of antimony it was found desirable to limit the current to one-half ampere because larger currents tended to give poorly-adherent deposits. The potential for deposition of bismuth was maintained initially at a value little above its deposition potential, then allowed to rise to the value necessary for complete deposition.

Results obtained in determinations of bismuth alone are summarized in Table IV. Sulfate was detected turbidimetrically in solutions of some of the bismuth deposits. Experiments involving pure antimony are summarized in Table V. Tin determinations are shown in Table VI. Typical deposition (time-current) curves are shown in Figures 3, 4, and 5. Table VII

TABLE III

DEPOSITION FROM NITRATE SOLUTION

Element	Depolarizer[a]	pH	Temp. (°C.)	Potential (S.C.E.)	Time (min.)	Amount, mg. Taken	Found	Diff.
Bi[b]	HYH	5.5	28	-0.5	70	103.1	99.0	-4.1
Bi	HAH	3	70	-0.3	20	99.6	98.9	-0.7
Bi	HAH	4	70	-0.35	20	112.7	112.1	-0.6
Sb	HYH	<1[c]	65	-0.3	29	103.5	100.7	-2.8
Sb	HYH	3	66	-0.5	41	124.6	123.4	-1.2
Sb	HYH	2	65	-0.5	52	112.0	109.0	-3.0
Sn	HYH	<1[c]	40	-0.7	69	126.9	126.4	-0.5
Sn	HYH	<1[c]	35	-0.7	86	120.6	117.3	-3.3
Bi	HYH	3	65	-0.3	19	123.8	122.5	-1.3
Sb		<1[c]	68	-0.6	39	110.3	45.1	-65.2
Sn		<1[c]	29	-0.7	153	102.6	138.1	+35.5

[a]HYH = hydrazine hydrochloride; HAH = hydroxylamine hydrochloride.
[b]0.25 M. sodium tartrate present. 0.2 M. sodium citrate used in all other experiments.
[c]0.9-1.3 M. in HCl.

TABLE IV

DETERMINATIONS OF BISMUTH IN SULFATE-CITRATE SOLUTION[a]

Citrate (M.)	Temperature(°C)	Amounts, mg. Taken	Found	Diff.
0.3	Room	166.0[b]	165.7	-0.3
0.1	"	107.0	108.5	+1.5
0.1	"	120.3	121.9	+1.6
0.2	"	125.9	131.1	+5.2
0.2	"	128.7[c]	131.7	+3.0
0.2	"	109.3[d]	228.0	+118.7
0.2	"	252.4[e]	244.9	+2.5
0.1	66	108.4	110.5	+2.1
0.1	60	201.7	203.9	+2.2
0.1	70	130.2	131.0	+0.8
0.1	70	105.3	104.8	-0.5
0.1	71	214.7	216.6	+1.9
0.2	78	200.7	200.7	0.0
0.3	78	160.7	160.3	-0.4
0.15	70	63.6	66.5	+2.9
0.15	71	164.4	165.8	+1.4
0.15	71	108.4	108.8	+0.4
0.15	72	101.8	101.8	0.0
0.35	69	104.6	105.9	+1.3
0.35	64	120.5	122.4	+1.9
0.2	74	109.2	110.8	+1.6
0.2[f]	71	236.2	237.8	+1.6

[a]Depolarizer, 3 g. HAH. Cathode potential -0.3 (S.C.E.), pH 3 unless noted otherwise. Time required thirty minutes or less, in general.
[b]pH 2.7.
[c]Potential -0.25 volt.
[d]pH 5. Potential -0.45. White salt deposited on cathode.
[e]pH 2. Potential -0.25.
[f]Three g. oxalic acid added.

TABLE V

DETERMINATIONS OF ANTIMONY IN SULFATE-CITRATE[a] SOLUTION

Depolarizer Weight[b]	pH	Chloride (M.)	Temp. (°C.)	Cathode Potential	Amounts, mg. Taken	Found	Diff.
1	3	0	Room	-0.75	108.4	105.8	-2.6
1	2.7	0	"	-0.75	124.8	123.1	-1.7
1	0.5	0	"	-0.4	177.3	167.0	-10.3
5	0.4	0	"	-0.3	199.9	194.3	-5.6
5	---	0.9	"	-0.4	110.5	104.6	-5.9
5	---	0.9	"	-0.4	126.3	120.5	-5.8
1	0.5	0	47-68	-0.4	134.5	127.4	-7.1
3	3	0	68	-0.75	133.6	133.9	+0.3
3	3	0	67	-0.6	177.3[c]	178.4	+1.1
3	0.5	0	68	-0.4	113.7	112.2	-1.5
5	0.4	0	42-74	-0.4	145.6	144.8	-0.8
3	0.4	0	48-75	-0.4	255.5	254.0	-1.5
3	0.4	0	42-67	-0.4	275.2	260.6	-14.6
1	---	0.9	45-64	-0.4	122.7	115.0	-7.7
1	---	0.9	44-61	-0.3	171.1	153.8	-17.3
5	---	0.9	44-74	-0.4	160.1	158.7	-1.4
5	---	0.9	42-69	-0.4	145.9	144.0	-1.9
5	---	0.9	47-77	-0.35	132.6	130.5	-2.1
5	---	0.9	43-68	-0.4	132.9	132.2	-0.7
5	---	0.9	42-70	-0.4	105.7	104.5	-1.2
1	---	1.3	67	-0.3	115.5[de]	115.1	-0.4
1	---	1.3	64	-0.3	160.4[d]	162.0	+1.6
---	---	1.3	65	-0.3	111.5[df]	110.5	-1.0
1	---	0.9	64	-0.3	116.2[deg]	116.1	-0.1
---	---	1.3	64	-0.3	104.3[dfh]	104.3	0.0
3	---	1.3	57	-0.3	226.8[dh]	227.5	+0.7

[a]Citrate 0.3 M. unless indicated otherwise.
[b]In grams. HAH used except where HYH indicated.
[c]0.1 M. citrate.
[d]0.2 M. citrate.
[e]Hydrazine hydrochloride used as depolarizer.
[f]3 g. HAH + 1 g. HYH used.
[g]Reduced with H_2SO_3 after dissolution.
[h]0.5 g. hydrazine sulfate added to H_2SO_4 before dissolution.

