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A CURRENT EFFICIENCY STUDY AND METHOD OF ANALYSIS
FOR MICRO QUANTITIES OF SILVER

DISSERTATION
Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
Gerald L. Weiss, B.A., M.S.

* * * * * *

The Ohio State University
1965

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INTRODUCTION

The purpose of this investigation was to obtain information concerning the application of radiochemical methods and electrochemical methods to the determination of small quantities of electrodepositable materials.

Constant current coulometric electrodepositions of radioactive silver solutions were used to study the effects of a number of variables on the current efficiency for the electrodeposition of silver. Silver was chosen because of its desirable radiochemical and electrochemical properties.

A method for the determination of small quantities of electrodepositable material was developed utilizing the isotope dilution principle and information from the current efficiency studies.
CHAPTER I

HISTORICAL REVIEW

Introduction

Electrodeposition and radiochemical methods were used in the present investigation. Much of the recent progress in these fields of research can be attributed to the development of electronic instrumentation and the increased availability of radiochemicals.

Outline of the history of electrodeposition

A historical account of the entire field of electrolytic analysis has been given by H. O. Heisey in the thesis "A History of Electrolytic Analysis" (1).

The first account of an electrodeposition was the electrolysis of water in May of 1800 by Nicholson and Carlisle (2). Shortly afterward, W. Cruickshank electrolytically deposited copper (3). The quantitative separation and identification of arsenic, zinc, antimony and manganese followed these original papers in a period extending to 1857.

Concurrently with the discovery that metallic elements could be separated and identified by electrolytic methods, the basic concepts of coulometry were elucidated by Michael Faraday. In the section "On the Power of Metals and the Solids to Induce the Combination of Gaseous Bodies" (4), he noted that the amount of chemical decomposition was proportional to the quantity of electricity passed; and in the section
"On a New Measure of Volta-electricity" (5), he defined the electrochemical equivalent weight of a substance. Michael Faraday also introduced the electrolytic nomenclature we use today.

It was not until October 1864 that the first quantitative electroanalysis was reported by Wolcott Gibbs (6). He used this technique for the determination of copper in the copper-nickel alloy employed for making coins. Carl Luckow (7) published a series of three papers in 1865 on "electro-metal analysis" which also dealt with the quantitative separation of metals.

The significance of the potential in separation of metals was pointed out by Kiliani in 1883 (8). By control of the electromotive force he was able to effect the separation of silver and copper. Previous to this time the separations were made possible by the reduction of a second material which would not deposit on the electrode. The reduction of the second material prevented the reduction potential from becoming negative enough for the electrodeposition of another metal. An example is the separation of copper from zinc in an acid solution. The copper deposits, but the zinc does not because hydrogen is reduced before the cathode potential becomes negative enough for the reduction of zinc.

The theoretical basis for electrochemistry began in the 1830's with Faraday's experiments. The next contribution to the theory of electrochemistry was 50 years later where the importance of the electrode potential was explained by Nernst. Van't Hoff's paper (9) on the theory of solutions in 1887 paved the way for Arrhenius's paper (10) on the electrolytic dissociation theory, and in two years Nernst (11) explained the nature and origin of the potential difference in a voltaic cell.
Since the development of the fundamentals for electrochemistry in the latter part of the nineteenth century, the number of investigations and methods using these fundamentals have steadily increased. Both the theoretical understanding and analytical methods have grown to complement each other. The publications of Tobias and Delahay (12,13) and the papers presented at a Symposium of the Theoretical Electrochemical Division of the Electrochemical Society in Philadelphia in May of 1959 (14) contain discussions of theoretical electrochemistry. General references to analytical electrochemistry are found in Delahay's text (15), in the fourth volume of part one in the Kolthoff and Elving series (16), and in Lingane's book (17).

The origin of coulometric analysis can be attributed to Grower (18), who determined the thickness of tin coatings on copper wire by measuring the number of coulombs required to strip the tin from the copper with a more or less controlled potential technique. The quantity of electricity passed was measured with a gas coulometer. Constant current coulometry began with the work of Evans and co-workers (19,20). In this type of measurement the quantity of current is the product of current intensity and the time of the run. However, the current efficiencies for deposition are not generally 100 percent. To correct for this, Zbiden (21) electrodeposited copper and then anodically stripped it from a platinum electrode, the amount of copper being calculated from the current of the anodic process. Szebeldedy and Somogyi (22) published a series of papers that introduced coulometric intermediates which were used as titrants. The next addition to coulometric methods was made in
1945 when Lingane (23) introduced constant potential coulometry for the determination of copper, bismuth, lead and picric acid.

The number of publications on coulometric methods are numerous enough to warrant review articles each year by various authors. The review of coulometry by Kies (24) was extensive and provided a historical background. Bard (25,26) reviewed books, research literature, and other review articles on the subject of electroanalysis and coulometric analysis from 1960 to 1964.

Outline of the history of radiochemistry

The discovery of radioactivity was a more or less accidental event. Previous to the identification of radioactivity as a means of causing phosphorescence, there was general scientific interest in phosphorescence caused by sunlight and ultraviolet light. Edmund Becquerel had purified some potassium uranyl sulfate which phosphoresced under the influence of ultraviolet light. However, he did not live long enough to discover that phosphorescence can be caused by radiations from the radioactive decay process. W. C. Roentgen discovered X-rays in 1895, and these experiments led Henri Becquerel, Edmund Becquerel's son, to perform similar experiments with buttons of uranium salts. The darkening of a photographic plate without sunlight by the buttons of uranium salts led to a series of experiments which he published in 1896 (27). The last of the series was entitled "Emission of New Radiations by Metallic Uranium." Marie Sklodowska Curie concluded that the radiation from uranium was an atomic phenomenon in 1898, and she introduced the term radioactivity. Other naturally occurring radioactive elements besides uranium were
identified in 1898. Owens, Professor of Electrical Engineering at McGill University in Montreal, discovered that thorium was radioactive, and Pierre and Marie Curie separated polonium and radium from pitchblende as other radioactive elements. Rutherford was responsible for the classification of the radiations into alpha rays, beta rays, and gamma rays through his experiments which measured their penetration abilities and their deflections in a magnetic field. The results of his experiments were published in the Philosophical Magazine for January 1899. Rutherford and Soddy in further studies recognized that activity of radioactive substances did not continue indefinitely, but diminished in intensity with a time scale characteristic of the substance, and that radioactive processes were accompanied by a change in the chemical properties of the active atoms.

The developments in the latter part of the nineteenth century laid the foundations for radiochemistry. The physicist has studied radioactive disintegrations for the purpose of discovering the mysteries of the atom. The physical chemist has used radiolysis (the breakdown and reforming of a chemical system subjected to high energy particles) for elucidating the kinetics and mechanisms of chemical reactions. The analytical chemist has used activation analysis (the production of radioactive species of the elements in order to qualitatively and quantitatively determine them) and tracer techniques (the addition of a known amount of activity associated with a particular element to qualitatively trace small quantities of materials and quantitatively determine the amounts of material by isotopic dilution relationships).
In the year of 1919, Rutherford produced and identified the first artificial nuclear transformation. An artificial isotope was produced by using the alpha particles from radium C to bombard nitrogen $^{14}$. The production of another radioactive species was identified by the scintillations produced on a zinc sulfide screen by the protons from the ($\alpha$,p) reaction. The protons were not identified as protons during the first experiments, but it was reasoned that the scintillations could not be produced by the alpha particles transversing the material between the source and the sulfide screen. Therefore, the scintillations must be produced by another particle given off from the induced radiochemical transformation.

The first tracer experiments were performed with a material called radium D which was a radioactive product obtained from uranium transformations. This product once mixed with lead could not be separated, and was used to trace lead in its reactions. Hevesy (28) was the first to use radium D for radiotracer experiments in the determination of the solubilities of lead chromate and lead sulfide. This was probably the first isotope dilution experiment. Various types of isotope dilution experiments developed since then are discussed by Christian and Pinajian (29). The advantage of isotope dilution experiments is that the total quantity of a certain substance can be calculated by knowing the activity associated with a small but accurately known part of the total material.

A period of 20 years passed before further developments of any significance for the analytical chemist were made. The experiment of Curie and Joliot (30) in which aluminum was activated with alpha particles
sparked a series of investigations on how to produce radioactive isotopes. The neutron discovered by Chadwick in 1932 was used by Fermi and his associates as another particle to activate a number of elements (31). Neutron activation was advantageous because the radioactive species was an isotope of the element bombarded. This made possible the production of a source of radioactive isotopes of almost every element. Hevesy (32) was quick to appreciate the fact that extremely small quantities of materials were needed for neutron activation, and he proceeded to develop the method of neutron activation for the determination of rare earths in minerals.

The combination of radiochemistry and electrochemistry

Hevesy (33) was also recognised as the first to combine electrodeposition with radiochemical methods. He separated lead and the tracer radium D from a solution by anodic oxidation to lead dioxide. The work of Hevesy was of great importance in the advancement of radiochemistry as an analytical method. A collection of his papers translated into English appeared in two volumes (34).

Both anodic and cathodic electrolytic depositions were used in this laboratory for the separation of zinc or cobalt from a solution, and the total quantities of zinc or cobalt were calculated from the mass and radioactivity measurements of the deposit (35,36,37,38).

Rusicka (39) and Rusicka and Bemus (40) have also combined radiochemistry and electrodeposition in the determination of silver.
Developments in the electrochemistry of silver

The historical development of the electrodeposition of silver dates back to 1801 when Cruikshank (41) electroanalysed solutions containing silver and copper salts, and he suggested that electrodeposition could be used for the qualitative identification of these metal ions present in solution. Nickles (42) found that large quantities of silver could be separated from cyanide solutions in 1862.

Luckow (7,43) discovered that silver could be quantitatively separated from the solutions Nickles used, and he proposed the quantitative separation as a method of analysis for silver. Tschawadarov (44) determined the optimum conditions of potential, current, and supporting electrolyte necessary for a complete deposition. He demonstrated that the percent deposition increased from 99.94 percent to 100.00 percent when formaldehyde was included in the electrolyte to prevent the formation of peroxide.

The importance of the potential control for separation of different metals was pointed out in 1883 by Killiani (8). Freudenberg (45) more fully elaborated on the method of separating silver, cadmium, zinc and nickel by control of the potential and he theoretically justified it. Sand (46) introduced the auxiliary reference electrode for control of the cathode potential, and he tried to reduce the resistance of solution by placing the electrodes closer together and stirring the solution. Rosa and his co-workers proceeded to determine the accurate value of the Faraday by the electrodeposition of silver after a series of preliminary investigations (47, 48, 49, 50). Rogers and his co-workers
(51, 52, 53, 54, 55, 56, 57, 58) studied voltammetry relationships for silver over an extended range of concentrations. Through his investigations he has been able to derive an expression which corrects the Nernst equation for electrodes which have less than a monomolecular layer of deposited silver. The recent development of electronic measuring and recording instruments has made controlled potential coulometry available to the analytical chemist as a method with reasonable accuracy and speed. Bard and Solon (59, 60) developed a high speed coulometric determination which was based on a voltage to frequency converter. Numerous other electronic methods can be found in the reviews by Bard (25, 26).
CHAPTER II

PROPERTIES OF SILVER

Silver is a white metal which is malleable, ductile, and has the greatest conductivity of any metal at 0°C. Crystalline structures of face-centered cubes are electrolytically deposited from nitric acid solutions, but the presence of colloidal material in an electrolyte will interfere with the formation of the cubic structures. Silver is usually obtained as a solid mass which is hard drawn, rolled, or made into soft wire, but it can also be found in nature or produced by man as a filament-like structure called filiform, moss, or hair silver. Some of the purest silver is made in the form of a powder of 325 mesh by electrodeposition at high current densities from a concentrated silver solution (61). Silver has a density of 10.5 grams per square centimeter at 20°C, a melting point of 960.5°C, and boiling point of 1950°C. Mellor (62) gives the tensile strength under various conditions and a number of other physical properties.

There are four different oxidation states for silver, Ag(0), Ag(I), Ag(II) and Ag(III). The Ag(II) and Ag(III) are very powerful oxidising agents, and they are reduced by water (63). The Ag(III) state exists in some complex compounds, in strong oxidising solutions (64), and possibly as the solid oxide (65). The Ag(II) ion, ordinarily unstable in aqueous solutions, has been stabilized in highly acid
solutions at low temperatures by Noyes and co-workers (66, 67, 68, 69, 70). They also studied methods of production of Ag(II), its reactions, and potential properties in nitric acid solutions. Mier and Swift (71) electrolytically produced Ag(II) in a perchloric acid solution, and they used it as an intermediate in a coulometric analysis. Lingane and Davis (72, 73) determined manganese, cerium and chromium by a titration with Ag(II) in 4 N HNO₃. They also studied the effect of the current density on the percent current efficiency for the production of Ag(II) in highly acid solutions at different temperatures, and electrode surfaces. Rechnitz studied Ag(II) to try to determine the type of complexes which were formed in perchloric acid (74) and sulfuric acid solutions (75). Wales recently studied and determined the type of oxides which would be deposited on an anode from a basic solution of KOH (76).

Silver (I) forms soluble salts with nitrate, nitrite, fluoride, chlorate, perchlorate, bromate, sulfate, permanganate, acetate and tartrate anions. The fluoride anion is the only soluble silver halide.

Sunderman and Townley (78) listed the types of precipitates formed by silver and chloride, bromide, iodide, oxide, sulfide, chromate, dichromate, carbonate, phosphate, thiosulfate, iodate, oxalate, cyanide and benzosotriazole ions. Their solubilities in water and other solvents are also listed. The physical form of the precipitate can be drastically changed by the rate of precipitation. Rapid precipitation of silver chloride gives a curdy deposit which can be easily filtered, but prolonged digestion may cause very small crystals to form and a possible loss on filtration. A crystalline deposit of silver can be obtained by homogeneous precipitation (77). The precipitation of traces of silver
has been affected by reduction to the metal, as the oxide from basic solutions, and as a halide by the use of scavengers (78).

Complexes of silver are numerous and there has been an attempt to classify them as inorganic complexes, organic complexes, ion association complexes, coordination complexes, and chelate complexes (78,79,80,81,82,83,84). The references cover the theory and give the complexity constants for the majority of the silver complexes formed.

The electrolytic reduction potentials of silver ions and silver compounds have been listed by Latimer (63). For quick reference to equilibrium potentials which are a function of the hydrogen concentration, Delahay and co-workers (85) have published a potential-pH diagram, and they have listed the reactions and electrode potential equations for three classes of reactions which are homogenous reactions with oxidation, heterogeneous reactions involving two solids with oxidation, and heterogeneous reactions involving one solid with oxidation. A few of the oxidation potentials are listed in Table 1 to illustrate the variation in reduction potential between the different oxidation states, and the effect of the solvent (86). Rogers (87) and Laitinen (88) have described voltammetric curves on platinum wire electrodes.

The radioactive isotopes of silver are not available from nature. The first man-made isotopes were produced during the initial neutron activation experiments (31). Since that time, some 22 isotopes of silver have been produced (78) by neutron activation, proton activation, neutron activation, alpha particle activation, and induced fission reactions. The only two readily available sources of silver isotopes are silver-110m, produced by neutron activation of silver-109, and silver-111
### TABLE 1

Oxidation Potentials of a Few Silver Ions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous</td>
<td></td>
</tr>
<tr>
<td>$\text{Ag}^+ + e^- = \text{Ag}$</td>
<td>0.7995</td>
</tr>
<tr>
<td>$\text{Ag}^{+2} + e^- = \text{Ag}^+$</td>
<td>1.339</td>
</tr>
<tr>
<td>$\text{Ag}^0 + 2\text{H}^+ + e^- = \text{Ag}^{+2} + \text{H}_2\text{O}$</td>
<td>2.100</td>
</tr>
<tr>
<td>Nonaqueous</td>
<td></td>
</tr>
<tr>
<td>$\text{Ag}^+ + e^- = \text{Ag}$</td>
<td>0.58 to 0.64 (Acetonitril derivatives)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

produced by neutron activation of palladium-110 which forms palladium-111 and then disintegrates by beta emission to silver-111. The most complete accumulation of data on radioactive isotopes can be found in the Nuclear Data Sheets which were printed by the Publications Office, National Academy of Sciences, National Research Council, Washington 25, D.C.
CHAPTER III

ANALYTICAL METHODS FOR THE DETERMINATION OF SILVER

There are many well known methods for the determination of silver. Most of these methods can be characterized as gravimetric, volumetric, spectrometric, electrolytic, radiochemical methods or a combination of these. One of the most thorough collection of methods for the determination of silver is presented in the series by Wilson and Wilson (89,90).

The gravimetric methods include deposition of silver as a metal, inorganic precipitates, organic precipitates or combination of these. The metallic state is achieved by fire assay, electrolytic reduction, and chemical reduction. The fire assay method for alloys and ores is a classical method which is described in detail by Furman (91). The method of determining silver in organic compounds also relies on the reduction of silver to the metallic state over a source of heat (92). Methods of electrolytic reduction are discussed under electrolytic methods.

Chemical reductions can be effected by metals with higher oxidation potentials such as zinc (93) or organic reducing agents such as formic acid, formaldehyde, and ascorbic acid. Extremely small quantities of silver can be deposited quantitatively by using a 2\% aqueous solution which must be heated to boiling. After the precipitate is filtered, washed and dried, it is ignited at 700°C (94,95). Chloride ion is the
most generally used inorganic anion for precipitation of silver. The silver compounds of bromide and iodide are much more insoluble than the chloride, but they are much more light sensitive (96,97,98,99). Quantitative precipitation for both macro and micro determinations of silver can be accomplished with benzo -1,2,3-trisole (100), but Versene in an ammonical solution is necessary to prevent the precipitation of normal hydrous oxides (101,102).

Volumetric titrations for silver may be classified as direct or indirect. The following examples rely upon color changes for detecting the end point of the titration. The Volhard method (103,104) is a direct titration where the end point is distinguished by the pink appearance of the ferric thiocyanate complexes after all of the silver ions are precipitated by the thiocyanate. Examples of the use of an oxidation reaction to indicate the end point are given in titrations with KI in which an oxidizing reagent such as KMnO₄, K₂Cr₂O₇ or CeNH₄(SO₄)₂ is present and it only oxidizes iodide ions in concentrations in excess of that supplied by the ionisation of silver iodide (105,106,107). An example of an adsorption indicator used to detect the end point was given by Fajans titration of silver with bromide ions and using rhodamine 6 G. Back titrations of excess halide ions are found in the Mohr method when the excess chloride is titrated with a standard solution of silver ions where the precipitation of silver chromate is used to detect the end point (108). Titrations of an excess of iodide is also accomplished by oxidizing the excess iodide to iodine with ferric chloride and then titrating the iodine with a thiosulfate-starch solution (109). If the silver iodide precipitate is separated from the solution with an excess
of iodide ions, either the iodide ion of the precipitate can be determined by first oxidizing it to the iodate ion with an excess of bromine then boil out the excess of bromine and determine the iodate in a thiosulfate-starch titration (110), or the silver ion of the precipitate can be used to displace the nickel in a potassium nickel cyanide complex and the displaced nickel is determined by an EDTA titration with murexide indicator (111).