TABLE VI

DETERMINATION OF TIN IN SULFATE-CITRATE SOLUTION[a]

Citrate (M.)	Temperature(°C)	Potential (S.C.E.)	Time (min.)	Amounts, mg. Taken	Found	Difference
0.3	40-71	-0.8	90	142.3	140.8	-1.5
0.3	Room	-0.8	110	138.0	135.3[b]	-2.7
0.1	Room	-0.8	39	122.5	13.7[c]	--
0.1	Room	-0.8	212	122.8	122.5	-0.3
0.1	Room	-0.8	85	204.7	201.6	-3.1
0.1	58	-0.8	70	108.7	105.0[b]	-3.7
0.1	Room	-0.7	90	199.2	198.2[b]	-1.0
0.1	Room	-0.7	109	105.1	105.8[b]	+0.7
0.2	55	-0.65	60	169.0	169.6[d]	+0.6
0.2	Room	-0.65	70	232.7	231.9[d]	-0.8

[a]0.9-1.3 M. hydrochloric acid. Three g. HAH unless specified
[b]Solution neutralized with NH_4OH before removal of cathode
[c]pH value was 1. Too slow; incomplete
[d]0.5 g. hydrazine sulfate added to H_2SO_4 before dissolution. Electrolyte washed out of beaker before removal of cathode

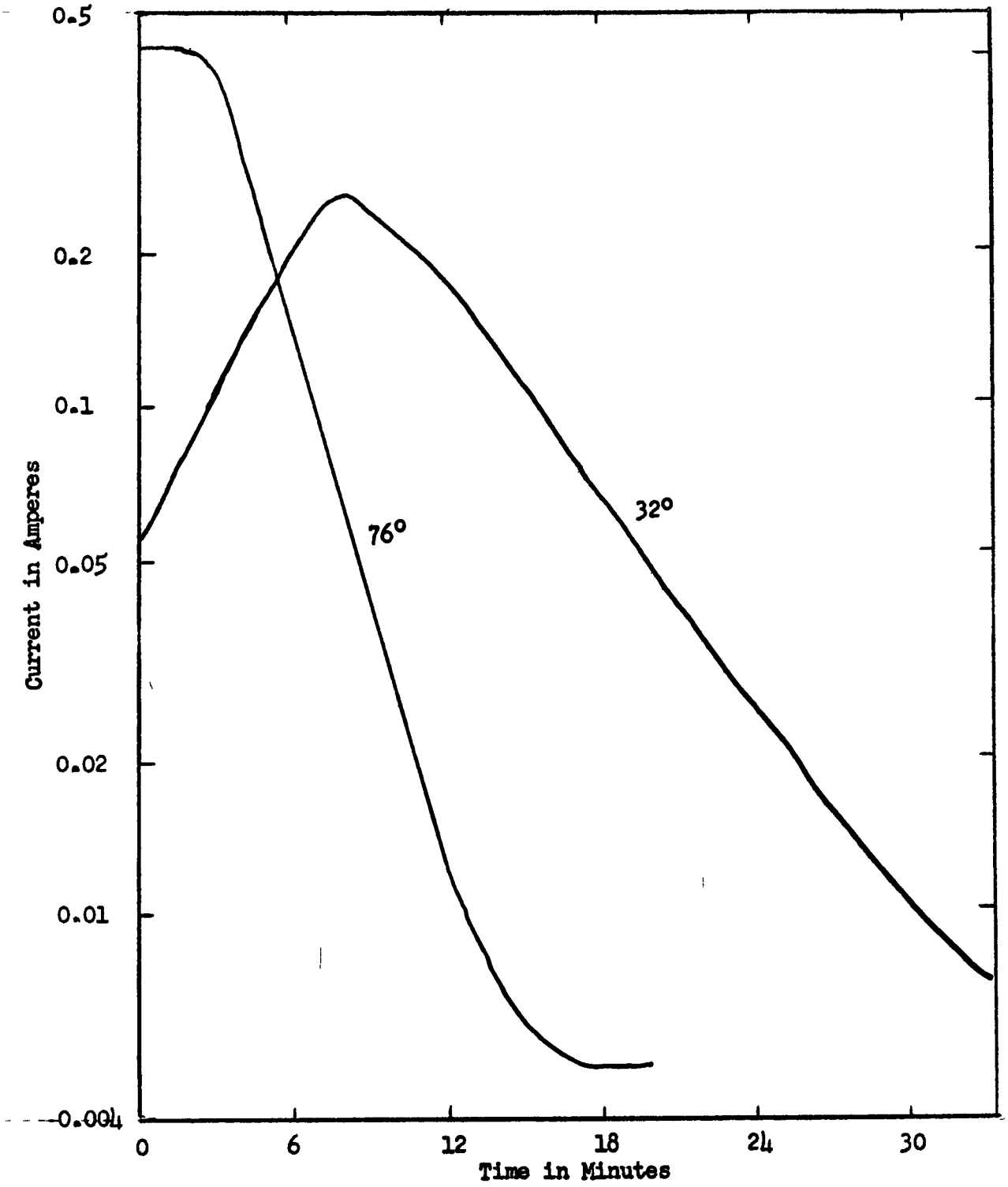


Figure 3. - Typical Deposition Curves for Bismuth

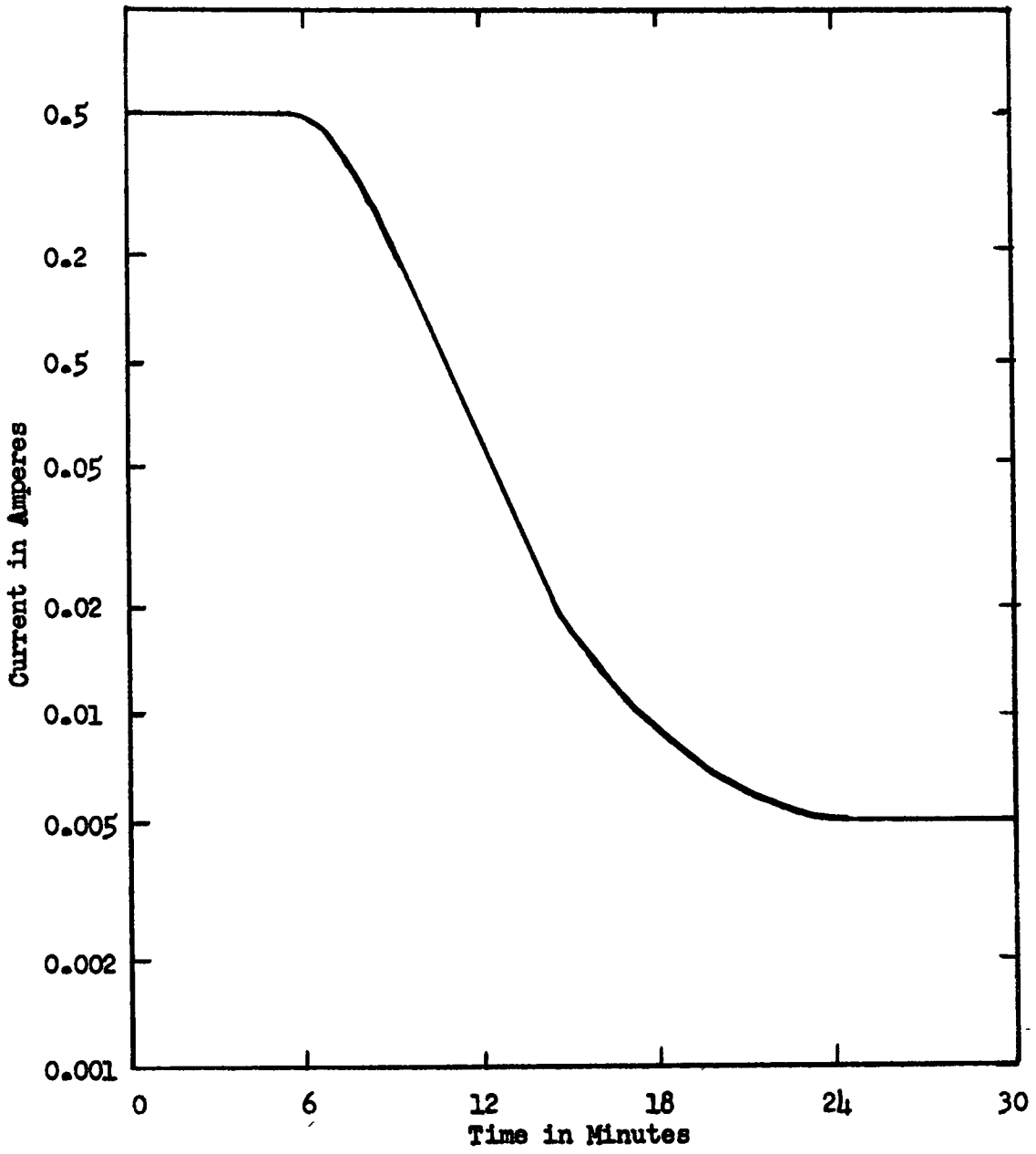


Figure 4. - Typical Deposition Curve for Antimony

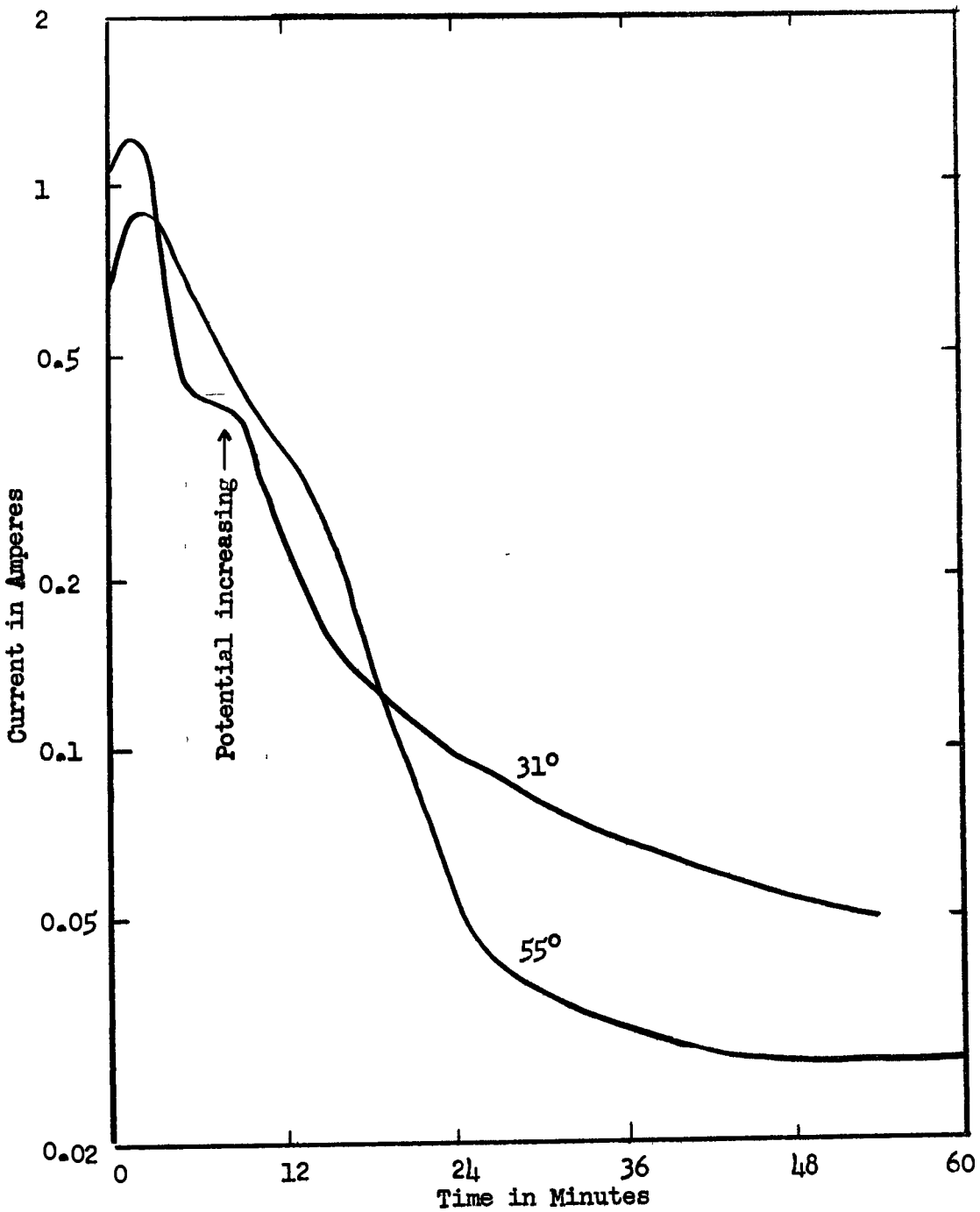


Figure 5. - Typical Time-Current Curves for Tin

summarizes experiments in analysis of mixtures of bismuth and antimony, while Tables IX and X give results of analysis of antimony-tin and ternary mixtures.

It was found that tin appeared to deposit with antimony from sulfate-citrate solutions containing no hydrochloric acid (see table VIII). It was noted that the antimony results were high by a roughly constant percentage, regardless of the amount of tin present. This phenomenon occurred at potentials lower than that of a tin-coated platinum electrode in the system. It may be that hydrolyzed tin salts were present and were deposited on the cathode with the antimony. On the other hand, the metals are known[62] to form antimony-rich solid solutions, in which tin is soluble to the extent of about five per cent. It may be that the deposition of such a solid solution is the reason for this anomalous behavior. The presence of hydrochloric acid prevents the codeposition of tin with antimony (Tables IX and X).

b. Citrate-Versene. Faucherre and Souchay[63] determined bismuth and copper polarographically in the presence of tin and antimony by use of a supporting electrolyte containing citrate and "Versene," the sodium salt of ethylenediamine tetracetic acid. The results of a brief investigation are summarized in Table XI.