Optical methods of analysis depend on the adsorption, emission of reflection of electromagnetic radiation which is proportional to the quantity of silver present. The species which absorb electromagnetic radiation can be the metal itself, colored complexes of the metal, or another species which is formed in a quantity proportional to the quantity of silver present. Silver can be determined in amounts from 0.01 to 0.1 ppm by atomic absorption methods (112,113). In this method the metallic ions themselves which have been vaporized in a flame absorb electromagnetic radiations at 338 millimicrons, and the absorption is proportional to the amount of silver present. Silver may also be determined by absorption spectrophotometry. For this purpose the two most used complexing agents are diethyldithiocarbamate and dithiones (83,114). The complexes can be extracted into carbon tetrachloride and the light absorption is proportional to the silver concentrations down to 1 ppm. The light absorbing properties of another compound can also be used to determine the concentration of silver ions when the second compound's concentration is proportional to the silver ion. Silver has a catalytic effect on the oxidation of the manganous ion by the per sulfate ion, and by proper adjustment of the experimental conditions 0.01 micro grams to
0.24 micro grams of silver can be determined (115). Emission spectroscopy has been applied to the determination of very small quantities of silver by D-C arc and flame excitation. Using a D-C arc with a carbon electrode 0.1 micro grams of silver can be determined (117). Flame photometric methods can be used to determine quantities of silver down to 0.01 ppm (118). When the light is partially reflected, turbidimetric methods measure the light transmitted, and nephelometric methods measure the light reflected. The turbidimetric determination of silver was suggested by de Brouckere and Petit. They precipitated the silver as a silver sulfide colloid and used a Dubosq colorimeter (119). Sandell refers to the nephelometric determination of silver when it was precipitated as a colloid of silver chloride (120). This type of determination is applicable to a narrow range of silver concentrations, from $2 \times 10^{-5}$ to $5 \times 10^{-4}$ molar, because the colloid is only stable in this range.

Electrolytic methods can be classified partly by the variables controlled, partly by the variables measured, partly by the mode of mass transfer, and partly by the electrode systems. Reilley and Murray have developed an "operational classification of electroanalytical methods" which includes thirty-three categories (121). These categories are divided among three groups which are methods using potential excitation, methods using current excitations, and methods using titrant excitations. Some examples of potential excitation methods and current excitation methods are found in the historical development of the electrochemistry of silver under constant potential electrodepositions and constant current electrodepositions. The methods of constant potential and constant current electrodepositions rely on the deposition of significant quantities of the silver present. In other current and potential excitation systems an
electrical property of the system is used which is proportional to the concentration of the silver ion concentration, and the proportionality constant is determined by using a series of known concentrations of silver. These methods rely on the rate of transfer of the silver ion through a solution to an electrode, or they rely on the potential gradient developed at an interface: but they do not depend on transfer of significant quantities of silver. Cava and Hume (122) have determined the concentration of silver by polarographic techniques which use less than a tenth of a percent of the silver present to develop a current that is proportional to the concentration of the silver ion. Nisbet and Bard (123) have determined the concentration of silver ion by chronopotentiometric techniques. Rechnits (124) claimed the concentration of silver ions can be determined by metal ion sensitive glass electrodes.

In titrant excitation methods there are two independent systems. The titrant system provides the source for excitation of a response, and the response measuring system excites some property which is proportional to the response of the titrant system that can be recorded. The source for excitation can be a standard solution of some titrant, and the response of the material being titrated at the end point has a sharp change in its concentration. The response measuring system must record this change in concentration by exciting some measurable property of the system which changes when the concentration of the material being titrated changes. If the titrant is a standard solution, the primary name of the titration method is derived from the method of measuring the response. If the titrant is a measured quantity of electricity, it is called a coulometric titration. There are three types of coulometric
titrations with a potentiometric end point for silver. The first method relies on the dissolution of the silver plate from another base metal, and at the end of the coulometric titration the potential of the electrode surface changes from that of a silver electrode to that of the base metal. Examples of determining silver on copper, brass, mild steel and nickel have been demonstrated by Mathur and Karuppanan (125). The second method relies on the reduction of a silver compound on the surface to metallic silver so the potential of the surface changes from that of the silver compound to that of a silver electrode. Campbell and Thomas (126) have determined surface films from less than a monomolecular layer to layers of 1000 angstroms thick of silver sulfide and silver sulfate.

A third method depends on the coulometric production of a titrating agent which causes the disappearance of a species in the solution. The disappearance of this species is recorded by a potential change on an indicating electrode. Anson and his associates (127) have determined an unknown quantity of silver by a coulometric titration with cyanide ions.

In 0.1 F solution of sodium sulfate $\text{Ag}_2(\text{CN})_2$ and $\text{Ag}(\text{CN})_2^-$ are soluble and the $\text{Ag}_2(\text{CN})_2$ controls the potential at the silver indicating electrode when it is present. Cyanide ions are effectively added to the solution by reducing the complexed silver ion to the metal. When the cyanide concentration becomes large enough, all the silver in solution is changed to the $\text{Ag}(\text{CN})_2^-$ complex and the indicating electrodes potential changes to the more negative value. The method used involves a coulometric pretitration of a solution containing $\text{Ag}_2(\text{CN})_2$ and $\text{Ag}(\text{CN})_2^-$ to a potential at the silver indicating electrode corresponding to the depletion of the $\text{Ag}_2(\text{CN})_2$ complex. The potential is measured against a
saturated calomel reference electrode. Addition of an unknown quantity of silver causes $\text{Ag}_2\text{(CN)}_2$ to be formed and the indicating electrode reverts back to the more positive value. The number of equivalents of electricity needed to liberate enough cyanide ions to bring the potential of the indicating electrode back to an equivalent potential value in the pretitration is the number of equivalents of silver added in the unknown.

An amperometric titration of silver using a standard chloride solution was described by Leitinen and Koltzoff (128). The indicating electrode was a rotating platinum micro electrode, and the reference electrode was an external large saturated calomel electrode. The current was measured by the potential drop across a 10,000 ohm resistor. Potentiometric titrations of silver with inorganic as well as organic titrants are followed by a number of indicating electrodes. Koltzoff and Lingane (129) used potassium iodide as the titrant. The indicating electrode was a silver iodide electrode and the reference electrode was a calomel electrode connected through a salt bridge. Meloche and Kalbus (130) used dithio-oxamide as the titrant. The indicating electrode was a silver wire and the reference electrode was a glass electrode. Rechnitz (131) and his co-workers used calcium tetraphenylboron as their titrant. The indicating electrode was a cation sensitive glass electrode and the reference electrode was a calomel electrode. Examples of other methods of following a titration are conductometric methods and high frequency methods. Koltzoff (132) described a conductometric method of following a titration of silver with lithium oxalate. Hara and West (133) described a high frequency method of following a titration of silver (in the
presence of an equal quantity of EDTA) with sodium hydroxide. They were also able to show that the silver EDTA complex was very weak.

Radiochemical methods used in analytical chemistry are classified as methods using neutron activation or methods using radioactive isotopes. The activation analysis of silver depends upon the production of radioactive isotopes in an amount which is proportional to the quantity of silver present.

The sources for neutron activation analysis are listed in Table 2. The production of the neutrons depends on fission type of reactions, or induced radiochemical decay which eliminates a neutron. The radiochemical decay is induced by bombardment of beryllium or tritium with a high energy particle. The particle can come from the radioactive decay of another element such as plutonium or it can be a deuterium ion which has been accelerated in an electrostatic field. The quantity of silver that can be detected by activation with 14 Mev neutrons from a Cockcroft Walton portable source are listed in Table 3. The irradiation times were four times the half life or one hour whichever was the shorter time.

Some examples of activation analysis of silver are found in the following articles. Berlaman (137) determined the amount of silver left on du Pont's film #510 after chemical development and he compared the quantities to densitometer readings. Morris and Killick (138) determined silver in galene-blende which gave a sensitivity of 1 ppm.

Radioactive isotopes are used in three types of analysis. These are tracer analysis, isotope dilution analysis and radiometric analysis. If silver is used as a tracer, the analysis shows where the silver
TABLE 2

Neutron Sources for Neutron Activation Analysis (134, 135)

<table>
<thead>
<tr>
<th>Type of Source</th>
<th>Nuclear Reaction</th>
<th>Fast Flux (n/cm²·sec)</th>
<th>Thermal Flux (n/cm²·sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutron Howitzer</td>
<td>Be⁹(α,n)C¹²</td>
<td>--</td>
<td>10⁴</td>
</tr>
<tr>
<td>Sealed Tube</td>
<td>T(d,n)He⁴</td>
<td>10⁶ to 10⁷</td>
<td>10⁴ to 10⁶</td>
</tr>
<tr>
<td>Van de Graaff</td>
<td>T(d,n)He⁴</td>
<td>4 x 10⁸</td>
<td>1 to 2 x 10⁸</td>
</tr>
<tr>
<td></td>
<td>Be⁹(d,n)B¹⁰</td>
<td>--</td>
<td>5 x 10⁸</td>
</tr>
<tr>
<td>Cockcroft Walton</td>
<td>T(d,n)He⁴</td>
<td>2 x 10⁹</td>
<td>0.5 to 1.0 x 10⁹</td>
</tr>
<tr>
<td>Small Reactor</td>
<td>Fission</td>
<td>--</td>
<td>10¹²</td>
</tr>
</tbody>
</table>

TABLE 3

Sensitivities for Activation Analysis with 14 Mev Neutrons (136)

<table>
<thead>
<tr>
<th>Isotopic Percentage</th>
<th>Isotope Reaction</th>
<th>Half Life (t₁/₂)</th>
<th>Time of Irradiation</th>
<th>Sensitivity (micro grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>51.4%</td>
<td>Ag-109(n,2n)Ag 108</td>
<td>2.3 min</td>
<td>10 min</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>Ag 109(n,p)Pd 109</td>
<td>13.6 hrs</td>
<td>1 hour</td>
<td>1,180</td>
</tr>
<tr>
<td>48.7%</td>
<td>Ag 107(n,2n)Ag 106</td>
<td>24 min</td>
<td>1 hour</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Isotope travels. Frierson and his co-workers (139) used radiotracers in their work on radiocontaminents in biological studies. If isotope dilution methods are applied, the tracer studies can give quantitative information as in Suzuke’s work (140) in the analysis of trace elements in the living body. Radiometric analysis involves tracer methods for the
quantitative determination of materials other than the amount of the radioactive species used. Langer (141) determined the quantity of chloride and bromide in a solution by addition of specific quantities of known amounts of silver solutions that had radioactive isotopes of silver. After each addition, the activity of a portion of the solution is measured and the data are plotted as a function of the added milliliters of the known silver solution. In this way only a few points need be taken before and after the end point, and the two lines drawn between the points before and after the end point may be extrapolated to the end point volume. Goyanes and co-workers (142) used a similar technique for the determination of phosphate and arsenate with a solution of thalium and silver isotopes.

Electrodeposition of silver with a constant current was not favored as a method for quantitatively depositing silver because the cathode potential became more negative as the deposition proceeded. When the potential became negative enough for the deposition of other elements, silver would be contaminated by the co-deposited material. Two methods of preventing the deposition of other elements were by limiting the current density and using a chemical which would limit the cathode potential to a more positive value than that needed for the deposition of another element. Limiting the current density effectively permitted the reduction of silver to proceed at a rate which was less than the limiting current of a voltammetric plot, and at a potential close to the Nernst potential. The chemicals used to limit the potential of the cathode would be reduced to a soluble form or a gas which would not interfere with the deposition of the silver. Adams and Hlaedel (143)
have limited the current to 1 milliamperere and less, and have used ammonium nitrate as the cathodic depolarizer for their separation of silver from copper. They have also pointed out that the reduction of water to hydrogen caused flaky nonadherent deposits, and the nitrate ion was necessary as a cathodic depolarizer to eliminate this trouble.

Since the stripping analysis proceeds at approximately 100 percent, it has been used to define the most accurate value of the Faraday in 1960 by Craig and his co-workers (144), and Rogers and his associates (145) used a stripping analysis to determine electrolytically deposited quantities of silver ranging from $1 \times 10^{-8}$ grams to $5 \times 10^{-10}$ grams. The silver was predeposited by a constant potential exhaustive electrodeposition.

A large number of analytical methods for the determination of silver are reported in the literature. However, examination of the reported analyses for trace amounts of silver in the National Bureau of Standards alloys demonstrates the difficulty of accurately determining silver in the presence of large amounts of other metals. When silver is present in trace amounts, losses by adsorption and interferences from other elements are especially important. In most methods losses due to adsorption of the silver on glass ware or precipitates are not taken into account, and interferences from complex mixtures are difficult to correct.

These sources of error are eliminated by using isotope dilution methods. Salyer and Sweet (36,37,38) determined zinc and cobalt by separation of the element for measurement by electrodeposition, and calculating the total quantity of metal present by isotope dilution calculations using the measurements of activity and mass. This method
was limited only to the time necessary for deposition of enough mass to measure accurately. In addition, a minimum quantity of the element being determined must be present in the unknown in order to use mass measurements. If the number of coulombs could be used to determine the quantity of silver deposited, much smaller quantities of silver could be determined in a much shorter time using the isotope dilution principle.
INTRODUCTION TO THE CURRENT EFFICIENCY STUDIES

Definitions

Faraday's law expresses an exact relationship between the number of coulombs of electricity and number of chemical equivalents. If all the electricity passed was used to deposit silver ions on the electrode, the number of coulombs of electricity passed would be a direct measure of the number of equivalents of silver deposited. The primary objective was to determine the physical, electrochemical and chemical conditions which would permit the application of Faraday's law in the determination of very small quantities of silver that were electrolytically deposited.

Current efficiency and percent current efficiency were used to express the portion of electricity delivered by the coulometer which was used to deposit silver on the cathode. The current efficiency is defined by Equation (1), and the percent current efficiency is defined by Equation (ii).

\[
\text{Current Efficiency} = \frac{\text{Number of equivalents of silver deposited on the electrode}}{\text{Number of moles of electrons that flowed through the electrode}} \quad (1)
\]

\[
\text{Percent Current Efficiency} = (100)\left(\text{Current Efficiency}\right) \quad (ii)
\]

The effects of physical, electrochemical, and chemical properties on the current efficiency were studied by holding all of the variables constant except one. This variable was systematically changed in the
electrolytic cells connected in a series circuit, and prepared solutions were electrolysed. After the cathode was removed from the cell, it was rinsed, and quantity of silver deposited was determined by the change of the electrode mass or the radioactivity on the electrode. The percent current efficiency was then calculated by substituting the moles of electrons the coulometer delivered, and the equivalents of silver deposited into Equations (i) and (ii).

The equivalents of silver deposited was determined from mass measurements by dividing the mass deposited by the equivalent weight of silver, 107.88 grams per equivalent. The equivalents of silver deposited were calculated from the activity measurements by Equation (iii). The tracer solution had an extremely high specific activity.

\[
\frac{\text{Equivalents of Silver Deposited}}{\text{Activity deposited}} = \frac{\text{Equivalents of silver originally present}}{\text{Total activity added}}
\]  

\[(iii)\]

and was treated as a carrier free solution.

**Experimental**

The electrolytic solutions were prepared from reagent-grade chemicals and demineralized double distilled water. The processed high specific activity Ag-110m was purchased from Oak Ridge National Laboratory, and it was checked for radioactive impurities as well as the concentration of silver. High purity nitrogen was obtained from the Liquid Carbonia Company for deaeration of the electrolytic solutions.
The apparatus may be classified into electrodeposition equipment, volumetric ware, mass measuring equipment, radioactivity measuring equipment, and miscellaneous supporting equipment.

The equipment used for the electrodeposition is represented by the block diagram, Figure I. It includes the equipment associated with the electrical circuits, the cells for electrodeposition, and the reservoirs for the electrolytic solutions and wash solutions.

The equipment associated with the electrical circuits included a Leeds and Northrup #7960 Coulometer, a set of resistors with known resistances, a Sargent SR strip recorder or a Varian strip recorder, 18 gauge plastic coated wires, and alligator clips. The coulometer delivered a constant current when it was in operation, and had a time integrated read out register that recorded the number of moles of electrons passed during its operation. The current output was checked by the potential developed across the known series resistances. The potential drop across the resistor was recorded from just prior to the run until just after the run on a strip recorder, and the potential drop was accurately determined periodically with a potentiometric circuit using a Rubicon Student Potentiometer model 2760, a Rubicon galvanometer, and a Weston cell.

The detailed cell assembly is shown in Figure II. Four of the five-cell covers were made from #10-1/2 neoprene rubber stoppers, and the fifth was a polyethylene cover supplied with the Leeds and Northrup #7961 Coulometric Titration Cell Kit. The covers were prepared to hold the electrodes, nitrogen bubblers, glass tubes for rinse water, and to provide an escape hole for the gases. The holes for all the apparatus were bored perpendicular to the bottom of the stopper except the hole
FIGURE I

Block Diagram of Apparatus for Electrodeposition
**Recorder Coulometer**

- Vacuum
- Waste containers
- Reservoir for Electrolyzed solutions
- Electrodeposition cells

**Diagram Components:**
- Recorder
- Coulometer
FIGURE II

Electrodeposition Cell Assembly

List of parts:

1. Ring stand
2. Magnetic stirrer
3. Titration cell which includes
   a. Magnetic stirring bar
   b. Nitrogen bubbler
   c. Clamp
   d. Neoprene rubber stopper
   e. Corks as holders for the anode and cathode
4. Anode
5. Cathode
6. Tygon tube for the nitrogen supply
7. Tygon tube for the rinse water
8. Screw clamp
9. Pinch clamp
10. Reservoir for rinse water
11. Stopcock
12. Tygon sleeve used as a connector between glass tubes
13. Electrolytic solution reservoir which includes
    a. Electrolytic beaker (180 milliliters)
    b. Neoprene rubber stopper
    c. Inlet glass tube from electrolytic cell
    d. Exit tube to the vacuum system
14. Filter flask
15. Vacuum tubing
For the nitrogen bubbler. The hole for the nitrogen bubbler was angled slightly towards the center of the stopper as it was bored from the bottom edge of the stopper. This was done in order to maintain a perpendicular position for the nitrogen bubbler when the cell was assembled. The opening of the hole at the bottom of the stopper would shift towards the center of the stopper as the lower section of the stopper was compressed into the electrolytic beaker. The electrodes were friction fitted into cork stoppers which fitted into the holes of the cell cover. The corks were prepared for the stems of the platinum electrodes by boring a hole with a #2 syringe needle, and cutting a groove in the side of the cork for the anode. This groove was the escape hole for the gases. The cathode was a standard platinum micro-gauze electrode weighing approximately one gram. The anode was a standard platinum quantitative analysis gauze electrode weighing approximately 11.6 grams. The gauze part was 5.2 centimeters high and 3.6 centimeters in diameter. The cell body was a modified 180-milliliter electrolytic beaker with a heavy walled #2 standard tapered stopcock affixed to the bottom side for rapid drainage. The bottom of the beaker was flattened and heat treated to permit the stirring bar to ride more smoothly and prevent the bottom of the cells from breaking. The bottoms of the cells as supplied from the glass companies have many strains in the glass and break easily if not heat treated. The magnetic stirrers were teflon-coated bars 13/16 inches long and 5/16 of an inch in diameter. An asbestos board was placed on top of the magnetic stirrers to prevent the stirrers from heating the electrolytic solutions. These are not shown in the diagram.
The reservoirs were 180-milliliter electrolytic beakers and liter filtering flasks. The 180-milliliter electrolytic beakers were used to catch the partially electrolyzed electrolytic solutions, and the liter filtering flasks were used to catch the rinses. Instead of using a three-way stopcock as was indicated in the block diagram, the vacuum tubing used for draining the cells was manually shifted from the 180-milliliter electrolytic beakers to the electrolytic cell. The electrolytic solutions and the rinse solutions were directed into their respective reservoirs by a vacuum supplied by an aspirator. Other apparatuses not mentioned are standard laboratory equipment.