c. Tartrate. Results of depositions of bismuth, antimony, and tin (as well as lead and copper) from sulfate-tartrate solution are shown in Table XII.

---

(62) Lyman, T., "Metals Handbook," American Society for Metals, Cleveland, O., 1948, p. 1239.

(63) Faucherre, J., and Souchay, P., Bull. Soc. Chim. France, 1949, 722.

TABLE VII

ANALYSIS OF MIXTURES OF BISMUTH AND ANTIMONY[a]

Citrate (M.)	pH	Bismuth Potential (S.C.E.)	Bismuth Amounts, mg. Taken	Bismuth Amounts, mg. Error	Antimony[b] Potential (S.C.E.)	Antimony[b] Amounts, mg. Taken	Antimony[b] Amounts, mg. Error
0.3	2.7	-0.3	134.5	-1.5	-0.65	100.3	+0.5
0.2	3	-0.3	122.6	+1.2	-0.3	118.2	-1.3
0.2	3	-0.3	150.2	+0.8	-0.3	167.3	-2.5
0.3	3	-0.3	216.8	-0.3	-0.3	224.2	-2.4
0.3	3	-0.3	173.2	-0.2	-0.3	138.2	-5.1
0.2	4	-0.35	66.4	+2.8	--	105.5	--
0.2	4	-0.35	50.8	+2.6	--	207.3	--
0.2	3	-0.3	45.7	+2.1	-0.3[c]	116.3	-0.8
0.35	3	-0.3	58.6	+2.1	-0.3[c]	107.9	+0.4
0.2	5	-0.4	54.9	+2.8[d]	-0.3[c]	110.4	+0.7
0.2	3	-0.3	103.7	+1.7	-0.3[c]	104.2	-1.2

[a]Deposition temperatures 62-82° for Bi; 59-69° for Sb (except first experiment, which was at room temperature) HAH used as depolarizer except when indicated otherwise
[b]Solution 0.9-1.3 M. in HCl except in first experiment
[c]1 g. HYH added before deposition of Sb
[d]Use of Sb tracer showed approximately 0.02% Sb codeposited