The volumetric ware included micro pipets made by Misco, "A" grade pipets from 1-milliliter to 50-milliliters made by Kimax, and "A" grade volumetric flasks made of pyrex glass. The solutions were transferred by aid of propipets for the milliliter sizes, and a Hamilton syringe was used with the micropipets. Solutions were stored in Boston Round soft glass bottles fitted with poly seal caps.

A Metler H-5 Analytical Balance with a maximum capacity of 160 grams, and a Metler M-5 Micro Analytical Balance with a maximum capacity of 20 grams were used. A set of masses standardized by the National Bureau of Standards was used for calibration purposes.

The radioactive measuring equipment consisted of survey meters and scintillation measuring equipment. The survey meters included a portable Tracer Lab Alpha-Beta-Gamma Survey Meter Model SU-14, and a Class Master Model #1613A made by Nuclear Chicago. The scintillation equipment included a 2 x 2-inch NaI (Tl) crystal and a 5-inch NaI (Tl) well crystal mounted on photomultipliers supplied by Harshaw. The preamplifier model N352 was made by Hammer for the 2 x 2-inch crystal and
the preamplifier for the 5-inch well crystal was made in the laboratory. The output of the preamplifiers was fed into a scaler made by Radiation Instrument Development Laboratory model 49-54. The connecting cables were shielded coaxial cables.

The miscellaneous supporting equipment included a stroboscopic light made by General Radio Company, a Beckman model G pH meter, a Rubicon Student Potentiometer model 2760, a Rubicon galvanometer, a timer made by Time It, a constant temperature water bath made by Heto, and a Friden Calculator.

The experiments were designed so that only one variable was changed during each series of runs.

The procedure used to prepare each cell for electrodeposition was as follows:

1. Fifty or 100 milliliters of the prepared solution was poured into the 180-milliliter electrolytic cells.

2. The cover of the cell was fastened in position, and the nitrogen gas adjusted with a screw clamp to give a fine stream of bubbles.

3. The magnetic stirrer was turned on to approximately 400 rpm.

4. The electrodes were adjusted so the large anode was a centimeter above the magnetic stirring bar and the small cathode was in the center of the solution. The gauze part of the cathode was just below the agitated surface.

5. The solution was deaerated with nitrogen for half an hour.

6. The stirring rate was adjusted to 400 rpm with a stroboscopic light and the positions of the cathodes were checked.

The procedure for the electrodeposition was as follows:

1. The strip recorder and coulometer were turned to warm up.

2. The wires were connected in series between the cells, the known resistance, the strip recorder, and one lead of the coulometer.
The aspirator was turned on and all stoppers and hoses were checked for air leaks.

A rough check of the electrode positioning, stirring rate, smoothness of stirring, and vacuum was made.

The strip recorder was turned to operation, and the second wire from the coulometer was attached to the first cell completing the series circuit.

The coulometer and an auxiliary timer were turned on for the specific time of the run.

The timer, coulometer, and magnetic stirrers were turned off.

One lead in the series circuit was disconnected and the strip recorder was turned off.

The procedure for the removal of the electrolyzed solution and the subsequent rinses were as follows:

1. The cells were drained of the electrolyzed solution by turning the stopcock of the drain at the bottom of the cell.

2. The vacuum hoses were shifted to the electrolytic cell and the drain stopcocks were closed.

3. The rinse distilled water was allowed to enter from the top until the cell was filled and then the rinse water was directed to the liter filter flasks.

4. Step #3 was repeated.

5. The nitrogen was turned off and the cells were disconnected from the wires, nitrogen tubing, and rinse water tubing.

6. The cells were dismantled and the cathode was put in a counting tube.

7. A couple of milliliters of distilled water was added to the counting tube by directing the stream of water against the side of the counting tube.

8. The electrode was removed from this rinse solution and placed in a fresh, dry counting tube for counting.

The micro-gauge platinum electrodes and all test tubes were cleaned prior to their use as a cathode for the deposition of silver by
the procedure described below. The cleaning procedure was performed in a
hood so that the concentrated nitric acid fumes and small amount of HCN
would be eliminated from the vicinity.

1. Concentrated nitric acid was added to the counting tube until
the level of the nitric acid was a few millimeters above the top of the
gauze part of the electrode.

2. The counting tube was picked up with a brass wire test tube
holding and the contents were heated to boiling over a micro burner. A
shaking in and out of the flame motion prevented the solution from boiling
out of the counting tube.

3. The solution was allowed to cool and it was then discarded
into a radioactive waste bottle.

4. The counting tube was then filled almost to the top with
concentrated nitric acid and the contents were heated to boiling. The
solution was then transferred to a second counting tube with another
electrode for a similar treatment. After all of the counting tubes were
risened with the concentrated nitric acid it was discarded in the above
mentioned waste bottle.

5. All the counting tubes were thoroughly rinsed with distilled
water. The last portion of water was removed by removing the electrode
and inverting the test tube.

6. The KCN-NH₄OH solution (5 grams of KCN, 5 milliliters of
concentrated NH₄OH, and 25 milliliters of water) was added to the first
counting tube until the liquid level was close to the top and it was
heated to boiling. The solution was then transferred to the other test
tubes for the same treatment. After the last test tube was rinsed, the
solution was put in a separate container for basic radioactive wastes.

7. The test tubes were filled with distilled water and the rinse
was discarded in the cup sink of the hood where there was a stream of
water flushing down the contents.

8. The final traces of cyanide were removed by addition of acidifi-
cated water to the test tubes and discarding it in the sink.

9. One more rinse with distilled water was used and the test
tubes were measured for activity in the 5-inch well crystal.
Details about some of the apparatus

The Metler M-5 micro analytical balance is a single pan semi-automatic constant load balance located in an air-conditioned balance room on a specially built table to reduce vibrations. There are four control knobs on the face of the balance which will simultaneously remove masses from the constant load and record the masses removed on a mechanical dial. The mechanically controlled masses were checked against a standard set of masses, and the difference was rarely more than three micro grams. One dial controlled the removal of a ten-gram mass, while the other three dials controlled the removal of 1.0 grams to 9.0 grams, 0.1 grams to 0.9 grams, and 0.01 grams to 0.09 grams, respectively. The illuminated automatic scale registered an amount of mass between 0.0000 grams and 0.0135 grams and a vernier gave the mass between the fifth and sixth place past the decimal point. The values registered on the automatic scale may be in error by as much as 35 micro grams for full-scale deflection. The variation in the number of micro grams was corrected by calibration. The variation was not constant, and changed with the humidity and temperature of the room. Therefore, the sliding scale was calibrated each day.

The Leeds and Northrup Coulometer was standardized according to the procedure described in the pamphlet provided with the instrument. The current output of the instrument was calculated from the potential developed across a standard resistor by means of Ohms Law. The current output was adjustable for the 64.3 milliampere and 6.43 milliampere scale by means of a potentiometer on the rear panel, but there was no
adjustment for the 0.643 milliampere scale. The calculated currents for each of the scales are listed in Table 4.

<table>
<thead>
<tr>
<th>Current Scale (mA)</th>
<th>Temperature °C</th>
<th>Number of NBS Resistor</th>
<th>Resistance (Internal Ohms)</th>
<th>Current Calculated (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>64.330</td>
<td>30.2</td>
<td>534246</td>
<td>10.000</td>
<td>64.330 ± 0.005</td>
</tr>
<tr>
<td>6.4330</td>
<td>30.2</td>
<td>759242</td>
<td>99.952</td>
<td>6.4337 ± 0.0055</td>
</tr>
<tr>
<td>0.64330</td>
<td>30.2</td>
<td>761848</td>
<td>100.52</td>
<td>0.64339 ± 0.00005</td>
</tr>
</tbody>
</table>

The current delivered in each of the experiments was checked by the potential developed across a known resistor which was recorded on a strip chart recorder. The Sargent S3 Recorder registered potentials which deviated less than a percent from the expected value. If the Sargent S3 Recorder was not available, a Varian Recorder was used. The potential value recorded by the Varian Recorder would drift a percent during the electrodeposition. If there was any indication that the coulometer was not operating properly, the exact current was determined by measuring the potential drop across a known resistance with a student potentiometer.

Some of the volumetric ware was calibrated. The class (A) pipets and volumetric flasks were not calibrated. The error in the volume contained in class A flasks was less than 0.3% of the rated volume. The 100-milliliter pipet did not have a class A rating and the volume of solution delivered from the factory etched ring was found on calibration.
to be 99.086 milliliters. The volumes of the micro pipets were found to be within a half of a percent of the rated volumes. The results of calibrating the micro pipets are listed in Table 5.

**Table 5**

Calibration of the Micro Pipets

<table>
<thead>
<tr>
<th>Rated Volume (ml)</th>
<th>Temperature °C</th>
<th>Volume Determined (ml)</th>
<th>Rated Volume (ml)</th>
<th>Temperature °C</th>
<th>Volume Determined (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>25</td>
<td>1.0022</td>
<td>0.100</td>
<td>24</td>
<td>0.1001</td>
</tr>
<tr>
<td>0.900</td>
<td>25</td>
<td>0.9058</td>
<td>0.090</td>
<td>24</td>
<td>0.0905</td>
</tr>
<tr>
<td>0.250</td>
<td>25</td>
<td>0.2495</td>
<td>0.025</td>
<td>24</td>
<td>0.0250</td>
</tr>
<tr>
<td>0.200</td>
<td>24</td>
<td>0.1999</td>
<td>0.020</td>
<td>25</td>
<td>0.0198</td>
</tr>
</tbody>
</table>

The equipment associated with the measuring of the radioactivity consisted of the radioactivity detecting equipment, the counting equipment, and the scales. The detection equipment produces electrical pulses which are proportional in number and size to the decay particles entering the detector. These electrical pulses are transmitted by means of special connectors and coaxial cables to the scaler. The scaler selects and records the pulses of electrical energy which are of interest.

Associated with the detector are the holder for the radioactive sample, a shield to protect the detector from radioactive contamination, metallic absorbers for beta particles, the scintillator to change the detected particles into light pulses, a photomultiplier to change the light pulses into electrical pulses, and a pre amplifier to amplify the electrical pulses for transmission. Figure III is a diagram of the detector assembly associated with the 2 x 2-inch crystal.
FIGURE III

The Detector Assembly
Preamplifier
Power supply
High voltage
Output
Pre Amplifier
Glass cover
Sample holder attached to glass cover
Crystal
Aluminum absorber
Photomultiplier
A 5-inch well crystal was also used. An aluminum cup was fitted into the hole of the well, and this cup acted as the holder, shield, and absorber for the radioactive sample.

The function of the holder was to present the active samples to the crystal in a reproducible geometrical arrangement for the most efficient detection. The movement of the sample in the sample holder was minimized by making the holder just large enough so that the sample vial or counting tube could fit into it. The holder was positioned so the center of activity in the sample coincided with the center of the crystal face. Even though the active sample container could be positioned to within 0.05 centimeters of the same place, the unevenly distributed deposit of silver on the platinum electrode did not permit the activity in the active sample container to be positioned with the same exact geometrical presentation from electrode to electrode. The effect on the count rate of turning the sample container with an active electrode was demonstrated in Table 6.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Rotation of the Stem of the Electrode</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0° (c/m)</td>
<td>90° (c/m)</td>
<td>180° (c/m)</td>
<td></td>
</tr>
<tr>
<td>2 x 2-inch</td>
<td>26,787</td>
<td>26,492</td>
<td>26,138</td>
<td></td>
</tr>
<tr>
<td>5-inch well</td>
<td>150,167</td>
<td></td>
<td>149,956</td>
<td></td>
</tr>
</tbody>
</table>
The variation of the count rate was as high as 2.5 percent when the electrode was turned 180 degrees in the sample holder of the 2 x 2-inch crystal holder, but the variation of the count rate in the well crystal was insignificant. Another important geometrical difference was the larger solid angle of the radioactive particles reaching the 5-inch well crystal than the 2 x 2-inch crystal, and this was manifested in the six-fold increase in the counting efficiency for the 5-inch well crystal.

It was not advisable to measure count rates of much over 200,000 counts per minute, and the lower counting efficiency of the 2 x 2-inch crystal permitted the measurement of samples which were too active to measure on the 5-inch well crystal. When the 2 x 2-inch crystal was used a sample was picked which could be accurately measured on the 5-inch well crystal, and it was used to obtain a conversion factor to correct the count rates of the highly active samples measured on the 2 x 2-inch crystal to comparable count rates on the 5-inch well crystal. The geometry of the sample used for obtaining the conversion factor was as close as possible to the geometry of the highly active samples. In the cases where the activity was deposited on an electrode, the stems of the electrodes were all turned towards the crystal face.

The 5-inch well crystal eliminated the counting variation in the horizontal plane, but there was a counting variation associated with the vertical position of the radioactive sample. The count rate of a sample was measured as a function of its distance from the bottom of the 5-inch well crystal, and the results were plotted in Figure IV. The variation in terms of the percent difference from the highest value measured was listed on the axis opposite the count rate in Figure IV.
FIGURE IV

The Height of a Sample in the Well Crystal vs the Count Rate or Percent Decrease in the Count Rate
The purpose of the absorbers was to eliminate any variation due to absorption of the weaker beta particles by the platinum electrode. Since the deposit had been shown to be non-symmetrical, there was the possibility that a difference in the distribution of the deposits on two electrodes might cause a difference in absorption of the weak beta particles.

The crystal is mounted in a container with a thin aluminum window on one end and an optical glass window on the other end which fits against the photomultiplier. If no sealing material or dirt gets between the crystal and the photomultiplier and no light leaks appear, the crystal should operate as it was designed. The radiations which get into the crystal can be regulated by the geometry, type of shielding, and position of the crystal.

The correct operating potential for the photomultiplier was determined by the manufacturer. The correct potential provided linear amplification of the original pulse from the photo-electrical emitter on the face of the photomultiplier. If the tube is operated at too high a voltage, some stages in the photomultiplier may arc; and the operation of the tube will become erratic. If the potential is too low, the electrical pulses are not linearly amplified.

The electrical pulses from the photomultiplier are amplified again by a pre-amplifier attached to the photomultiplier socket and sent to the scaler. The scaler has another amplifier which has a range of amplifications (1, 1/4, 1/2, 1/8, 1/16) that can be set by a dial on the front of the instrument, and a setting of 1/8 was chosen. Pulses associated with meaningless radiations of low energies are eliminated by proper
adjustment of the discriminator. The following procedure was used to determine the correct setting of the discriminator:

1. A series of counts of the background were taken with the discriminator set at zero and intervals of 0.50 until 10.00 was reached.

2. A series of counts of the active silver were taken with the same settings.

3. A ratio of the counts of the silver sample to the background counts for each discriminator setting were calculated and plotted as a function of the discriminator setting.

4. Steps 1 through 3 were repeated in the range of the maximum at intervals of 0.25 units.

5. The discriminator setting which gave the maximum ratio was used.

The crystal and the photomultiplier are capable of producing much higher pulse rates than the scaler is capable of registering. Since the dead time of the scaler was given as 0.5 micro seconds or \(8.333 \times 10^{-8}\) minutes, the true number of counts were calculated according to Equation (iv).

\[
R^f = \frac{R}{1 - R\tau}, \quad \text{(iv)}
\]

where \(R^f\) is the true count rate, \(R\) is the count rate measured, and \(\tau\) is the dead time. After subtracting the background, \(R^f\) should give the correct rate within 0.5 percent of the actual value for count rates as high as 200,000 counts per minute.

The over-all precision of the radioactive measurements was demonstrated in Table 7 by the calculation of the activity of a stock solution in terms of the activity per lambda. The errors which entered into the calculated activity per lambda of the stock solution were volumetric
errors, transfer errors, absorption errors, and radioactive measuring errors.

### TABLE 7

Evaluating Radioactivity Metering and Measuring Procedure

<table>
<thead>
<tr>
<th>Volume of Activity (ml)</th>
<th>R (c/m)</th>
<th>R' (c/m)</th>
<th>Corrected for Background (c/m)</th>
<th>Activity per Lambda</th>
<th>Absolute Deviation from Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>24,815.3</td>
<td>24,866</td>
<td>24,330</td>
<td>973.20</td>
<td>3.12</td>
</tr>
<tr>
<td>70</td>
<td>67,597.3</td>
<td>67,979</td>
<td>67,443</td>
<td>963.47</td>
<td>6.61</td>
</tr>
<tr>
<td>80</td>
<td>77,666.2</td>
<td>78,171</td>
<td>77,655</td>
<td>970.43</td>
<td>0.35</td>
</tr>
<tr>
<td>90</td>
<td>87,247.8</td>
<td>88,495</td>
<td>87,959</td>
<td>977.32</td>
<td>7.24</td>
</tr>
<tr>
<td>100</td>
<td>96,752.6</td>
<td>97,539</td>
<td>97,003</td>
<td>979.03</td>
<td>0.05</td>
</tr>
<tr>
<td>200</td>
<td>190,666.8</td>
<td>193,745</td>
<td>193,209</td>
<td>966.05</td>
<td>4.03</td>
</tr>
</tbody>
</table>

Average 970.08 3.57

Therefore, the average deviation can be expected to be within 3.7 parts per thousand or within 0.4 percent of the average value and the standard deviation was 4 parts per thousand.

**Evaluation of the Methods for Measurement of the Silver Deposited**

The quantity of silver deposited during any one analysis was very small, and therefore a small deviation in the measurement of the quantity of silver deposited could cause a large relative error. The methods of measuring the quantity of silver deposited by radioactive measurements and mass measurements were evaluated.

Whenever a sample was measured for activity, a standard was measured under the same conditions. The standard was used to correct for any variations in the counting efficiency of the detection system, and
the decay of the radioactive isotope. Three types of standards made and
tested were a dried aliquot in a test tube, a five milliliter aliquot in
a 3-dram sealed vial, and a liquid aliquot in a sealed counting tube.

If the standard was a dried aliquot of the radioactive silver
solution on the bottom of a test tube, and the silver deposit was dis-
tributed over the gauge of the electrode, the center of activity of the
standard was lower than the center of activity of the deposited silver.
According to the variation in count rate due to the height of the activity
in the well (see Figure IV), the counting efficiency for the standard
should be slightly higher than the counting efficiency of the deposited
silver. This geometrical variation could be eliminated if the activity
was presented to the detector in the same shape and form as the standard.
This was accomplished by preparing a 5-milliliter aliquot of the dis-
solved silver from the electrode in a 3-dram screw cap vial. The
standard was five milliliters of acidified silver nitrate solution with a
measured quantity of the radioactive stock solution in a similar vial.
The procedure for removal of the silver activity from the electrode was
as follows:

1. One and a half milliliters of concentrated nitric acid was
added to the counting tube with the active electrode, and heated to a
boil.

2. The solution was transferred to a 10-milliliter volumetric
flask with the aid of a small funnel. The lip of the counting tube and
the funnel were rinsed with a few drops of nitric acid.

3. Step 1 was repeated with a few drops of 0.1 molar silver
nitrate added in addition to the nitric acid.

4. Step 2 was repeated.

5. Steps 1 and 2 were repeated twice more.
6. The flask was stoppered and allowed to cool for a few hours.

7. The volume of the solution was adjusted to the ten milliliter mark, and five milliliters were pipeted into a 3-dram screw cap vial.

The electrodeposited silver from $1 \times 10^{-3}$ molar silver nitrate at a current density of 0.306 milliamperes per square centimeter was used in the evaluation of the method for measuring the quantity of silver deposited. The three methods of measuring the quantity of silver deposited were measurement of the activity of the metallic silver deposit, the determination of the activity of an aliquot of dissolved silver, and measurement of the mass of the silver deposited. The effect of the duration of the run and the concentration of the sodium nitrate are discussed later in this section.

The percent current efficiencies calculated from the activity of the silver deposit and the activity of the aliquot of dissolved silver are summarized in Table 8.

### TABLE 8

The Current Efficiency Calculated from Activity Measurements of the Metallic Deposits and Dissolved Activity

<table>
<thead>
<tr>
<th>From Electrode Activity (percent)</th>
<th>From Solution Activity (percent)</th>
<th>From Electrode Activity (percent)</th>
<th>From Solution Activity (percent)</th>
<th>From Electrode Activity (percent)</th>
<th>From Solution Activity (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>94.6</td>
<td>91.3</td>
<td>97.8</td>
<td>95.1</td>
<td>94.3</td>
<td>89.6</td>
</tr>
<tr>
<td>96.5</td>
<td>98.5</td>
<td>97.2</td>
<td>97.3</td>
<td>95.2</td>
<td>88.8</td>
</tr>
<tr>
<td>92.5</td>
<td>93.3</td>
<td>93.0</td>
<td>93.5</td>
<td>94.2</td>
<td>94.2</td>
</tr>
<tr>
<td>95.6</td>
<td>96.5</td>
<td>92.9</td>
<td>94.3</td>
<td>94.0</td>
<td>96.5</td>
</tr>
<tr>
<td>90.5</td>
<td>90.1</td>
<td>97.7</td>
<td>100.3</td>
<td>97.7</td>
<td>100.2</td>
</tr>
<tr>
<td>82.6</td>
<td>82.1</td>
<td>95.8</td>
<td>97.5</td>
<td>95.8</td>
<td>97.9</td>
</tr>
<tr>
<td>80.1</td>
<td>73.0</td>
<td>97.0</td>
<td>97.5</td>
<td>96.2</td>
<td>97.4</td>
</tr>
<tr>
<td>131.4</td>
<td>128.7</td>
<td>99.2</td>
<td>98.2</td>
<td>101.2</td>
<td>99.7</td>
</tr>
<tr>
<td>114.3</td>
<td>109.2</td>
<td>98.3</td>
<td>99.0</td>
<td>97.6</td>
<td>98.7</td>
</tr>
</tbody>
</table>
From these data it is apparent that—

1. Eleven runs had higher calculated percent current efficiencies using the activity measurements of the metallic deposit.

2. Fifteen runs had higher calculated percent current efficiencies using the activity measurements from the aliquot of dissolved silver.

3. One run had the same calculated current efficiency from the measurements of the activity from the metallic silver deposit and the aliquot of dissolved silver deposit.

4. When the current efficiencies were higher using the measurements from the solutions, the percent current efficiencies ranged from 0.1 percent to 2.6 percent higher.

5. When the current efficiencies were higher using the measurements from the metallic deposits, the percent current efficiencies ranged from 0.4 percent to 7.1 percent higher.

The larger absolute values of the percent current efficiencies represented by the measurement of the activity of the metallic deposit can be attributed to experimental errors. Since the overall average of each of the two methods did not differ significantly, the method of dissolving the activity from the electrode was discontinued.

The third type of standard was a liquid aliquot in a sealed counting tube. It was prepared in the following way:

1. A test tube was thoroughly cleaned so the liquid drops would not adhere to the sides of the test tube.

2. The open end was constricted and drawn out in the form of a neck.

3. The following solutions were added: 0.5 ml of dilute nitric acid, five drops of 0.1 molar silver nitrate, an aliquot of the radio-active stock solution, two rinses of the pipet used to deliver the active isotope, and concentrated nitric acid to raise the level of the liquid to the top of the gauze part of the micro-platinum gauze electrode placed in a similar adjacent test tube.

4. The neck of the test tube was sealed with an oxygen torch.
The advantages of this type of standard were that--

1. The geometry of the active standard is approximately the same as the geometry of the radioactive silver deposited on the electrode.

2. The geometry of the sample activity does not change due to reduction by foreign matter in some specific area of the test tube (e.g., the paper liners of the screw caps, cork stoppers, or dust particles).

3. The percentage of active silver adsorbed on the walls of the test tube is very small as a result of the large amount of carrier present.

The dried aliquot type of standard was used in the early part of this investigation and the results were comparable to the results using the sealed aliquot type of standard. However, the sealed aliquot standard was used after it was developed.

The current efficiencies were calculated from the mass measurements of the same silver deposits used in the calculation of the current efficiencies in Table 8. The masses were obtained by the difference of the weight of the electrodes before and after the removal of the silver. Before each weighing, the electrodes were dried by rinsing them with absolute alcohol and irradiating them with an infrared lamp for 15 minutes. After they came to temperature equilibrium in the balance room, they were placed on a plastic support which rested on the balance pan. The plastic support was used to prevent any direct contact of the balance with the radioactive deposit. The percent current efficiencies were calculated by dividing the observed mass by the mass calculated from the number of coulombs of electricity passed, and then multiplying the quotient by 100.

The percent current efficiencies calculated by the mass measurements were plotted as a function of the duration of the run in Figure V.
and the percent current efficiencies calculated from the radioactivity
measurements of the deposits were plotted as a function of the duration
of the run in Figure VII. The following observations were made by
examination of these plots:

1. The deviations from 100 percent current efficiency were
   negative when the mass measurements were used.

2. With a few exceptions the deviations from 100 percent current
   efficiency were negative when the radioactive measurements were used.

3. The positive deviations from 100 percent current efficiency
   obtained by mass measurement were larger than the negative deviations
   from 100 percent current efficiency obtained by activity measurements for
   the electrolytic depositions which lasted five minutes or less and were
   in solutions with added sodium nitrate.

4. The positive deviations from 100 percent current efficiency
   decreased as the total quantity of mass deposited increased.

5. The negative deviations from 100 percent current efficiency
   increased slightly as the total quantity of silver deposited increased.

By calculating the quantity of mass associated with the number
of coulombs of electricity delivered, and subtracting this mass from the
mass measured, an excess quantity of mass was found in the deposit. The
excess quantity of mass and its effect on the calculation of the current
efficiency for deposition where the total quantity of mass varied by
twenty fold are summarized in Table 9.
FIGURE V

The Percent Current Efficiency as a Function of Time Calculated from the Activity of the Deposit

Shows the effect of the concentration of the supporting electrolyte
% Current efficiency

Time (min.)

- 1.0 M NO₃⁻
- 0.1 M NO₃⁻
- X-0.002 M NO₃⁻

[Ag⁺] = 1 x 10⁻³
FIGURE VI

The Percent Current Efficiency as a Function of Time
Calculated from the Mass of the Deposit

Shows the effect of the concentration
of the supporting electrolyte
\[ [\text{Ag}^+] = 1 \times 10^{-3} \]
TABLE 9

The Effect of Additional Mass on the Current Efficiency

<table>
<thead>
<tr>
<th>Number of Equivalents of Electricity Passed (micro equivalents)</th>
<th>The Mass of Silver Equivalent to the Number of Equivalents of Electricity Passed (micro grams)</th>
<th>Mass of Silver Deposited (micro grams)</th>
<th>Difference of Mass (micro grams)</th>
<th>Current Efficiency (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.202</td>
<td>21.8</td>
<td>32</td>
<td>10.2</td>
<td>147</td>
</tr>
<tr>
<td>0.202</td>
<td>21.8</td>
<td>31</td>
<td>9.2</td>
<td>142</td>
</tr>
<tr>
<td>0.202</td>
<td>21.8</td>
<td>30</td>
<td>8.2</td>
<td>138</td>
</tr>
<tr>
<td>0.401</td>
<td>43.2</td>
<td>54</td>
<td>10.8</td>
<td>125</td>
</tr>
<tr>
<td>0.401</td>
<td>43.2</td>
<td>44</td>
<td>0.8</td>
<td>102</td>
</tr>
<tr>
<td>0.401</td>
<td>43.2</td>
<td>53</td>
<td>9.8</td>
<td>122</td>
</tr>
<tr>
<td>0.802</td>
<td>86.3</td>
<td>74</td>
<td>-8.7</td>
<td>86</td>
</tr>
<tr>
<td>0.802</td>
<td>86.3</td>
<td>91</td>
<td>4.7</td>
<td>105</td>
</tr>
<tr>
<td>0.802</td>
<td>86.2</td>
<td>85</td>
<td>-0.7</td>
<td>99</td>
</tr>
<tr>
<td>1.602</td>
<td>173</td>
<td>198</td>
<td>25</td>
<td>114</td>
</tr>
<tr>
<td>1.602</td>
<td>173</td>
<td>187</td>
<td>14</td>
<td>108</td>
</tr>
<tr>
<td>1.602</td>
<td>173</td>
<td>196</td>
<td>23</td>
<td>113</td>
</tr>
<tr>
<td>2.002</td>
<td>216</td>
<td>241</td>
<td>25</td>
<td>112</td>
</tr>
<tr>
<td>2.002</td>
<td>216</td>
<td>226</td>
<td>10</td>
<td>105</td>
</tr>
<tr>
<td>2.002</td>
<td>216</td>
<td>222</td>
<td>6</td>
<td>103</td>
</tr>
<tr>
<td>4.001</td>
<td>432</td>
<td>435</td>
<td>3</td>
<td>100.7</td>
</tr>
<tr>
<td>4.001</td>
<td>432</td>
<td>444</td>
<td>12</td>
<td>103</td>
</tr>
<tr>
<td>4.001</td>
<td>432</td>
<td>447</td>
<td>15</td>
<td>104</td>
</tr>
</tbody>
</table>
From the data in Table 9 it is apparent that--

1. The overall averaged quantity of excess mass was 10 micro grams.

2. The excess mass for the smallest quantity of silver deposited and the largest quantity of silver deposited was approximately 10 micro grams.

3. The quantity of excess mass became less significant in the calculation of percent current efficiency as the total mass increased.

Since there was approximately 10 micro grams of excess mass in the deposits whose total mass increased 20 fold, the most likely place the mass was entrapped was at the metallic interface. If excess mass was entrapped in the silver deposit, there should have been a systematic increase in the quantity of mass entrapped with an increase of the quantity of silver deposited.

The method of mass measurements was not used to determine the quantity of silver deposited, because of the inaccurate measurements associated with small quantities of mass.
CHAPTER V

THE EFFECTS OF PHYSICAL, ELECTRICAL, AND CHEMICAL
PROPERTIES ON THE PERCENT CURRENT EFFICIENCY

The effect of the presence of platinum oxide on the cathode

If a layer of platinum oxide was formed on the cathode surface, the platinum oxide would be reduced prior to the reduction of the silver. The number of equivalents of platinum oxide per square centimeter was determined under different conditions by Anson and Lingane (146). The oxide layer was formed by anodic oxidation or chemical oxidation of platinum sheets with Ce(SO₄)₂, Ce(ClO₄)₂, and AgO. In some of their experiments anodic oxidation was allowed to proceed until the potential of the electrode reached 1.23 volts (vs a saturated calomel electrode). Anson and Lingane determined that a mono layer of platinum oxides covered the surface when the potential reach this value. If the anodic oxidation was allowed to continue, a maximum quantity of platinum oxides would be formed. The same maximum quantity of platinum oxides was formed by a strenuous chemical oxidation. The amount of platinum oxide formation was analysed by stripping the platinum oxides from the surface of the platinum in the form of chloroplatinates, and the chloroplatinates were determined spectrophotometrically. The residual amount of oxides which did not strip from the surface were determined coulometrically. If the surface of the platinum micro-gauge electrode used in the present
work was completely covered with a platinum oxide coating, the percentage of the current that would be used to reduce this coating was calculated by Equation (v) and is given in Table 10.

\[
\text{Percentage of current used for reduction of platinum oxides} = \frac{(\text{Equivalents/cm}^2)(\text{Area of the electrode})(100)}{(\text{Equivalents of electricity used in the determination})} \tag{v}
\]

The surface of the electrode was 2.1 square centimeters, and 0.40 micro equivalents of electricity was generally used for an analysis.

\begin{table}
\centering
\caption{The Effect of Platinum Oxide on the Current Efficiency}
\begin{tabular}{lcc}
\hline
Method of Production & Equivalents/cm$^2$ & Current Used in the Reduction of Platinum Oxides \\
\hline
Anodic oxidation (Mono layer formation) & $6.91 \times 10^{-9}$ & 3.6\% \\
Chemical or anodic oxidation (Maximum formation) & $12.1 \times 10^{-9}$ & 6.3\% \\
\hline
\end{tabular}
\end{table}

Since the silver was removed from the electrode by a chemical oxidation with concentrated nitric acid, the formation of platinum oxide coatings was very probable. However, the ammonium hydroxide-potassium cyanide treatment most probably stripped all the platinum oxides from the surface.

The decrease in the current efficiency due to the formation of platinum oxide was investigated. All of the electrodes were cleaned according to the procedure on page 38, and then the electrodes were
boiled in a fresh solution of ammonium hydroxide-potassium cyanide solution followed by the treatments described in Table II. After these treatments they were rinsed with demineralised double distilled water and used in the electrolysis of a silver nitrate solution at a current density of 0.306 milliamperes per square centimeter for one minute.

**TABLE II**

The Effect of Platinum Oxide Formation on the Current Efficiency

<table>
<thead>
<tr>
<th>Trial Number</th>
<th>Electrode Treatment</th>
<th>Duration of Treatment (minutes)</th>
<th>Concentration of Silver Nitrate Electrolyzed (moles/liter)</th>
<th>Current Efficiency (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Boiled in conc. HNO₃</td>
<td>1.0</td>
<td>$1 \times 10^{-4}$</td>
<td>74.4</td>
</tr>
<tr>
<td>(2)</td>
<td>Room temp. conc. HNO₃</td>
<td>0.1</td>
<td>$1 \times 10^{-4}$</td>
<td>92.5</td>
</tr>
<tr>
<td>(3)</td>
<td>Room temp. dil. HClO₄</td>
<td>1.0</td>
<td>$1 \times 10^{-4}$</td>
<td>93.6</td>
</tr>
<tr>
<td>(4)</td>
<td>Boiled in conc. HNO₃</td>
<td>1.0</td>
<td>$1 \times 10^{-3}$</td>
<td>96.0</td>
</tr>
<tr>
<td>(5)</td>
<td>Room temp. conc. HNO₃</td>
<td>0.5</td>
<td>$1 \times 10^{-3}$</td>
<td>97.7</td>
</tr>
<tr>
<td>(6)</td>
<td>Room temp. dil. HClO₄</td>
<td>1.0</td>
<td>$1 \times 10^{-3}$</td>
<td>97.7</td>
</tr>
</tbody>
</table>

Evidence that there is a decrease in current efficiency caused by processes other than the reduction of platinum oxides was supported by the following observations from Table II:

1. The decrease in the current efficiency for all of the depositions made from $1 \times 10^{-4}$ molar silver nitrate was larger than the maximum expected according to Table 10.
2. Treatment of platinum surfaces with concentrated nitric acid at room temperature did not significantly decrease the current efficiency for the deposition of silver.

3. The decrease in the current efficiency by decreasing the concentration of silver nitrate was larger than the decrease expected from reduction of platinum oxides.

When the electrode was prepared according to the procedure regularly used throughout this work (see Table 11, No. 5), the maximum quantity of platinum oxides on the surface of the cathode should be less than a mono layer because the 2.3 percent decrease in the current efficiency from the $1 \times 10^{-3}$ molar silver nitrate solution was less than the 3.6 percent decrease expected if the surface was covered with a mono layer of platinum oxides.

The effects of other metallic surfaces

A metallic surface that would be useful for the deposition of silver should meet the following requirements: the surface must be as noble or more noble than silver, the silver deposit must be removable from the metal, and the metal must be available. If the metal was less noble than silver, some silver would be deposited by internal electrolysis prior to the coulometric electrodeposition. Gold is more noble than silver, but alloys of silver and gold could form (147) which would cause difficulties in removal of the deposited silver. A silver surface was the only other surface besides platinum that would meet the above requirements.

A silver surface should be superior to any other surface, because the basic lattice for growth was present. This condition should permit
a very adherent deposit to form, and eliminate to a large extent entrapment of foreign materials.

Since silver is a noble metal, one might expect the surface to be inert. Rollin (148) demonstrated that an exchange took place in two hours between the silver ions in a 0.03 molar silver nitrate solution and 10 atomic layers of a silver electrode. If a similar solution of 0.03 molar silver nitrate was made 0.3 molar in sodium nitrate, an exchange took place in one hour between the silver ions in solution and 100 to 150 atomic layers of the silver electrode. He was unable to explain this increase in rate of exchange. Gerschler and Tischer (149,150) studied the exchange of silver between silver perchlorate solutions and silver surfaces. They found that two atomic layers of the silver exchanged in ten minutes at 0°C, and four atomic layers of silver exchanged in ten minutes when the temperature ranged from 25°C to 65°C. Increasing the time of the exchange only caused a small increase in the number of layers which exchanged. They also pointed out that there was a high exchange current at the electrode surface which was 0.15 (± 0.02) amperes per square centimeter for 1 x 10⁻³ molar silver perchlorate solutions. The exchange rate increased with an increase in the concentration.

The method of isotope dilution relies on the separation of a known quantity of silver, and the separated silver must have a specific activity which is a function of the silver originally present and the silver added by the radioactive tracer. The exchange reaction from an inactive silver electrode would preclude the use of isotope dilution methods because the specific activity of silver in solution would be altered. However, if the specific activity of the solution was the same
as the specific activity of an adherent coat of silver deposited on an electrode, the method of isotope dilution could be used. In this procedure, the base material for the analysis must be predeposited from the solution to be analysed, cleaned of any loose material, and its activity measured. The difference in the activity between the base coat and the final coat would be the activity deposited during the analysis, and the quantity of silver deposited in the analysis could be obtained by mass measurements or the number of coulombs of electricity used. This method involving predeposition was not used because it would increase the quantity of silver needed for a determination and decrease the accuracy. The lower limit of the quantity of silver that could be determined would be raised because there would have to be enough silver in the solution to deposit two coats of silver without the current efficiency changing drastically. The quantity of activity associated with the deposit for analysis would be the difference of two activity measurements, and this would be less accurate than either of the measured activities.

The effect of adsorbed silver on a platinum surface

The cleaned platinum micro-gauge electrodes were introduced into radioactive solutions of silver for 20 minutes. During this time the solutions were stirred with a magnetic stirring bar, and they were continuously deaerated with high purity nitrogen. At the end of 20 minutes the active solutions were removed from the electrodes, and the electrodes were rinsed two times in the cells with distilled water. No electrical contacts were made to the electrodes during the above procedure. The electrodes were then removed from the cells, the stems of the electrodes
were rinsed with distilled water that flowed off the stem end, and the activity of the electrodes were measured. The adsorption of silver on the platinum was measured as a function of the silver ion concentration in sodium sulfate and sodium nitrate solutions. The silver ion concentration, specific activity of the silver, activity adsorbed, and grams adsorbed are listed in Table 12 for silver sulfate solutions, and in Table 13 for silver nitrate solutions. If the adsorbed silver ions were entrapped and not reduced in a 0.4 micro equivalent electrodeposition, the increase in the current efficiency that would be expected was included in these tables.