TABLE VIII

ANOMALOUS CODEPOSITION OF TIN WITH ANTIMONY

Citrate (M.)	pH	Antimony[a] Potential (S.C.E.)	Antimony[a] Taken (mg.)	Antimony[a] Error mg.	Antimony[a] Error %	Tin[b] Taken (mg.)	Tin[b] Error (mg.)
0.3[c]	1.5	-0.5	178.7	+10.2	+5.7	125.8	--
0.3[c]	1.5	-0.55	146.1	+6.0	+4.1	213.6	--
0.3[c]	1	-0.5	105.9	+11.2	+10.6	154.1	--
0.1	1.5	-0.5	116.3	+4.7	+4.0	124.5	-5.7
0.1	1	-0.4	108.0	+3.1	+2.8	116.4	-6.2
0.1	1	-0.4	124.7	+2.6	+2.1	107.8	-6.7
0.1	1	-0.4	112.7	+1.8	+1.8	142.3	-4.1
0.1	1	-0.35	201.0	+3.6	+1.8[d]	207.2	-3.8
0.1	0.6	-0.35	98.0	+3.1	+3.1[e]	147.8	-2.0
0.1	0.4	-0.3	200.4	+2.5	+1.2	270.6	-5.3
0.1	0.6	-0.4	37.1	+0.8	+2.1	509	--
0.1	0.6	-0.4	97.4	+4.8	+4.7	201	--
0.1	0.6	-0.4	200.4	+4.5	+2.2	221	--
0.1	0.6	-0.4	54.4	+2.2	+3.9	203	--
0.1	0.6	-0.4	112.8	+2.2	+1.9	63	--
0.1	0.6	-0.4	220.4	+4.1	+1.8	66	--

[a]No HCl added before deposition
[b]0.9-1.3 M. HCl. Deposited at -0.7 volt (S.C.E.)
[c]Room temperature. Others at 64-71°
[d]Tin tracer indicated 1.6% of tin codeposited.
[e]Tin tracer indicated 0.9% of tin (1.3 mg.) codeposited.

TABLE IX

ANALYSIS OF TIN-ANTIMONY MIXTURES[a]

Citrate (M.)	Antimony				Tin[b]	
	Temperature (°C)	Potential (S.C.E.)	Amounts, mg. Taken	Amounts, mg. Error	Amounts, mg. Taken	Amounts, mg. Error
0.1	42-66	-0.4	111.1	-0.2	143.0	-3.2
0.2	42-69	-0.4	152.0	+0.2	103.1	-4.4
0.1	67	-0.3	113.9	0.0	104.0	-0.2
0.1	66	-0.3	250.9	-2.1[c]	122.8	-0.7
0.1	67	-0.3	212.1	-0.2	202.0	-4.6[c]
0.1	65	-0.3	249.4	+1.7	166.6	-2.8

[a]Sulfate-citrate system, 0.9-1.3 M. in hydrochloric acid
[b]Deposited at a cathode potential of -0.7 (S.C.E.)
[c]Slightly non-adherent deposit

TABLE X

ANALYSIS OF MIXTURES OF BISMUTH, ANTIMONY, AND TIN[a]

	Bismuth[b]		Antimony[c]		Tin[c]	
pH	Amounts, mg. Taken	Error	Amounts, mg. Taken	Error	Amounts. mg. Taken	Error
3	110.4	+0.2	107.6	--	101.7	--
3	105.0	-1.6	106.6	-0.5	129.3	-0.1
3.3	136.7	+1.6	192.6	-0.3	105.4	-0.7
3	104.4	+0.2	110.6	+0.1	116.0	-1.8[d]
2.7[e]	61.4	+3.7	122.1	-2.9	169.0	-0.7
3.1	121.8	+2.3	98.3	-2.1	101.9	-1.6
3[fg]	100.3	+1.6	108.3	-4.6	104.5	-0.9
3[fh]	101.8	+2.1	200.1	-1.9	225.2	-1.8

[a]0.2 M. citrate
[b]Deposited at -0.3 volt (S.C.E.), 65-75°
[c]0.9-1.3 M. HCl. Sb deposited at -0.3 volt; 55-70°; Sn at -0.65 to -0.7 volt (S.C.E.)
[d]Not neutralized
[e]Tin tracer indicated ~0.07% Sn in Sb, 1.0% left in solution.
[f]0.5 g. hydrazine sulfate added before dissolving
[g]Sb tracer indicated ~0.09% Sb in Bi, 3.3% in Sn.
[h]Sn tracer indicated ~0.02% Sn in Bi, ~0.03% in Sb.

TABLE XI

DEPOSITIONS FROM CITRATE-VERSENE-SULFATE SOLUTION

Metal	Citrate (M.)	Versene (M.)	pH	Potential	Amounts, mg. Taken	Error
Sb[a]	0.25	0.1	3	-0.8	108.2	-10.7
Sb[b]	0.25	0.1	--	-0.45	186.3	-35.9
Bi[c]	0.25	0.1	9.1	-0.8	118.2	+2.1
Bi[d]	0.2	0.07	0.7	-0.4	128.9	+1.4
Bi[de]	0	0.04	3	-0.6	112.8	+3.9

[a]Reduced with SO_2 after dilution of H_2SO_4. Deposition at room temperature
[b]5 ml. sulfuric acid added to electrolyte. Deposition at room temperature
[c]Deposition at room temperature
[d]Deposition at 63-73°
[e]HYH used as depolarizer. HAH used in other experiments

TABLE XII

DEPOSITIONS FROM SULFATE-TARTRATE[a] SOLUTIONS

Metals	pH	Potential (S.C.E.)	Amounts, mg. Taken	Error
Sb	<1	-0.4	102.7	-6.4
Bi	5.4	-0.5	114.4	-0.3
Sb[b]	--	-0.4	108.9	-25.4
Bi	5.4	-0.4	120.8	-1.1
Sb[c]	--	-0.4	116.0	-0.8
Bi	6	-0.5	130.1	+7.8
Sb[d]	--	-0.4	103.0	-13.1
Sn[d]	--	-0.65	105.8	-1.5
Cu[e]	6	-0.4	16.1	-1.5
Pb	5	-0.65	9.1	+1.3
Sb	2.7	-0.75	37.3	+35.3
Sn[d]	--	-0.65	441.2	-44.0
Sb[d]	--	-0.4	129.7	-10.3
Sb[d]	--	-0.4	128.2	-8.2
Sb[d]	--	-0.4	137.0	-11.1
Bi	5.5[f]	-0.4	106.5	-19.0