**TABLE 12**

The Effect of Adsorbed Silver on the Current Efficiency

The Silver Was Adsorbed on a Platinum Surface from a Sulfate Solution

<table>
<thead>
<tr>
<th>Trial No.</th>
<th>Silver Concentration (moles/liter)</th>
<th>Specific Activity (c/min-gram)</th>
<th>Activity Adsorbed (c/min)</th>
<th>Grams Adsorbed</th>
<th>Current Efficiency Increase in 0.40 Micro Equivalents of Silver (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.0 \times 10^{-3}$</td>
<td>$5.0 \times 10^8$</td>
<td>989.6</td>
<td>$2.0 \times 10^{-6}$</td>
<td>4.5</td>
</tr>
<tr>
<td>2</td>
<td>$1.0 \times 10^{-3}$</td>
<td>$5.0 \times 10^8$</td>
<td>711.1</td>
<td>$1.4 \times 10^{-6}$</td>
<td>3.3</td>
</tr>
<tr>
<td>3</td>
<td>$1.0 \times 10^{-4}$</td>
<td>$5.0 \times 10^8$</td>
<td>286.0</td>
<td>$5.7 \times 10^{-7}$</td>
<td>1.3</td>
</tr>
<tr>
<td>4</td>
<td>$1.0 \times 10^{-5}$</td>
<td>$5.0 \times 10^8$</td>
<td>229.2</td>
<td>$4.6 \times 10^{-7}$</td>
<td>1.1</td>
</tr>
<tr>
<td>5</td>
<td>$1.0 \times 10^{-3}$</td>
<td>$5.0 \times 10^8$</td>
<td>1,011.9</td>
<td>$2.0 \times 10^{-6}$</td>
<td>4.6</td>
</tr>
</tbody>
</table>
The ratio of the sulfate ion concentration to the silver ion concentration was 100 to 1 for the experiments 1 through 4, and it was 1000 to 1 for experiment 5. The sulfate ion concentration was adjusted with sodium sulfate in the first four experiments, and it was adjusted by ionisation of 1 molar copper sulfate in the last experiment.

The observations from the results in Table 12 were—

1. The amount of silver adsorbed on the platinum electrode from a sodium sulfate solution increased with the concentration of silver.

2. If the adsorbed silver was entrapped and not reduced, the increase in the percent current efficiency would be about 1.0 percent to 4.5 percent for a 0.40 micro equivalent deposit of silver in the range of silver sulfate concentrations studied.

3. The presence of 1 molar copper sulfate did not affect the adsorption of silver ions.

**TABLE 13**

The Effect of Adsorbed Silver on the Current Efficiency

The Silver Was Adsorbed on a Platinum Surface from a Nitrate Solution

<table>
<thead>
<tr>
<th>Trial No.</th>
<th>Silver Concentration (moles/liter)</th>
<th>Specific Activity (c/min-g)</th>
<th>Activity Adsorbed (c/min)</th>
<th>Grams Adsorbed</th>
<th>Current Efficiency Increase in 0.40 Micro Equivalents of Silver (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.40 x 10^{-5}</td>
<td>5.18 x 10^9</td>
<td>2,495</td>
<td>4.7 x 10^{-7}</td>
<td>1.11</td>
</tr>
<tr>
<td>2</td>
<td>9.40 x 10^{-5}</td>
<td>5.18 x 10^9</td>
<td>2,404</td>
<td>4.6 x 10^{-7}</td>
<td>1.07</td>
</tr>
<tr>
<td>3</td>
<td>4.96 x 10^{-4}</td>
<td>1.04 x 10^9</td>
<td>338.2</td>
<td>3.3 x 10^{-7}</td>
<td>0.75</td>
</tr>
<tr>
<td>4</td>
<td>1.09 x 10^{-3}</td>
<td>5.18 x 10^8</td>
<td>1,147</td>
<td>2.2 x 10^{-6}</td>
<td>5.1</td>
</tr>
<tr>
<td>5</td>
<td>1.64 x 10^{-3}</td>
<td>3.46 x 10^8</td>
<td>126.0</td>
<td>3.7 x 10^{-7}</td>
<td>0.84</td>
</tr>
<tr>
<td>6</td>
<td>2.20 x 10^{-3}</td>
<td>2.59 x 10^8</td>
<td>185.6</td>
<td>7.2 x 10^{-7}</td>
<td>1.7</td>
</tr>
</tbody>
</table>
The solutions which were used to study the adsorption of silver ions from a nitrate solution were 1 molar in cupric nitrate. The contact time was increased to one hour for all of these solutions.

The observations from the results in Table 13 were—

1. The quantity of silver adsorbed was relatively constant for a 20-fold change in the concentration of silver nitrate.

2. If the adsorbed silver was entrapped and not reduced, the increase in the percent current efficiency would be approximately 1 percent for a 0.40 micro equivalent deposit of silver in the range of silver nitrate concentrations studied.

3. The quantity of silver adsorbed from a nitrate solution was generally much smaller than the quantity of silver adsorbed from a sulfate solution.

The effect of the presence of adsorbed silver on a silver surface

Since there are many references in the literature regarding the concentration of adsorbed silver ions on a silver surface, the concentration of adsorbed silver ions on silver was not determined in the present work. The majority of the studies claim that the silver ion concentration adsorbed on a silver surface is relatively constant for the range of silver concentrations studied. King and Schochet demonstrated that this was only true if the concentration of the silver salt was high enough. Figure VII was constructed from the data of King and Schochet (151). The data which a number of investigators reported as the concentration of adsorbed silver on a silver surface are summarized in Table 14, and the increase in the percent current efficiency for a 0.40 micro equivalent deposit on 2.1 square centimeters of silver are included.
TABLE 14

The Effect of Adsorbed Silver on the Current Efficiency

The Silver Was Adsorbed on a Silver Surface from Various Solutions

<table>
<thead>
<tr>
<th>Reference</th>
<th>Salt</th>
<th>[Ag⁺]</th>
<th>Method of Measurement</th>
<th>Concentration (moles/cm²)</th>
<th>Increase in Current Efficiency (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mehl &amp; Bockris (152)</td>
<td>AgClO₄</td>
<td>0.1</td>
<td>Chronopotentiometric</td>
<td>90 x 10⁻¹¹</td>
<td>0.46</td>
</tr>
<tr>
<td>Gerischer (153)</td>
<td>AgClO₄</td>
<td>0.1</td>
<td>Chronopotentiometric</td>
<td>20 x 10⁻¹¹</td>
<td>0.11</td>
</tr>
<tr>
<td>Despic &amp; Bockris (154)</td>
<td>AgClO₄</td>
<td>0.1</td>
<td>Chronopotentiometric</td>
<td>3 x 10⁻¹¹</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>160 x 10⁻¹¹</td>
<td>0.8</td>
</tr>
<tr>
<td>King &amp; Schochet (151)</td>
<td>AgClO₄</td>
<td>0.1</td>
<td>Titration</td>
<td>100 x 10⁻¹¹</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>AgClO₄</td>
<td>0.01</td>
<td>Titration</td>
<td>40 x 10⁻¹¹</td>
<td>0.21</td>
</tr>
<tr>
<td>Lorenz (155)</td>
<td>Ag(NH₃)₂NO₃</td>
<td>0.1</td>
<td>Impedence</td>
<td>3 x 10⁻¹¹</td>
<td>0.016</td>
</tr>
<tr>
<td>King &amp; Schochet (151)</td>
<td>Ag₂SO₄</td>
<td>0.1</td>
<td>Titration</td>
<td>120 x 10⁻¹¹</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>Ag₂SO₄</td>
<td>0.01</td>
<td>Titration</td>
<td>100 x 10⁻¹¹</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>AgNO₃</td>
<td>0.1</td>
<td>Titration</td>
<td>77 x 10⁻¹¹</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>AgNO₃</td>
<td>0.01</td>
<td>Titration</td>
<td>16 x 10⁻¹¹</td>
<td>0.084</td>
</tr>
</tbody>
</table>

*Activated by positive and negative pulses.

All the data shown in the table demonstrate that the quantity of silver adsorbed on the silver surface would not increase the percent current efficiency as much as 1 percent. The trend of decreased adsorption as the concentration of silver decreases for a silver nitrate solution as shown in Figure VII indicates that the quantity of silver adsorbed in the
FIGURE VII

Concentration of Adsorbed Silver Ions on a Silver Surface
Concentration of silver salt

\[ \times 10^{10} \text{ equivalents per square centimeter} \]
solutions used in this investigation would cause an increase in the percent current efficiency of less than 0.08 percent. This means that the quantity of silver adsorbed on a silver surface would be insignificant.

The effect of additional rinses on the amount of adsorbed silver on the platinum surface

The electrodes which were used to determine the amounts of silver adsorbed on the platinum surface were treated with a variety of rinsing procedures to determine the effectiveness of the rinse procedure and different types of rinse solutions. The treatment of the electrodes, the activity of the adsorbed material left after each treatment and the percent of the total amount of silver removed are recorded in Table 15.

The following observations were made from the data in Table 15:

1. Absolute alcohol removed approximately the same amount of activity as the water rinse. (However, the addition of alcohol to a surface with adsorbed water caused a great amount of agitation by dilution of the solvent at the surface. This agitation was noticed to cause flaking off of loose deposits in other experiments.)

2. The efficiency of different solvents to remove the adsorbed activity decreases in the following order: ammonium hydroxide-potassium cyanide, concentrated nitric acid, concentrated ammonium hydroxide, acetic acid, water and absolute alcohol.

3. Successive one minute rinses with water removed approximately four to five percent of the remaining activity for each rinse.

4. The percent of the activity removed by a water rinse doubles if the adsorbed activity was left in contact with the water over an extended time.

5. The adsorbed activity cannot be removed by a simple rinsing procedure with water.

6. The only procedure which will remove all the silver from the electrode was the ammonium hydroxide-potassium cyanide treatment with heating.
### TABLE 15

The Effect of Rinses on the Adsorbed Silver

The Silver Was Adsorbed on a Platinum Surface from a Sulfate Solution

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Activity on the Electrode (c/min)</th>
<th>Activity Which Was Removed (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before additional rinses</td>
<td>989.6</td>
<td>--</td>
</tr>
<tr>
<td>Absolute alcohol</td>
<td>939.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Water</td>
<td>879.0</td>
<td>5.0</td>
</tr>
<tr>
<td>A 3 normal acetic acid</td>
<td>791.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Concentrated nitric acid and heat</td>
<td>24.0</td>
<td>97.0</td>
</tr>
<tr>
<td>Before the additional rinses</td>
<td>711.1</td>
<td>--</td>
</tr>
<tr>
<td>Water (four times)</td>
<td>583.0</td>
<td>18.0</td>
</tr>
<tr>
<td>Water (over night)</td>
<td>535.0</td>
<td>8.3</td>
</tr>
<tr>
<td>Concentrated ammonium hydroxide</td>
<td>348.0</td>
<td>35.0</td>
</tr>
<tr>
<td>Ammonium hydroxide-potassium cyanide and heat</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Before the additional rinses</td>
<td>286.0</td>
<td>--</td>
</tr>
<tr>
<td>Water (over night)</td>
<td>246.8</td>
<td>14.0</td>
</tr>
<tr>
<td>Concentrated ammonium hydroxide</td>
<td>161.7</td>
<td>35.0</td>
</tr>
<tr>
<td>Ammonium hydroxide-potassium cyanide and heat</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Before the additional rinses</td>
<td>229.2</td>
<td>--</td>
</tr>
<tr>
<td>Water (over night)</td>
<td>207.8</td>
<td>9.3</td>
</tr>
<tr>
<td>Concentrate ammonium hydroxide</td>
<td>140.4</td>
<td>33.0</td>
</tr>
<tr>
<td>Ammonium hydroxide-potassium cyanide and heat</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Before the additional rinses</td>
<td>1,011.9</td>
<td>--</td>
</tr>
<tr>
<td>Water (four times)</td>
<td>792.8</td>
<td>21.6</td>
</tr>
<tr>
<td>Water (four times)</td>
<td>665.9</td>
<td>16.0</td>
</tr>
<tr>
<td>Water (four times)</td>
<td>636.7</td>
<td>4.4</td>
</tr>
<tr>
<td>Water (over night)</td>
<td>571.7</td>
<td>10.2</td>
</tr>
</tbody>
</table>
In conclusion, the adsorption of silver on a platinum surface is not a simple process because the adsorbed silver was not easily rinsed off. The final cleaning procedure used to remove silver must include an ammonium hydroxide-potassium cyanide treatment to remove all the silver from the electrode. The adsorbed cyanide ion should then be removed by a rinse with an acid solution, because the cyanide ion will complex the silver ions in solution, and possibly cause the dissolution of the platinum anode.

The effect of rinses on deposited silver

Since the quantity of silver adsorbed on a silver surface from silver nitrate solutions was shown to be insignificant in comparison to a 0.40 micro equivalent deposit of silver, the silver removed by rinsing should be very small if only adsorbed silver is removed. Therefore, the effect on the current efficiency of dissolution of the silver deposit by the rinses was studied.

The first two rinses in the electrolytic cell were discarded, because they probably involved washing away adsorbed silver ions and the electrolyte. The activity of subsequent rinse solutions or the activity of the electrode before and after rinsing was measured. The quantity of silver lost by the rinsing was obtained from the activity of the rinse solutions or the difference in activity of the deposit on the electrode. The accuracy of determining the quantity of silver lost was low, because the count rates of the silver dissolved were small.

The results of this study are summarized in Table 16. The rinses which were stirred with a vigorous up and down motion of the electrodes
were designated with a V. The other rinses were performed by allowing
the rinse water to flow down the inside of the counting tubes and over
the gauze part of the electrode. The electrode was then gently removed
and placed in another counting tube for measurement. All of the rinses
were performed with water except where stated. The depositions were made
from silver nitrate solutions.

**TABLE 16**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Number of Rinses</th>
<th>Duration of Rinse (min)</th>
<th>Current Efficiency of Deposition (percent)</th>
<th>Activity Removed (percent)</th>
<th>Decrease in Current Efficiency (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>49</td>
<td>1</td>
<td>0.3</td>
<td>96.5</td>
<td>0.21</td>
<td>0.20</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>0.3</td>
<td>97.2</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>51</td>
<td>1</td>
<td>0.3</td>
<td>95.2</td>
<td>0.30</td>
<td>0.28</td>
</tr>
<tr>
<td>196</td>
<td>1</td>
<td>0.3</td>
<td>92.8</td>
<td>0.17</td>
<td>0.16</td>
</tr>
<tr>
<td>197</td>
<td>1</td>
<td>0.3</td>
<td>95.4</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>198</td>
<td>1</td>
<td>0.3</td>
<td>98.5</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>352</td>
<td>1</td>
<td>0.3</td>
<td>85.5</td>
<td>0.31</td>
<td>0.26</td>
</tr>
<tr>
<td>354</td>
<td>1</td>
<td>0.3</td>
<td>6.4</td>
<td>4.20</td>
<td>0.27</td>
</tr>
<tr>
<td>358</td>
<td>1</td>
<td>0.3</td>
<td>83.4</td>
<td>0.15</td>
<td>0.12</td>
</tr>
<tr>
<td>359</td>
<td>1</td>
<td>0.3</td>
<td>87.3</td>
<td>0.36</td>
<td>0.31</td>
</tr>
<tr>
<td>360</td>
<td>1</td>
<td>0.3</td>
<td>86.1</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>Averaged</td>
<td>3</td>
<td>0.3 (V)</td>
<td>40.2</td>
<td>28.2</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.3</td>
<td>-1.3</td>
<td>-0.5</td>
<td>-0.2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.3</td>
<td>-0.4</td>
<td>-0.2</td>
<td>-0.2</td>
</tr>
<tr>
<td>149</td>
<td>3</td>
<td>0.3 (V)</td>
<td>64.1</td>
<td>28.0</td>
<td>17.9</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.3 (V)</td>
<td>7.5</td>
<td>4.8</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.3 (V)</td>
<td>5.5</td>
<td>5.5</td>
<td>3.5</td>
</tr>
<tr>
<td>150</td>
<td>3</td>
<td>0.3 (V)</td>
<td>131.4</td>
<td>2.4</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.3 (ethanol)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>overnight</td>
<td>0.4</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>57</td>
<td>3</td>
<td>0.3a</td>
<td>93.0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

*After washing the electrode and measuring its activity, it was placed back in the electrolyte for ten minutes.*
Observations from the data in Table 16 are as follows:

1. The average percent of silver removed in each rinsing procedure was 0.21 percent.

2. The average decrease in the percent current efficiency for the deposition of silver was 0.17 percent per rinse.

3. Vigorous stirring caused much greater losses from the deposit of silver than losses from gentle rinsings, and this was attributed to the dislodging of the soft silver deposit.

4. The losses did not increase beyond that expected from the additional rinses with water when the electrode was returned to the electrolytic solution for ten minutes.

5. No detectable activity was found in the ethanol rinse.

In conclusion, the water rinses appear to oxidise and remove $1 \times 10^{-9}$ moles of silver per rinse.

The effect of stirring rate

The percent current efficiency for the electrodeposition of silver was studied as a function of the stirring rate, and the results were plotted in Figure VIII. A one-minute electrodeposition at a current density of 0.306 milliamperes per square centimeter was performed on a $1 \times 10^{-4}$ molar silver nitrate solution.

The frequency of stirring was measured with a stroboscopic light. Since the lowest rate of flashing of the stroboscopic light was 600 times per minute, and it was impossible to distinguish between flash rates equal or twice the rate of stirring of a symmetrical stirring bar, the stirring rate was measured with flashing rates four times and two times the stirring rate. If the rate of flashing was four times the stirring rate, the stirring bar appeared in a cross configuration. When the rate
of flashing was twice or equal to the rate of stirring, the stirring bar appeared to be stopped in the solution.

Figure VIII indicates that the percent current efficiency for the deposition of silver is not affected to any significant amount by changes in the stirring rate when the stirring rate is above 300 revolutions per minute. Below 300 revolutions per minute the percent current efficiency decreased to 11 percent with no stirring.

The appearance of the electrodes were bright and shiny when the stirring rate was 400 revolutions per minute or higher, but the electrodes were dark gray or black for stirring rates between 400 to 100 revolutions per minute. The electrode was bright and shiny when the deposition was done with no stirring.

The slowest rate of stirring used in the following experiments was 400 revolutions per minute.

The effect of size and type of stirring bar

The stirring of the solution was less efficient when stirring bars with shorter lengths were used. When a stirring bar 1-1/4 inches long was used, the percent current efficiency was 90 percent, but it dropped to 60 percent when a 1/2-inch stirring bar was used.

Stirring bars with three types of coverings were used. Plastic or Teflon coverings were preferred over glass-covered bars because glass stirring bars are difficult to handle with tweezers. The plastic-coated stirring bars had a greater tendency to be contaminated than the Teflon stirring bars, but both of them could be cleaned when the correct procedure was used. The only stirring bars which were impossible to decontaminate were those with a crack in the outer covering.
FIGURE VIII

The Percent Current Efficiency as a Function of the Stirring Rate
The effect of rate of flow of nitrogen

The rate of nitrogen flow was adjusted so the bubbles issuing from the bubbler were approximately a millimeter in diameter or slightly less. Bubbles of this size would be swirled about the solution a number of times before they bubbled out, and they would not attach themselves to the magnetic stirring bar to any significant extent. The adjustment was made by supplying approximately 5 lbs of pressure with the regulator valve on the tank of nitrogen and a screw clamp at the inlet to the cell. The bubbler was 6-mm soft glass tubing which was gathered and drawn into a fine capillary. The capillary was successively shortened until the proper bubble size was produced. The solutions were deoxygenated for a half hour or longer before they were electrolyzed. The actual quantity of nitrogen used was not measured, and the results were not affected to any noticeable extent when the bubblers were broken during a run.

The effect of the current density

The current density is the current per unit area of the electrode. The current density was calculated by dividing the current output of the coulometer by the area of the micro-gauge electrode. According to the output selected, the coulometer delivered three different currents which were 64.3, 6.43 and 0.643 milliamperes per second. The area of the electrode was calculated from measurements of the diameter of the wires in the gauge, length, width and depth of each component of the electrode which was immersed in the electrolyte.

No literature was found on the effect of current density on the percent current efficiency for the deposition of silver from a silver
nitrate solution. Kudryavtsev and Bec (156) studied the effect of the current density on the percent current efficiency for the deposition of silver from a basic cyanide solution, and they demonstrated that an increase in the current density beyond a certain value caused the reduction of hydrogen. The reduction of hydrogen was prevented by addition of sodium nitrate, and a smooth deposit of silver was produced.

The effects of the current density on the percent current efficiency for the deposition of silver were studied using $1 \times 10^{-3}$ molar silver ions. The results obtained by using supporting electrolytes of 0.1 molar sodium sulfate, and sodium nitrate at different current densities are summarized in Table 17.

Observations from the data in Table 17 are as follows:

1. There was a small decrease in the percent current efficiency when the current density was increased from 0.306 to 3.06 milliamperes per square centimeter.

2. There was a large decrease in the percent current efficiency when the current density was increased from 3.06 to 30.6 milliamperes per square centimeter.

3. The above trends were the same for the different electrolytes if the time of deposition was the same.

The deposits produced by a current density of 0.306 milliamperes per square centimeter were all bright and shiny. Those produced by a current density of 3.06 milliamperes per square centimeter were dull but they had a metallic luster. Those produced by a current density of 30.6 milliamperes per square centimeter were black, and some of the deposits formed beard-like structures which hung from the bottom of the electrode. These structures were fragile and broke away from the electrode easily.

If the black structures were allowed to remain in water, they became
lighter in color which was probably due to rearrangement of the deposited silver into larger crystals with fewer defects.

TABLE 17

The Effect of the Current Density on the Current Efficiency

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time of Run (min)</th>
<th>Current Density (ma/sq cm)</th>
<th>Anion</th>
<th>Current Efficiency (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1</td>
<td>0.306</td>
<td>SO₄⁻</td>
<td>103.0</td>
</tr>
<tr>
<td>34</td>
<td>1</td>
<td>3.06</td>
<td></td>
<td>96.3</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>30.6</td>
<td></td>
<td>20.1</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>0.306</td>
<td>NO₃⁻</td>
<td>97.3</td>
</tr>
<tr>
<td>33</td>
<td>1</td>
<td>3.06</td>
<td></td>
<td>87.8</td>
</tr>
<tr>
<td>331</td>
<td>1</td>
<td>0.306</td>
<td></td>
<td>94.6</td>
</tr>
<tr>
<td>336</td>
<td>1</td>
<td>3.06</td>
<td></td>
<td>96.0</td>
</tr>
<tr>
<td>341</td>
<td>1</td>
<td>30.6</td>
<td></td>
<td>17.7</td>
</tr>
<tr>
<td>346</td>
<td>1</td>
<td>0.306</td>
<td></td>
<td>96.5</td>
</tr>
<tr>
<td>333</td>
<td>1</td>
<td>0.306</td>
<td></td>
<td>96.8</td>
</tr>
<tr>
<td>338</td>
<td>1</td>
<td>3.06</td>
<td></td>
<td>93.9</td>
</tr>
<tr>
<td>343</td>
<td>1</td>
<td>30.6</td>
<td></td>
<td>17.7</td>
</tr>
<tr>
<td>348</td>
<td>1</td>
<td>0.306</td>
<td></td>
<td>98.5</td>
</tr>
<tr>
<td>335</td>
<td>1</td>
<td>0.306</td>
<td></td>
<td>98.4</td>
</tr>
<tr>
<td>340</td>
<td>1</td>
<td>3.06</td>
<td></td>
<td>95.6</td>
</tr>
<tr>
<td>345</td>
<td>1</td>
<td>30.6</td>
<td></td>
<td>29.9</td>
</tr>
</tbody>
</table>

The effect of the duration of the run

The series of experiments used to obtain data for Figures V and VI are representative of runs with durations that ran from 0.5 to 10.0 minutes. The percent current efficiencies calculated from radioactivity measurements of the deposits from solutions with added sodium nitrate
indicated that there was a small decrease in the percent current efficiency with an increase in the duration of the run.

The percent current efficiencies for the depositions of silver up to 50.0 minutes at a current density of 0.306 milliamperes are listed in Tables 18 and 19. The electrolyte used in the deposition of the silver

**TABLE 18**

The Effect of the Duration of the Run on the Current Efficiency from a Nitrate Solution

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Duration of the run (min)</th>
<th>Current Efficiency (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>50.0</td>
<td>79.5</td>
</tr>
<tr>
<td>50, 52, 57</td>
<td>10.0</td>
<td>96.8 (average)</td>
</tr>
<tr>
<td>60</td>
<td>5.00</td>
<td>95.3 (average)</td>
</tr>
<tr>
<td>69</td>
<td>4.00</td>
<td>95.0</td>
</tr>
<tr>
<td>72</td>
<td>2.00</td>
<td>99.2</td>
</tr>
<tr>
<td>66</td>
<td>1.00</td>
<td>98.3</td>
</tr>
<tr>
<td>63</td>
<td>0.50</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 19**

The Effect of the Duration of the Run on the Current Efficiency from a Sulfate Solution

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Duration of the run (min)</th>
<th>Current Efficiency (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>39</td>
<td>50.0</td>
<td>88.2</td>
</tr>
<tr>
<td>41</td>
<td>25.0</td>
<td>97.4</td>
</tr>
<tr>
<td>100</td>
<td>1.00</td>
<td>103.0</td>
</tr>
<tr>
<td>103</td>
<td>0.25</td>
<td>107.5</td>
</tr>
</tbody>
</table>
for Table 18 was $1 \times 10^{-3}$ molar silver nitrate, and 0.1 molar sodium nitrate. The electrolyte used in the deposition of the silver for Table 19 was $1 \times 10^{-3}$ molar silver sulfate, and 0.1 molar sodium sulfate.

Observations from the data in Tables 18 and 19 are as follows:

1. There was an overall 0.4 percent decrease in the percent current efficiency per minute of run for both supporting electrolytes.

2. There was approximately an 8 percent increase in the percent current efficiency for the depositions from the sulfate solution over the depositions from the nitrate solutions.

**The effect of separating the anode compartment**

A possible explanation for the observed current efficiencies was the production of a reducible species at the anode which was transferred to the cathode and reduced there. This was checked by observing the effect of separating the anode and cathode compartments. The anode compartment was separated from the cathode compartment by means of an ammonium nitrate solution, using the equipment supplied with the Leeds and Northrup #7961 Coulometric Titration Cell Kit. The anode was a platinum wire. The concentration of the silver ion in the electrodeposition compartment was $1 \times 10^{-3}$ molar, and the deposition was carried out in ten minutes with a current density of 0.306 milliamperes per square centimeter. The results of this study are listed in Table 20. The data indicate that the products of the anode reaction were not responsible for the decrease in the percent current efficiency.

The technique of using separate compartments was discontinued because of the negligible effect on the percent current efficiency and the excess potential requirements from the coulometer. The output
TABLE 20

The Effect of Separating the Anode Compartment on the Current Efficiency

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Concentration of NaN₃ (molar)</th>
<th>The Current Efficiency with the Electrodes in the</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Same Compartment (percent)</td>
<td>Different Compartments (percent)</td>
</tr>
<tr>
<td>46</td>
<td>$1 \times 10^{-3}$</td>
<td>94.6</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>$1 \times 10^{-1}$</td>
<td>97.8</td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>10</td>
<td>94.3</td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>$1 \times 10^{-3}$</td>
<td>96.5</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>$1 \times 10^{-1}$</td>
<td>97.2</td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>10</td>
<td>95.2</td>
<td></td>
</tr>
</tbody>
</table>

Potential needed for the potential drop developed across the porous glass discs, together with the other resistances of a series, exceeded the suggested operating potential of the coulometer.

The effect of the cathode potential

Since the deposition was a constant current electrodeposition, the potential of the electrode was free to vary, and it assumed the potential of the reaction taking place. The potential of the cathode was measured with a student potentiometer against a saturated calomel electrode which was separated by an ammonium nitrate solution in a bridge tube from the Leeds and Northrup Titration Cell Kit #7961. Since there was a slight current flow during the adjustment of the potentiometric circuit, the slight current flow caused the current efficiencies to vary on the electrodes used for the potential studies, and the percent current
efficiencies were calculated from other cells in the series circuit. The results are summarized in Table 21.

\textbf{TABLE 21}

<table>
<thead>
<tr>
<th>Silver Concentration (molar)</th>
<th>Potential Measured (volts vs SCE)</th>
<th>Over Potential (millivolts)</th>
<th>Current Efficiency (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 10^{-3}$</td>
<td>0.3493</td>
<td>31</td>
<td>95</td>
</tr>
<tr>
<td>$1 \times 10^{-4}$</td>
<td>0.2752</td>
<td>46</td>
<td>90</td>
</tr>
<tr>
<td>$5 \times 10^{-5}$</td>
<td>-0.2598</td>
<td>563</td>
<td>85 and 32</td>
</tr>
<tr>
<td>$1 \times 10^{-5}$</td>
<td>-0.4100</td>
<td>672</td>
<td>20</td>
</tr>
</tbody>
</table>

Observations from the above data are as follows:

1. The percent current efficiency decreased with increasing negative potential of the cathode.

2. The current efficiency was erratic for the $5 \times 10^{-5}$ molar silver nitrate solution.

3. The potential of the lowest concentration of silver has a low current efficiency, but the potential only approaches the reduction potential of the next species in the solution which can be reduced. (The Nernst potential for the reduction of $1 \times 10^{-3}$ molar hydrogen is $-0.419$ (vs SCE) and the over voltage for the reduction of hydrogen varies from 0.097 where hydrogen evolution is first observed to 0.3 volts at a current density of 0.01 amperes per square centimeter.)

In order to determine the potential of a possible competing reaction which might cause the decrease in current efficiency, an exhaustive electrodeposition of 10 micro equivalents of silver was performed and the potential of the cathode was observed throughout this electrodeposition. The electrolytic solution of 100 milliliters was $1 \times 10^{-4}$ molar in silver nitrate, 0.01 molar in sodium nitrate, and $\text{HNO}_3$. 
was used to bring the pH to 4.11. The potential was measured with a saturated calomel electrode which was separated from the electrolytic solution by an ammonium nitrate solution. The current density for the electrodeposition was 0.306 milliamperes per square centimeter. See Figure IX.

Observations from Figure IX are as follows:

1. Concentrations of $5.0 \times 10^{-5}$ molar silver nitrate and higher permit the cathode potential to remain approximately 0.28 volts positive with respect to a saturated calomel electrode, or 0.52 volts positive with respect to a normal hydrogen electrode.

2. For concentrations of silver from $4.5 \times 10^{-5}$ molar to the depletion of the silver ion concentration the potential was approximately -0.42 volts with respect to a saturated calomel electrode, or -0.18 volts with respect to a normal hydrogen electrode.

3. The potential of the cathode decreased approximately 0.10 volts upon the depletion of the silver ions in the solution.

4. The rate of decrease in the electrode potential was approximately 0.006 volts per micro equivalent of electricity passed when silver ions were present under observations #1 and #2.

5. The rate of decrease in the electrode potential after the depletion of the silver-ion concentration was approximately 0.01 volts per micro equivalent of electricity passed.

6. The potential of the cathode was approximately 70 millivolts more positive than the equilibrium Nernst potential for the hydrogen-ion concentration for the duration of the slightly negative plateau discussed under observation #2.

7. The length of the second plateau (discussed under observation #2) was approximately 12 micro equivalents long whereas the quantity of silver ions left in the electrolyte was approximately 3.5 micro equivalents at the start of the plateau.

In conclusion, the potential and the current efficiency data indicate that three electrode reactions were taking place.
FIGURE IX
Cathode Potential as a Function of the Current Passed
The effect of temperature

The effect of temperature on the current efficiency for the electrodeposition of silver was studied at 0°C, 25°C, 50°C, and 75°C. Solutions of $5 \times 10^{-5}$ and $1 \times 10^{-5}$ molar silver nitrate were prepared by dilution of a stock solution which contained $1 \times 10^{-4}$ molar silver nitrate, $1 \times 10^{-2}$ molar sodium nitrate, and $1 \times 10^{-3}$ molar nitric acid. The current density was 0.306 milliamperes per square centimeter, and 0.402 micro equivalents of electricity were passed. The results of this study are given in Table 22.

**TABLE 22**

The Effect of Temperature on the Current Efficiency

<table>
<thead>
<tr>
<th>Concentration of Silver Ions (molar)</th>
<th>Temperature of the Solution (°C)</th>
<th>Current Efficiency (percent)</th>
<th>Appearance of the Electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.023 \times 10^{-4}$</td>
<td>73.3</td>
<td>100.7</td>
<td>shiny</td>
</tr>
<tr>
<td>$1.023 \times 10^{-4}$</td>
<td>50.00</td>
<td>99.8</td>
<td>gray</td>
</tr>
<tr>
<td>$1.023 \times 10^{-4}$</td>
<td>24.45</td>
<td>94.6</td>
<td>greenish-gray</td>
</tr>
<tr>
<td>$1.023 \times 10^{-4}$</td>
<td>00.05</td>
<td>93.0</td>
<td>brownish-black</td>
</tr>
<tr>
<td>$5.115 \times 10^{-5}$</td>
<td>75.3</td>
<td>100.7</td>
<td>dull</td>
</tr>
<tr>
<td>$5.115 \times 10^{-5}$</td>
<td>50.00</td>
<td>99.5</td>
<td>gray</td>
</tr>
<tr>
<td>$5.115 \times 10^{-5}$</td>
<td>25.20</td>
<td>32.0</td>
<td>shiny</td>
</tr>
<tr>
<td>$5.115 \times 10^{-5}$</td>
<td>0.00</td>
<td>43.1</td>
<td>shiny with a greenish tint</td>
</tr>
<tr>
<td>$1.023 \times 10^{-5}$</td>
<td>75.0</td>
<td>48.7</td>
<td>shiny</td>
</tr>
<tr>
<td>$1.023 \times 10^{-5}$</td>
<td>50.00</td>
<td>40.1</td>
<td>shiny</td>
</tr>
<tr>
<td>$1.023 \times 10^{-5}$</td>
<td>25.25</td>
<td>20.0</td>
<td>shiny</td>
</tr>
<tr>
<td>$1.023 \times 10^{-5}$</td>
<td>0.05</td>
<td>15.4</td>
<td>shiny</td>
</tr>
</tbody>
</table>

Observations from the above data are as follows:

1. There was a systematic decrease in the percent current efficiency with a decrease in the temperature.
2. The electrodeposition of $5 \times 10^{-5}$ molar silver nitrate at 75°C and 50°C had the same current efficiencies as the electrodepositions of $1 \times 10^{-4}$ molar silver nitrate, but the current efficiencies for electrodepositions from $5 \times 10^{-5}$ molar silver nitrate were much lower at the lower temperatures.

3. In general, the appearance of the electrodeposits progressed from shiny to dull, gray, greenish-gray, black and shiny as the current efficiency decreased.

Since the results from the $5 \times 10^{-5}$ molar silver nitrate were erratic, only the logarithms of the activities of $1 \times 10^{-4}$ and $1 \times 10^{-5}$ molar silver nitrate solutions were plotted against the inverse of the absolute temperature in Figure I. Straight lines with different negative slopes are obtained for each concentration of silver nitrate. This indicates that at least two different reactions are taking place at the cathode.

The effect of certain anions

The anions studied were the sulfate ion, perchlorate ion and nitrate ion. None of these caused precipitates or strong complexes with the silver ions. The current efficiencies for the deposition of $1 \times 10^{-3}$ molar silver ions in the presence of 0.1 molar salts of these anions at a pH of 2.3 are listed in Table 23.

The increase in the current efficiencies for the different anions was in the same order as the increase in adsorption of the silver salts on silver surfaces shown in Figure VII. The fact that the current efficiency for silver deposition from silver sulfate solutions is higher than that for other salts could be attributed to the larger positive adsorption and entrapment at the cathode.
FIGURE X

The Activity of the Deposited Silver as a Function of the Inverse of the Absolute Temperature
**TABLE 23**

The Effect of Certain Anions on the Current Efficiency

<table>
<thead>
<tr>
<th>Duration of the run (min)</th>
<th>Current Density (ma/sq cm)</th>
<th>Current Efficiency Ag₂SO₄ (percent)</th>
<th>Current Efficiency AgClO₄ (percent)</th>
<th>Current Efficiency AgNO₃ (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.06</td>
<td>92.6</td>
<td>90.7</td>
<td>87.8</td>
</tr>
<tr>
<td>50</td>
<td>0.306</td>
<td>86.2</td>
<td>82.4</td>
<td>79.5</td>
</tr>
</tbody>
</table>

The effect of nitrate on the current efficiency was studied with $2 \times 10^{-3}$, 0.1, and 10 molar nitrate solutions. The $2 \times 10^{-3}$ molar nitrate solutions were obtained by preparing a solution $1 \times 10^{-3}$ molar in silver nitrate and $1 \times 10^{-3}$ molar in nitric acid. Other solutions were made with the addition of sodium nitrate. The current density was 0.306 milliamperes per square centimeter. The current efficiencies calculated from the measurements of the activity on the electrode and the activity of solutions prepared by dissolving the silver from the electrode are listed in Table 24. The average of the current efficiencies for each concentration are plotted as a function of the duration of the electrodeposition in Figure XI.

Observations from Figure XI and Table 24 are these:

1. When the nitrate ion concentration was very low the results were erratic.

2. When the nitrate ion concentration was increased by addition of sodium nitrate the erratic behavior decreased.

3. As demonstrated in Figure XI, the erratic behavior also tended to diminish as the quantity of silver deposit increased.