[a]Tartrate 0.2-0.25 M.
[b]5 ml. sulfuric acid added
[c]5 ml. hydrochloric acid added
[d]10 ml. hydrochloric acid added
[e]National Bureau of Standards sample 54b
[f]HYH used as depolarizer; HAH used in other experiments. Temperature 67°; others at room temperature

d. Fluoride. Depositions of antimony were attempted from sulfate solutions which were about 0.07 M. in hydrofluoric acid. The results were 15-20 per cent low, even though the cathode was maintained at a potential considerably more negative than that of an antimony-plated electrode in the system. In one experiment the weight of antimony deposited indicated that 16 per cent remained in solution, while tracer antimony-124 indicated 18 ± 2 per cent. It was necessary to apply high potentials to the electrolysis cell. with the probable result that antimony was oxidized anodically to the pentavalent state, which forms a stable complex with fluoride ion[64].

Copper and bismuth were found to deposit together from the fluoride-sulfate system.

---

(64) Diehl, H., "Electrochemical Analysis with Graded Cathode Potential Control," G. F. Smith Chemical Co., Columbus, O., 1948, p. 40.

CHAPTER IV

DISCUSSION

The attempt to devise an electrochemical procedure for the separation and determination of bismuth, antimony, and tin has succeeded to only a limited extent. A number of electrolyte systems have been studied with the results presented in Chapter III and discussed below.

Deposition from perchloric acid yielded satisfactory results for bismuth (and copper), but separations were not feasible (Table I). Difficulties in dissolution of samples were noted. Use of the hydrochloric-sulfuric acid system gave generally good results for bismuth, but separations of bismuth and antimony were impossible (Table II). Similarly, use of the nitrate-citrate electrolyte gave fair results for bismuth and tin, but oxidation of antimony during dissolution caused difficulties (Table III).

Deposition from citrate-versene-sulfate offered no advantages over the simpler citrate-sulfate system discussed below. Bismuth results were high, probably because of the deposition of basic compounds, and antimony analyses were low (Table XI). Analytical results were generally unsatisfactory when a sulfate-tartrate (Table XII) or sulfate-fluoride electrolyte was used.

Determinations of bismuth by depositing from a citrate-sulfate electrolyte were most successful and somewhat faster at high temperature (70-80°) than at room temperature, and at pH 3 and a potential of -0.3 volt (S.C.E.). Hydroxylamine hydrochloride was found to be a satisfactory depolarizer. Results were almost always high when good deposits were

secured. The bias was +1.3 mg. from 33 bismuth results in Tables IV, VII, and X, and was apparently independent of amount of bismuth plated. Subtraction of the bias from the results gave a mean deviation of 1.0 mg., satisfactory for rough quantitative analysis, especially since the bismuth determination is rapid.

In determination of antimony, best results were obtained when the solution in sulfuric acid was reduced with hydrazine sulfate. The reagent could be present during dissolution, or could be added to the concentrated acid solution after the metal had dissolved, and heating continued. A temperature of 50-70° was satisfactory for depositions. The potential was allowed gradually to attain -0.3 volt. It was found that hydrazine hydrochloride and hydrochloric acid should be present. No bias was shown by 16 antimony determinations under proper conditions, reported in Tables V, VII, IX, and X. The mean deviation was 0.7 mg., satisfactory for approximate quantitative analysis. Sulfur formed during dissolution of antimony-tin mixtures acted to prevent the oxidation of antimony[65].

Tin was best determined by depositing at -0.65 to -0.7 volt. The electrolyte was the same as that for antimony. Temperature did not affect the results except in length of time required for completion of plating. Tin results were low, probably because of incomplete deposition (small effect) and loss in washing[66]. The best washing procedure involved

---

(65) Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 70.

(66) Diehl, H., "Electrochemical Analysis with Graded Cathode Potential Control," G. F. Smith Chemical Co., Columbus, O., 1948, p. 49.

removal of electrolyte from the beaker (with potential still applied to the electrodes) by siphoning while adding water. Neutralization of the electrolyte before removal of the tin-coated electrode[67] did not allow as good results. The bias of 15 tin results (Tables VI, IX, and X) by both handling techniques was -1.2 mg., and the mean deviation (after correcting for bias) was 1.1 mg.

Use of tracers demonstrated that deposits of bismuth from solutions containing antimony and tin were essentially free of those elements, and that antimony was free of tin when deposited. However, the tin deposit sometimes contained antimony because of occasional incomplete deposition of the latter. It is believed that antimony and tin deposits obtained after removal of bismuth were free of the latter, because the weights were never significantly high.

The following procedure has been used for analysis of the single elements, binary mixtures, and ternary mixtures.

Procedure. Take a sample containing not over 100 mg. of bismuth (if antimony is present in large amount), and not over 250 mg. each of antimony and tin. Add 0.5 g. of hydrazine sulfate and 10 ml. of concentrated sulfuric acid. Heat without excessive boiling until all metal particles have disappeared. Allow the material to cool, and dilute with about 10-20 ml. of water. Add 30 ml. of 1 M. sodium citrate, 3 g. of hydroxylamine

---

(67) Diehl, H., "Electrochemical Analysis with Graded Cathode Potential Control," G. F. Smith Chemical Co., Columbus, O., 1948, p. 49.

hydrochloride, and neutralize to about pH 3 with 10 M. sodium hydroxide. Cool and dilute to 120-140 ml., and adjust to pH 3.0 with sodium hydroxide or sulfuric acid, measuring pH with a glass electrode-S.C.E. assembly. Heat to 70-80°, and deposit bismuth on a platinum gauze electrode, maintaining the potential at -0.2 volt (S.C.E.) at first, then allowing it to rise (in the reduction sense) to -0.3. Continue the electrolysis until the current falls to a small, constant value (usually requires about 25 min.). Remove the electrode, washing with water from a wash bottle, agitate in two separate beakers of water, then in acetone. Dry in a stream of filtered air or by heating. Weigh (cool if necessary) and subtract 1.3 mg. to obtain the weight of bismuth. To the electrolyte add 1 g. of hydrazine hydrochloride and 15 ml. of hydrochloric acid. On a clean cathode, deposit antimony at 50-70° and at an initial current not exceeding 0.5 amp. Limit the potential to -0.3 volt, and continue electrolysis until the current falls to a small, constant value (usually requires about 30-45 min.). Wash and dry the cathode as before. Determine the weight of antimony deposited. Using a clean cathode, deposit tin at a potential of -0.6 volt, allowing it to rise to -0.65 volt after about 15 min. (about an hour required). Remove the electrolyte by siphoning while diluting with water (about 400-500 ml.). Finally siphon all liquid out, wash and dry the cathode as before. Weigh, adding 1.2 mg. to obtain the weight of tin plated. The results should be accurate to about 1 mg. The total time required is about 3.5-4 hours. Copper deposits with bismuth, and lead with tin (if these metals are present).

CHAPTER V

SUMMARY

A study was made of the separation and determination of bismuth, antimony, and tin by electrochemical means, using controlled cathode potential. The effects of electrolyte composition, cathode potential, and temperature were investigated with respect to separations of the three metals and degree of recovery of each. Radioactive tracers were employed to a limited extent, and yielded useful information. Best results were obtained by use of an electrolyte containing sulfate and citrate. A procedure was devised which would serve for approximate analysis for bismuth, antimony and tin in the form of mixtures and alloys. Further investigation along similar lines might lead to improved analytical results.

BIBLIOGRAPHY

BIBLIOGRAPHY

Diehl, H., "Electrochemical Analysis with Graded Cathode Potential Control," G. F. Smith Chemical Co., Columbus, O., 1948.

Faucherre, J., and Souchay, P., Bull. Soc. Chim. France, 1949, 722.

Friedlander, G., and Kennedy, J. W., "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 109-114.

Goldberg, C., Metallurgia, 42, 108 (1950)

Grant, J., Analyst, 53, 626 (1928)

Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1953

Kny-Jones, F. G., Analyst, 64, 172, 575 (1939), 66, 101 (1941).

Kolthoff, I. M., and Lingane, J. J., "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946.

Latimer, W. M., "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952.

Lee, D., and Cook, G. B., British Atomic Energy Report AERE-C/R-430 (1950)

Lingane, J. J., and Auerbach, C., Anal. Chem., 23, 986 (1951)

Lingane, J. J., and Jones, S. L., Anal. Chem., 23, 1788 (1951)

Lyman, T., "Metals Handbook," American Society for Metals, Cleveland, O., 1948, p. 1239.

Meyer, R. J., "Gmelins Handbuch der Anorganischen Chemie," S-N 5, Verlag Chemie G. M. B. H., Leipzig-Berlin, 1926, p. 401.

Norwitz, G., Anal. Chem., 23, 386 (1951)

Norwitz, G., Analyst, 75, 473 (1950), 76, 423 (1950)

Sand, H. J. S., "Electrochemistry and Electrochemical Analysis," Vol. II, Blackie and Son, Glasgow, 1945.

Sand, H. J. S., J. Chem. Soc., 91, 373 (1907), 93, 1572 (1909)

Schleicher, A., "Elektroanalytische Schnellmethoden, Die Chemische Analyse, IV/V Band" (Boettger, W.,ed.), F. Enke, Stuttgart, 1947.

Schoch, E. P., and Brown, D. J., J. Am. Chem. Soc., 38, 1660, 1673 (1916).

Schweitzer, G. K., and Whitney, I. B., "Radioactive Tracer Techniques," D. Van Nostrand Co., New York, N. Y., 1949, pp. 112-113.

Treadwell, F. P., and Hall, W. T., "Analytical Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1937, pp. 161, 167.

Walton, H. F., "Principles and Methods of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1952.

Way, K., Fano, L., Scott, M. R., and Thew, K., "Nuclear Data," Circular of the National Bureau of Standards 499, U. S. Government Printing Office, 1950, pp. 133, 139.

Willard, H. H., and Diehl, H., "Advanced Quantitative Analysis," D. Van Nostrand Co., New York, N. Y., 1943.

Willard, H. H., and Furman, N. H., "Elementary Quantitative Analysis," D. Van Nostrand Co., New York, N. Y., 1940.

Willard, H. H., Merritt, L. L., and Dean, J. A., "Instrumental Methods of Analysis," D. Van Nostrand Co., New York, N. Y., 1951.