4. Except for the 1 and 0.5 minute runs, there was in general an increase in the percent current efficiency with an increase in concentration of the nitrate ion.
FIGURE XI

The Effect of the Concentration of Nitrate Ion on the Percent Current Efficiency
### TABLE 24

The Effect of Nitrate Ion Concentration on the Current Efficiency

<table>
<thead>
<tr>
<th>Time of Run (min)</th>
<th>Percent Current Efficiency</th>
<th>Electrode Solution</th>
<th>Electrode Solution</th>
<th>Electrode Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2x10^{-3} molar nitrate</td>
<td>0.1 molar nitrate</td>
<td>10 molar nitrate</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Electrocatalytic</td>
<td>Electrolytic</td>
<td>Electrolytic</td>
<td>Electrolytic</td>
</tr>
<tr>
<td></td>
<td>94.6</td>
<td>91.3</td>
<td>97.8</td>
<td>95.1</td>
</tr>
<tr>
<td></td>
<td>96.5</td>
<td>98.5</td>
<td>97.2</td>
<td>97.3</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>100.2</td>
<td>100.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>92.5</td>
<td>93.3</td>
<td>93.0</td>
<td>93.5</td>
</tr>
<tr>
<td></td>
<td>94.2</td>
<td>94.2</td>
<td>94.2</td>
<td></td>
</tr>
<tr>
<td>average</td>
<td>94.5</td>
<td>94.4</td>
<td>97.1</td>
<td>96.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>94.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>90.9</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td>97.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>96.5</td>
</tr>
<tr>
<td>5</td>
<td>95.6</td>
<td>96.5</td>
<td>92.9</td>
<td>94.3</td>
</tr>
<tr>
<td></td>
<td>97.7</td>
<td>100.2</td>
<td>97.7</td>
<td>100.2</td>
</tr>
<tr>
<td>average</td>
<td>93.1</td>
<td>93.3</td>
<td>95.3</td>
<td>97.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>95.9</td>
<td>98.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>97.1</td>
</tr>
<tr>
<td>4</td>
<td>82.6</td>
<td>82.1</td>
<td>95.8</td>
<td>97.5</td>
</tr>
<tr>
<td></td>
<td>82.4</td>
<td></td>
<td>95.8</td>
<td>97.9</td>
</tr>
<tr>
<td>2</td>
<td>80.1</td>
<td>73.0</td>
<td>97.0</td>
<td>97.5</td>
</tr>
<tr>
<td></td>
<td>76.6</td>
<td></td>
<td>96.2</td>
<td>97.4</td>
</tr>
<tr>
<td>1</td>
<td>131.4</td>
<td>128.7</td>
<td>99.2</td>
<td>98.2</td>
</tr>
<tr>
<td></td>
<td>130.1</td>
<td>98.7</td>
<td>101.2</td>
<td>99.7</td>
</tr>
<tr>
<td>0.5</td>
<td>114.3</td>
<td>109.2</td>
<td>98.3</td>
<td>99.0</td>
</tr>
<tr>
<td></td>
<td>113.8</td>
<td>98.7</td>
<td>97.6</td>
<td>98.2</td>
</tr>
</tbody>
</table>

The effect of certain cations

The effect of hydrogen-ion concentration on the percent current efficiency was studied with a solution 1 x 10^{-3} molar in silver nitrate and 0.1 molar in sodium perchlorate. The hydrogen-ion concentration was adjusted with perchloric acid. The hydrogen-ion concentration ranged from 0.3 molar to 1 x 10^{-6} molar. The calculated percent current efficiencies plotted as a function of the pH are shown in Figure XIII.
FIGURE XII

The Percent Current Efficiency for the Silver Ion as a Function of the Hydrogen-Ion Concentration
Each run was for ten minutes at a current density of 3.06 milliamperes per square centimeter. The effect of varying the pH from 6 to 0.5 was negligible.

The effect of the concentration of silver on the current efficiency was determined on the basis of 44 experiments. The solutions used for the deposition contained sodium nitrate at a concentration 100 times that of the silver-ion concentration and the pH of the solutions were approximately 2. The electrodeposition was carried out for one minute at a current density of 0.306 milliamperes per square centimeter. Each of the values plotted in Figure XIII were averages of the number of experiments indicated by a subscript.

The percent current efficiency was shown in Figure XIII to be approximately 95 percent for the range of concentration extending from $7 \times 10^{-3}$ molar to $2 \times 10^{-4}$ molar silver nitrate. Below $2 \times 10^{-4}$ molar silver nitrate the current efficiency decreased at an accelerated rate for further decreases in the concentration. When the concentration of silver dropped to approximately $4 \times 10^{-5}$ molar, the results became erratic.

The effect of 1 molar copper nitrate on the current efficiency for the deposition of silver was studied as a function of the concentration of silver nitrate. The electrodepositions were performed at a current density of 0.306 milliamperes per square centimeter, and 0.40 micro equivalents of electricity were used. The results were plotted in Figure XIV. Observations from this figure are—

1. The current efficiency decreased when 1 molar copper nitrate was present.
FIGURE XIII

The Percent Current Efficiency for Silver as a Function of the Silver Concentration
FIGURE XIV

The Percent Current Efficiency for Silver as a Function of the Silver-Ion Concentration in the Presence of One Molar Copper Nitrate
Silver concentration (molar)

1 x 10^{-5}

1 x 10^{-4}

1 x 10^{-3}

1 x 10^{-2}

% Current efficiency

0 20 40 60 80 100

1

2

1

2

0
2. The decrease in current efficiency with decreasing silver nitrate concentration was more pronounced when copper nitrate was present.

The effect of the copper nitrate concentration on the current efficiency for depositions of silver from $1 \times 10^{-4}$ molar silver nitrate was studied by plotting the current efficiencies for silver depositions as a function of the logarithm of the copper nitrate concentration in Figure XV. The current density was 0.306 milliamperes per square centimeter, and 0.40 micro equivalents of electricity were used. The following observations were made from Figure XV.

1. The decrease in the percent current efficiency for the deposition of silver was an exponential function of the copper-ion concentration.

2. The addition of small quantities of copper nitrate caused the current efficiency for the deposition of silver to increase above the value associated with pure silver nitrate solutions.

The depositions of silver from silver nitrate solutions at different concentrations of copper nitrate are summarised in Table 25. A current density of 0.306 milliamperes per square centimeter was used in a 0.40 micro equivalent electrodeposition at room temperature.

Since a temperature increase to $75^\circ$C increased the percent current efficiency to 100 percent for silver nitrate concentrations of $1 \times 10^{-4}$ and $5 \times 10^{-5}$ molar solutions, and to 50 percent for $1 \times 10^{-5}$ molar silver nitrate, the same concentrations of silver were used in a 3 molar copper nitrate solution. The same current density and quantity of electricity was used in these experiments as in the temperature studies and other copper nitrate interference studies. The results are summarised in Table 26.
FIGURE XV

The Percent Current Efficiency for Silver as a Function of the Copper-Ion Concentration
Copper concentration (molar)

% Current efficiency of pure silver solutions at this silver concentration

\[ [\text{Ag}^+] = 1 \times 10^{-4} \]
### TABLE 25
The Current Efficiency for the Deposition of Silver as a Function of the Copper-Ion Concentration and Silver-Ion Concentration

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Concentration of Copper</th>
<th>Anion</th>
<th>Concentration of Silver</th>
<th>Time of Run</th>
<th>Current Efficiency (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>357</td>
<td>3.00 molar</td>
<td>NO$_3^-$</td>
<td>1 x 10$^{-4}$ molar</td>
<td>1 min</td>
<td>6.3</td>
</tr>
<tr>
<td>382</td>
<td>3.00 molar</td>
<td></td>
<td>4 x 10$^{-4}$ molar</td>
<td></td>
<td>24.8$^a$</td>
</tr>
<tr>
<td>387</td>
<td>3.00 molar</td>
<td></td>
<td>4 x 10$^{-4}$ molar</td>
<td></td>
<td>4.5$^b$</td>
</tr>
<tr>
<td>392</td>
<td>3.00 molar</td>
<td></td>
<td>4 x 10$^{-4}$ molar</td>
<td></td>
<td>64.7</td>
</tr>
<tr>
<td>184</td>
<td>2.50 molar</td>
<td></td>
<td>4 x 10$^{-4}$ molar</td>
<td></td>
<td>77.1</td>
</tr>
<tr>
<td>189</td>
<td>2.50 molar</td>
<td></td>
<td>4 x 10$^{-4}$ molar</td>
<td></td>
<td>47.5</td>
</tr>
<tr>
<td>188</td>
<td>2.50 molar</td>
<td></td>
<td>5 x 10$^{-4}$ molar</td>
<td></td>
<td>48.3</td>
</tr>
<tr>
<td>185</td>
<td>2.50 molar</td>
<td></td>
<td>6 x 10$^{-4}$ molar</td>
<td></td>
<td>82.3</td>
</tr>
<tr>
<td>187</td>
<td>2.50 molar</td>
<td></td>
<td>8 x 10$^{-4}$ molar</td>
<td></td>
<td>50.7</td>
</tr>
<tr>
<td>186</td>
<td>2.50 molar</td>
<td></td>
<td>1 x 10$^{-3}$ molar</td>
<td></td>
<td>82.7</td>
</tr>
<tr>
<td>383</td>
<td>2.00 molar</td>
<td></td>
<td>1 x 10$^{-4}$ molar</td>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td>388</td>
<td>2.00 molar</td>
<td></td>
<td>1 x 10$^{-4}$ molar</td>
<td></td>
<td>1.4</td>
</tr>
<tr>
<td>376</td>
<td>1.00 molar</td>
<td></td>
<td>9.4 x 10$^{-5}$ molar</td>
<td></td>
<td>51.5</td>
</tr>
<tr>
<td>371</td>
<td>1.00 molar</td>
<td></td>
<td>1 x 10$^{-4}$ molar</td>
<td></td>
<td>54.4</td>
</tr>
<tr>
<td>384</td>
<td>1.00 molar</td>
<td></td>
<td>1 x 10$^{-4}$ molar</td>
<td></td>
<td>59.8</td>
</tr>
<tr>
<td>389</td>
<td>1.00 molar</td>
<td></td>
<td>1 x 10$^{-4}$ molar</td>
<td></td>
<td>37.8</td>
</tr>
<tr>
<td>377</td>
<td>1.00 molar</td>
<td></td>
<td>5 x 10$^{-4}$ molar</td>
<td></td>
<td>81.9</td>
</tr>
<tr>
<td>372</td>
<td>1.00 molar</td>
<td></td>
<td>5 x 10$^{-4}$ molar</td>
<td></td>
<td>78.2</td>
</tr>
<tr>
<td>378</td>
<td>1.00 molar</td>
<td></td>
<td>1 x 10$^{-3}$ molar</td>
<td></td>
<td>82.4</td>
</tr>
<tr>
<td>373</td>
<td>1.00 molar</td>
<td></td>
<td>1 x 10$^{-3}$ molar</td>
<td></td>
<td>82.9</td>
</tr>
<tr>
<td>379</td>
<td>1.00 molar</td>
<td></td>
<td>1.5 x 10$^{-3}$ molar</td>
<td></td>
<td>89.2</td>
</tr>
<tr>
<td>374</td>
<td>1.00 molar</td>
<td></td>
<td>1.5 x 10$^{-3}$ molar</td>
<td></td>
<td>86.4</td>
</tr>
<tr>
<td>380</td>
<td>1.00 molar</td>
<td></td>
<td>2 x 10$^{-3}$ molar</td>
<td></td>
<td>81.6</td>
</tr>
<tr>
<td>375</td>
<td>1.00 molar</td>
<td></td>
<td>2 x 10$^{-3}$ molar</td>
<td></td>
<td>88.4</td>
</tr>
<tr>
<td>385</td>
<td>0.50 molar</td>
<td></td>
<td>1 x 10$^{-4}$ molar</td>
<td></td>
<td>78.9</td>
</tr>
<tr>
<td>390</td>
<td>0.50 molar</td>
<td></td>
<td>1 x 10$^{-4}$ molar</td>
<td></td>
<td>72.4</td>
</tr>
<tr>
<td>367</td>
<td>0.30 molar</td>
<td></td>
<td>1 x 10$^{-4}$ molar</td>
<td></td>
<td>92.6$^c$</td>
</tr>
<tr>
<td>335</td>
<td>1.1 x 10$^{-3}$ molar</td>
<td></td>
<td>1 x 10$^{-3}$ molar</td>
<td></td>
<td>98.5$^c$</td>
</tr>
<tr>
<td>340</td>
<td>1.1 x 10$^{-3}$ molar</td>
<td></td>
<td>1 x 10$^{-3}$ molar</td>
<td></td>
<td>98.4$^c$</td>
</tr>
</tbody>
</table>

---

$^a$ Shorted momentarily.

$^b$ Bumped during removal.

$^c$ The percent current efficiency for silver nitrate solutions without copper nitrate ran in series with experiments 367, 335 and 340 were 92.4, 95.5 and 98.4, respectively. Each solution without copper nitrate had the same concentration of silver nitrate as the one with it.
TABLE 26
The Effect of 3 Molar Copper Nitrate on the Current Efficiency for the Deposition of Silver at 75°C

<table>
<thead>
<tr>
<th>Concentration of Silver Nitrate (molar)</th>
<th>Current Efficiency with No Copper Nitrate (percent)</th>
<th>Copper Nitrate (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 x 10^{-4}</td>
<td>100.7</td>
<td>1.72</td>
</tr>
<tr>
<td>5 x 10^{-5}</td>
<td>100.7</td>
<td>0.72</td>
</tr>
<tr>
<td>1 x 10^{-5}</td>
<td>48.7</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Observations from the above table are as follows:

1. The presence of copper nitrate in high concentrations at high temperatures radically decreases the current efficiency.

2. There is a systematic decrease in the current efficiency for the deposition of silver with a decrease in the concentration of silver nitrate.

3. When the current efficiency for the deposition of silver nitrate at 1 x 10^{-4} molar in the presence of 3 molar copper nitrate are compared at room temperature in Table 25 and at 75°C in Table 26, there was an indication that the current efficiency decreases with a rise in temperature.

If the copper was reduced with the silver, the percent current efficiency for the silver deposition would decrease. However, no copper color was noticed in the deposits, and the potential of the electrode was not negative enough for the deposition of copper at 1 x 10^{-4} molar silver.

In order to examine the possibility of codeposition of copper, solutions of silver and copper with radioactive Cu-64 were electrolyzed at different current densities. All the solutions were 1 x 10^{-3} molar in silver nitrate and 0.1 molar with respect to sodium nitrate. The
solutions containing copper were $1 \times 10^{-3}$ molar with respect to copper nitrate. The results are summarized in Table 27.

**TABLE 27**

Current Efficiencies Using Cu-64 and Ag-110

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Current Density (ma/sq cm)</th>
<th>Tracer Added</th>
<th>Current Efficiency for Silver (percent)</th>
<th>Current Efficiency for Copper (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>331</td>
<td>0.306</td>
<td>Ag-110</td>
<td>94.6</td>
<td>0.01</td>
</tr>
<tr>
<td>332</td>
<td>0.306</td>
<td>Cu-64</td>
<td>96.5</td>
<td>0.02</td>
</tr>
<tr>
<td>333</td>
<td>0.306</td>
<td>Ag-110</td>
<td>98.5</td>
<td></td>
</tr>
<tr>
<td>334</td>
<td>0.306</td>
<td>Cu-64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>335</td>
<td>0.306</td>
<td>Ag-110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>336</td>
<td>0.306</td>
<td>Ag-110</td>
<td>96.0</td>
<td>0.01</td>
</tr>
<tr>
<td>337</td>
<td>0.306</td>
<td>Cu-64</td>
<td>96.8</td>
<td>0.03</td>
</tr>
<tr>
<td>338</td>
<td>0.306</td>
<td>Ag-110</td>
<td>98.4</td>
<td></td>
</tr>
<tr>
<td>339</td>
<td>0.306</td>
<td>Cu-64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>340</td>
<td>3.06</td>
<td>Ag-110</td>
<td>94.6</td>
<td>0.02</td>
</tr>
<tr>
<td>341</td>
<td>3.06</td>
<td>Cu-64</td>
<td>93.9</td>
<td>0.07</td>
</tr>
<tr>
<td>342</td>
<td>3.06</td>
<td>Ag-110</td>
<td>95.6</td>
<td></td>
</tr>
<tr>
<td>343</td>
<td>3.06</td>
<td>Cu-64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>344</td>
<td>3.06</td>
<td>Ag-110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>345</td>
<td>3.06</td>
<td>Ag-110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>346</td>
<td>30.6</td>
<td>Ag-110</td>
<td>17.7</td>
<td>58.97</td>
</tr>
<tr>
<td>347</td>
<td>30.6</td>
<td>Cu-64</td>
<td>17.7</td>
<td>79.0</td>
</tr>
<tr>
<td>348</td>
<td>30.6</td>
<td>Ag-110</td>
<td>29.9</td>
<td></td>
</tr>
<tr>
<td>349</td>
<td>30.6</td>
<td>Cu-64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>30.6</td>
<td>Ag-110</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*1 x 10^-3 molar copper nitrate is present.

If the calculated percent current efficiencies were less than 0.1 percent, the activity on the electrodes was less than $1/2$ the background activity. This quantity of activity could be due to adsorption or entrapment of copper in the silver deposit.
Observations from Table 27 are as follows:

1. No copper was found in the deposit of silver when a current density of 0.306 or 3.06 milliamperes per square centimeter was used.

2. The current efficiency for the deposition of silver was greater when copper nitrate was present at a concentration of $1 \times 10^{-3}$ molar than when it was absent.

3. At the highest current density, copper deposited at a higher current efficiency than the silver, and they were present at the same concentration.

Since copper nitrate was reduced at a current density 100-fold the rate at which the majority of the electrodepositions were run, the potential of the electrode was not negative enough to reduce hydrogen or nitrate ions at the lower current densities. When copper ions were reduced, they were reduced from the (II) state to the metal.

The appearance of the electrodes changed as the current density increased. Shiny deposits of silver were produced at the lowest current density. Dull metallic deposits were produced at the middle current density, and spongy dark deposits were produced at the highest current densities.

Since high concentrations of copper nitrate were found to decrease the current efficiency for the deposition of silver, the effect of other cations at high concentrations were studied. The cations were representative of different families in the periodic table, and they had relatively high solubilities. The first series of electrodeposition of silver were made from $1 \times 10^{-4}$ molar silver nitrate solutions that were 3 molar with respect to the metal nitrate salt. If the solubilities of the salts were less than that required to produce a 3 molar solution, 1.50 molar or 1.00 molar solutions were used. No nitric acid was added to the solutions.
with high concentrations of nitrate salts because the pH of the solutions obtained from the dissolution of the salts ran from 0 to 4.29. Sodium nitrate was not added. The current density was 0.306 milliamperes per square centimeter, and 0.40 micro equivalents of electricity were used.

In order to determine the concentration effect of these selected cations on the current efficiency, a second series of electrodeposition were performed in solutions which were 1/10 the metal salt concentration used in the first series. The results are summarized in Table 28. The current efficiency for a similar solution of \(1 \times 10^{-4}\) molar silver nitrate without these cationic salts would be 93.5 percent.