APPENDIX

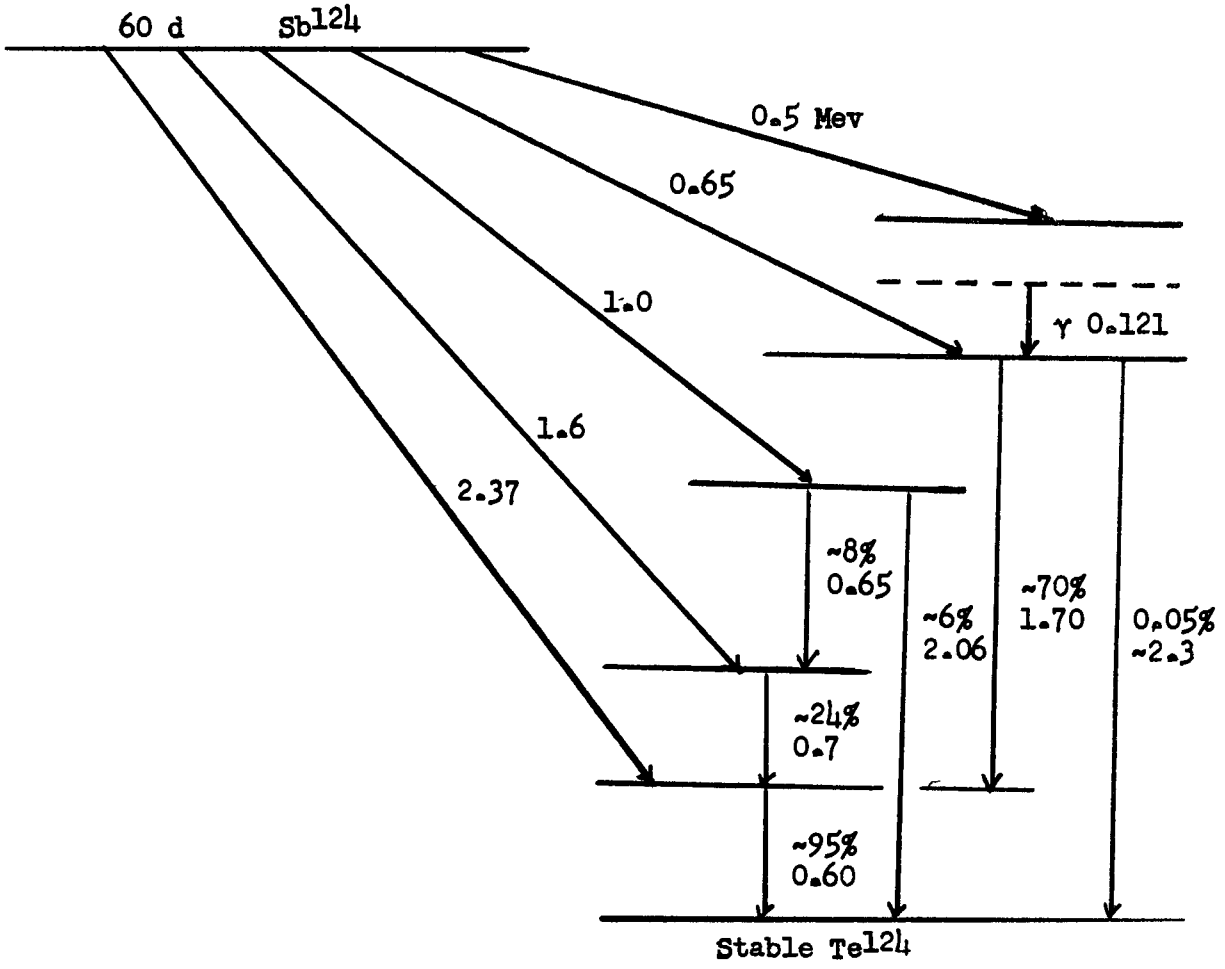


Figure 6. - Decay Scheme of Antimony-124

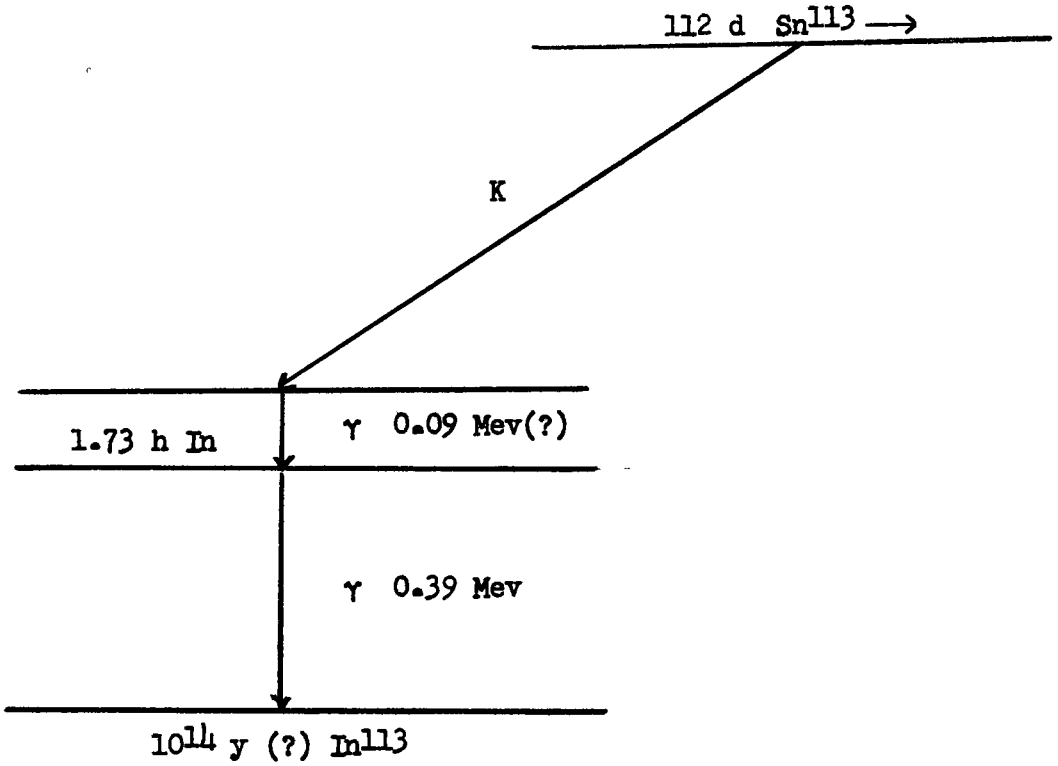


Figure 7. - Decay Scheme of Tin-113