**TABLE 28**

Current Efficiency for Silver in the Presence of High Concentrations of Other Cations

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration</th>
<th>Current Efficiency (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium (II)</td>
<td>3.00 molar</td>
<td>36.2</td>
</tr>
<tr>
<td></td>
<td>0.30 molar</td>
<td>88.3</td>
</tr>
<tr>
<td>Iron (III)</td>
<td>1.50 molar</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>0.15 molar</td>
<td>0.30</td>
</tr>
<tr>
<td>Cobalt (II)</td>
<td>3.00 molar</td>
<td>86.9</td>
</tr>
<tr>
<td></td>
<td>0.30 molar</td>
<td>89.5</td>
</tr>
<tr>
<td>Nickel (II)</td>
<td>3.00 molar</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>0.30 molar</td>
<td>94.8</td>
</tr>
<tr>
<td>Copper (II)</td>
<td>3.00 molar</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>0.30 molar</td>
<td>93.7</td>
</tr>
<tr>
<td>Aluminum (III)</td>
<td>1.50 molar</td>
<td>82.0</td>
</tr>
<tr>
<td></td>
<td>0.15 molar</td>
<td>91.9</td>
</tr>
<tr>
<td>Cadmium (II)</td>
<td>3.00 molar</td>
<td>85.8</td>
</tr>
<tr>
<td></td>
<td>0.30 molar</td>
<td>90.7</td>
</tr>
<tr>
<td>Lead (II)</td>
<td>1.00 molar</td>
<td>84.6</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>91.8</td>
</tr>
</tbody>
</table>
Observations from the data in Table 28 are as follows:

1. The current efficiency obtained with the highest concentration of metal nitrate salts was always below that obtained with no added metal nitrate.

2. The current efficiency increased in all of the solutions with a decrease in the added cation concentration.

3. There was no correlation between magnitude of decrease in the current efficiency and the charge on the cation.

4. The low current efficiencies experienced in the presence of iron (III) were attributed to its reduction to iron (II).

5. There was no systematic variation in the current efficiency which could be attributed to the periodic arrangement of the cations in the periodic table.

6. Nickel and copper were the only two elements which showed an extreme variation in their effect on the current efficiency with dilution.

All the cations used in this study have oxidation numbers of +2 or +3, and all of them caused a decrease in the current efficiency at the highest concentration. However, even higher concentrations of a cation with a +1 oxidation number such as sodium caused an increase in the current efficiency when it was present in 10 molar concentrations. (See the five-minute and ten-minute runs in Figure XI.)

The decrease in the percent current efficiency for the calcium (II) solution was attributed to a chloride impurity in the nitrate salt. Upon addition of silver nitrate to a clear solution of the salt a slight cloudiness was apparent. The chemical assay on the calcium nitrate bottle indicated there was 0.001 percent chloride in the salt, and this furnished enough chloride ion to exceed the solubility product of silver chloride in the quantity of salt used.
The effect of powdered silver formation

If a powdered form of the reduced silver was found in the electrolyte, this would account for a reduction in the measured current efficiency. The first two potential plateaus found during an exhaustive electrodeposition of 10 micro equivalents of silver nitrate (see Figure IX) corresponded to concentration ranges of the silver nitrate where the current efficiency for the deposition of silver was quite different, and it was desired to determine the quantity of powdered silver formed in each range.

The quantity of silver powder formed was separated from the electrolyzed solution by filtration, and its activity was measured. The activity due to the powdered silver was used to calculate the percentage of current it represented. The activity deposited on the electrode was used to determine the percentage of current it represented, and these were compared.

In order to investigate the possibility of powdered silver formation in the concentration ranges of the potential plateaus, the volume of solution which could be electrolyzed, concentration of silver nitrate, number of equivalents of electricity used for the deposition and the specific activity of the silver were considered relative to each other. The maximum volume of solution which could be safely handled in the electrolytic cells was 100 milliliters. The potential plateaus were found in the concentration ranges of $7 \times 10^{-3}$ to about $5 \times 10^{-5}$ molar silver nitrate and about $5 \times 10^{-5}$ molar nitrate and lower concentrations. By using 100 milliliters of $1 \times 10^{-4}$ and $5 \times 10^{-5}$ molar silver nitrate
solutions in a three micro equivalent electrodeposition and a current density of 0.306 milliamperes per square centimeter, the concentration of the silver nitrate should remain in the concentration ranges of the two potential plateaus. The specific activity of the silver solutions were adjusted so the quantity of activity which would be measured would give good statistical data. The specific activity of the $1 \times 10^{-4}$ molar silver nitrate solution used for investigation of the possibility of powdered silver was very high because the maximum estimated amount of the silver which could be found as silver powder would be 1.5 percent of the total present. Since the activity deposited on the electrode from the solution used to study the possibility of the formation of powdered silver would be approximately 18 times as much as the quantity of activity associated with the powdered silver, the activity of the silver deposited on the electrode would be too high for accurate measurement. Therefore, for each concentration of silver two solutions were prepared. One solution with a high specific activity for determination of the possibility of the formation of powdered silver, and a second with a lower specific activity for the determination of the quantity of silver deposited on the electrode.

In order to study the effect of the anode on the silver powder formation two series of electrodepositions were performed. In the first series the anode and the cathode were in the same compartment. In the second series the anode and cathode compartments were separated by the separators supplied with the Leeds and Northway #7961 Coulometric Titration Cell Kit. The platinum foil electrode supplied in this kit was used
as the anode, and the electrolyte used in the anode compartment was 20 percent ammonium nitrate.

In the first series of runs four cells were connected in series. Two of the cells contained $1 \times 10^{-4}$ and $5 \times 10^{-5}$ molar silver nitrate with high specific activities of silver for the study of powder silver formation, and the other two cells contained similar concentrations of silver nitrate with a lower specific activity for determination of the quantity of silver deposited on the electrode.

In the second series of runs the potential drop developed across the porous glass discs of the compartment separators eliminated the use of two or more cells in series, since they would require a potential output of the constant current coulometer which was larger than that recommended for the instrument. Therefore, both the quantity of silver deposited on the cathode and the amount of reduced silver in the solution were determined with the same cell. The amount of active silver in this single cell was adjusted to detect small amounts of reduced silver in the solution, and therefore, the activity of the silver deposited on the electrode was too large for accurate measurement. The most accurate measurements of the radioactivity were made with the five-inch well crystal and its associated electronic measuring equipment. For count rates that would be over 200,000 counts per minute on the five-inch well crystal, the activity was measured with a less sensitive $2 \times 2$-inch crystal and its associated electronic equipment. The $2 \times 2$-inch crystal was more subject to geometrical errors in counting, but they were minimised by placing the electrodes with radioactive silver in the most
reproducible position for measuring the activity. The count rate obtained on this crystal can be changed to the count rate which would be obtained on the five-inch well crystal by multiplying it with an appropriate conversion factor.

In previous attempts to separate powdered silver from the silver nitrate solution for measurement by means of a porous glass filter with an average pore size of 14 microns, no silver powder was detected. If this was due to the fact that the particles were small enough to pass through the filter, the use of a millipore filter with a pore size of 0.45 microns might filter them from the solution. However, some of the silver would be reduced by the filter because these filters were made of organic material. The activity due to the silver powder was determined by subtraction of the activity found on a blank from the activity found on the filters through which the electrolyzed solutions passed.

The solutions used for blanks should approximate the composition of the electrolyzed solutions. Therefore, solutions of $7.16 \times 10^{-5}$ and $2.05 \times 10^{-5}$ molar silver nitrate solutions were used for the preparations of the blanks, because 30 percent and 59 percent of the silver in the respective $1 \times 10^{-4}$ and $5 \times 10^{-5}$ molar silver nitrate was deposited on the electrodes.

The percent current efficiencies for the deposition of silver were calculated by using Equations i, ii, and iii. The quantity of powdered silver was also calculated in terms of the loss in percent current efficiency it represented. The radioactivity measured on the filters and the electrodes, and the calculated percent current efficiencies are summarized in Table 29.
<table>
<thead>
<tr>
<th>Silver Nitrate Concentration (molar)</th>
<th>Cell</th>
<th>Unit Measured</th>
<th>Activity Measured (c/m)</th>
<th>Activity from Powdered Silver</th>
<th>Current Efficiency (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>First Series:</strong> Anode and cathode are in the same compartment.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.023 × 10⁻⁴</td>
<td>1</td>
<td>Filter Hᵃ</td>
<td>137,773</td>
<td>48,533</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank</td>
<td>89,240</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Filter Tᵃ</td>
<td>34,737</td>
<td>-8,903</td>
<td>-0.1</td>
</tr>
<tr>
<td>1.023 × 10⁻⁴</td>
<td>2</td>
<td>Electrode</td>
<td>79,248</td>
<td></td>
<td>97.2</td>
</tr>
<tr>
<td>5.115 × 10⁻⁵</td>
<td>3</td>
<td>Filter H</td>
<td>729</td>
<td>- 438</td>
<td>-0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank</td>
<td>1,167</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Filter T</td>
<td>108</td>
<td>- 156</td>
<td>-0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank</td>
<td>264</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.115 × 10⁻⁵</td>
<td>4</td>
<td>Electrode</td>
<td>68,384</td>
<td></td>
<td>78.7</td>
</tr>
<tr>
<td><strong>Second Series:</strong> Anode is separated from the cathode compartment.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.023 × 10⁻⁴</td>
<td>5</td>
<td>Filter H</td>
<td>32,832</td>
<td>14,984</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank</td>
<td>17,848</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Filter T</td>
<td>10,085</td>
<td>1,357</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank</td>
<td>8,728</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electrodeᵇ</td>
<td>277,134</td>
<td></td>
<td>94.1</td>
</tr>
<tr>
<td>5.115 × 10⁻⁵</td>
<td>6</td>
<td>Filter H</td>
<td>1,367</td>
<td>200</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank</td>
<td>1,167</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Filter T</td>
<td>606</td>
<td>342</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank</td>
<td>264</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electrode</td>
<td>83,662</td>
<td></td>
<td>76.6</td>
</tr>
</tbody>
</table>

ᵃMilli pore filters, H for heavy filter and T for thin filter.

ᵇMeasured with a 2 × 2-inch crystal, the conversion factor for conversion to a count rate on the five-inch well crystal was 5.498.
The results of the powdered silver investigation were—

1. A significant quantity of silver was reduced by the filters during the filtration.

2. Although there was an indication that powdered silver was formed when the anode compartment was separated from the cathode compartment, the observed decrease in the current efficiency from 100 percent was not accounted for by the formation of powdered silver.

3. Separation of the anode compartment did not cause the formation of powdered silver to increase markedly.
CHAPTER VI

EXPLANATION FOR OBSERVED CURRENT EFFICIENCIES

The mechanism of entrapment

The following mechanism is proposed to explain why the addition of sodium nitrate to a silver nitrate solution decreased the erratic changes in the current efficiency, and why the measured current efficiency was above 100 percent in deposits from certain supporting electrolytes, and below 100 percent from other supporting electrolytes.

It was found that approximately 10 micro grams of mass was entrapped between the metallic surface of a platinum electrode and the silver deposit when the total silver deposited varied over a 40-fold range. Thus silver salts in the electrolyte could increase the quantity of silver in the deposit above the quantity of silver electrolytically deposited. This could cause the measured current efficiency to be above 100 percent under certain conditions. However, increases above 100 percent were not consistent and were quite erratic in some electrolytes.

The proposed mechanism of entrapment of silver salts in the deposit of the silver metal depends on the formation of tree-like structures which grow from the platinum surface and trap electrolyte at the base of the trees. Lingane (158) states the following: "From silver nitrate solution silver deposits in a coarsely crystalline form; at small current densities the deposit is tree-like or dendritic and individual crystals are discernible, while at large current densities a loose
filamentous or hairy deposit results." The strength and height of these
tree-like structures determine the quantity of electrolyte entrapped,
and the amount of silver salts entrapped depends on the concentration of
the silver in the electrolyte entrapped.

Both the growth of the silver deposit and the quantity of silver
salt entrapped were considered to be a function of the concentration of
the silver ions at the electrode surface. The concentration of the
silver ions on the platinum surface laid the foundation for the initial
growth of the deposit, and silver ions supplied by diffusion or migration
determined the subsequent growth of the deposit.

The effect of the platinum surface on the adsorption of silver
was studied in an indirect way by Rosa and his co-workers (48). If the
platinum surface influenced the adsorption of silver ions, the electro-
lytically deposited silver should show variations along a smooth surface
as irregularities in the crystalline structure of the deposit, and these
irregularities should reappear in each electrodeposition. The surface of
the platinum was marked with scratches, and each deposit on the platinum
surface was examined by means of a microscope. Irregularities in the
deposit were not reproducible, and the adsorption of the silver was
concluded to be a random process.

The effect of sodium ions or hydrogen ions on the adsorption of
silver was questionable, since the quantity of these ions adsorbed should
be very small (159, 160).

The effect of the anions on the adsorption of silver ions on the
platinum surface varied with the type of anion and the concentration of
the silver salt. According to the data and conclusions on pages 54 to 61,
the adsorption of silver ions from dilute solutions of silver nitrate was independent of the silver nitrate concentration, but the adsorption of silver ions from dilute solutions of silver sulfate was dependent on the concentration of silver sulfate. Silver salts with lower solubilities were also found to cause larger quantities of silver ions to adsorb on the metallic surfaces. If the charge of the adsorbed silver ions were delocalized as in the silver ion adsorption on a silver surface (161), negative ions would be electrostatically attracted to the surface forming a double layer. The quantity of positive charge induced on the platinum surface is probably a function of the number of silver ions adsorbed and the portion of its charge transferred. The silver salts with a stronger bond between silver and the anion did not transfer as large a positive charge to the platinum surface per silver ion adsorbed, and a larger number of silver ions were adsorbed before the positive charge on the surface limited the adsorption of additional silver ions.

The concentration of the silver ions at the electrode surface during an electrolysis was a function of the rate of reduction, release of the molecules of solvation attached to the silver ions prior to reduction, and transfer of silver ions from the body of the solution. Conway and Bockris (173) illustrated how each of the five water molecules of solvation were released from an adion prior to its reduction, and he assumed that the slow step in the reduction of silver was associated with the release of these molecules of water.

The reduction of the adsorbed silver ions on the platinum surface acted as the origins of the trunks of the tree-like structures. The silver atoms reduced on the platinum surface probably migrated into
monomolecular layer groupings along the surface of the platinum, and these groupings were projections into the solution. Since these projections from the electrode surface had a higher negative charge density than the smooth platinum surface, additional silver ions were preferentially attracted and adsorbed at these locations. The silver ions reduced on the silver groupings migrated to their proper lattice positions, and formed the trunk of a tree-like structure.

Silver ions adsorbed on the surfaces of the crystalline deposits of silver along the side of the projection were reduced and initiated the growth of a branch of the tree-like structure, or increased the thickness of the tree-trunk. The branching process increased as the deposit grew away from the surface of the platinum electrode, and the top of the trees grew together forming a continuous surface of silver with entrapped material at the base of the trees. If silver salts were trapped at the base of the tree, they were not reduced. The enclosure in which these salts were entrapped were at a constant potential, and the reduction of the silver would constitute a violation of the law of electroneutrality because the negative charge on the anion associated with the silver ion could not be neutralized by transferring another cation into the enclosure or the escape of the anion from the enclosure. The result of entrapment of additional silver ions in the deposit caused the quantity of silver measured to be larger than the quantity of silver represented by the number of coulombs of electricity used for the deposition.

In the presence of large amounts of sodium nitrate, entrapment of silver nitrate was not observed; and strong deposits were formed which did not flake away. The silver ions were believed to be supplied by a
process of diffusion, and the surfaces to the side as well as towards the solution were supplied with a fresh supply of silver ions at approximately the same rate. If sodium ions can exchange with the silver ions adsorbed on the surface of the deposit, under the influence of a potential field, the silver ions had a better chance to escape entrapment at the base of the tree-like structures.

In the absence of sodium nitrate, silver nitrate was entrapped, and weak deposits were formed which tended to flake away. The silver ions were believed to be supplied by a process of migration, and the branches which represented projections into the solution with a higher charge density attracted the silver ions in preference to the trunk of the tree. Therefore the branches grew faster than the tree trunk by adsorption and reduction of these silver ions. Therefore, these tree-like structures entrapped more electrolyte than the solutions with sodium nitrate (see Figure V). These structures were also more fragile (see the erratic results in Figure VI).

Entrapment of silver sulfate was observed in the presence of sodium sulfate because of the higher concentration of silver ions adsorbed at the surface.

In conclusion, the mechanism of entrapment explained why there was excess mass in the deposit, why the silver salts were found in some deposits and not in others, and why some deposits were held more tenaciously than others to the platinum surface of the electrode.
An explanation for the decrease in the current efficiency

An unexplained loss of current was observed in the majority of the electrodepositions of silver. It is felt that this loss in current is due to the reduction of hydrogen ions.

According to the investigations of Rosa and his co-workers (49) there is a 4 parts per million decrease in the quantity of silver deposited for each part per million of nitric acid added to a 0.1 molar silver nitrate solution in the range of 1 to 10 parts per million of nitric acid. Addition of larger amounts of nitric acid causes the decrease in the silver deposited to become less for each additional part per million of acid added. In the solutions used in the present investigation, the concentration of silver nitrate was much lower and the concentration of acid was normally much higher. Therefore, an increase of the acid strength in the concentration range which was used should not cause a significant variation in the current efficiency for the deposition of silver according to Rosa and his co-workers’ investigations, and this was in accord with the results from the pH study. During the exhaustive electrodeposition-potential studies of the present investigation, the pH of the solutions was observed to increase when the concentration of silver nitrate fell below $5 \times 10^{-5}$ molar. A pH change resulting from the reduction of hydrogen ions was not observed at higher concentrations of silver nitrate because the portion of the current used to reduce the hydrogen ions was too small to produce a measurable change.

The potential developed at a hydrogen electrode corresponds to the reaction at a specially prepared surface and a hydrogen pressure of
one atmosphere. In the silver solutions which were electrolyzed in this investigation, the hydrogen pressure was extremely small; and the surface was composed of platinum and silver crystals orientated in a random manner. Related studies on the reduction of hydrogen at a cathode indicate that its reduction is rather complicated.

Thon and his co-workers (162) report that there are three types of hydrogen formed during the electrodeposition of nickel. Each type is distinguished by its ability to be released from the deposit of nickel which is heated in a vacuum. Franklin and Matsuda (163) also report that there are three types of hydrogen formed during the electrodeposition of iron. Each type of hydrogen is distinguished and measured by a cyclic coulometric method. Franklin and Cooke (164) suggest that $H_2^+$, a fourth type of hydrogen, is formed at a platinum anode which is solvated. Uhlig and Krutenat (165) demonstrate that a soluble reduced species of hydrogen is formed at magnesium, platinum and mercury cathodes in sulfuric acid solutions when hydrogen is bubbled past the cathodes. The reducing species has a half-life of approximately five minutes, and they suggest that it may be hydrolyzed atomic hydrogen, $H_{aqua}$, or $H_2^+$.

Thon and his co-workers (166) state that the amount of hydrogen absorbed is directly proportional to the porosity of the electrodeposited metal. If the metal is deposited from a solution containing only inorganic ions, the only material released from the electrolytically deposited metal is hydrogen. According to Franklin and Sothern (167) organic nitriles appear to displace adsorbed hydrogen, and Franklin and Goodwyn (168) showed that a complicated relationship exists between the hydrogen and the organic compounds adsorbed in the metallic deposit.
The porosity of the metal electrolytically deposited on a surface on another metal is a function of the type of metal electrolytically deposited, the thickness of the deposit, and the preparation of the surface of the base metal. A metal deposited on a crystalline surface has approximately one-third the porosity that is found in a deposit on a mechanically polished surface (166). However, the metallic surface used for the base is the same metal which is to be electrodeposited, co-deposition of hydrogen might be eliminated by either chemically or mechanically polishing the surface (169).

In addition to the different types of hydrogen that are electrolytically deposited, each crystalline plane of a metallic surface can influence the reaction which takes place on a surface to a different degree as is shown in the reduction and adsorption of hydrogen and the variation of exchange rates between metallic atoms and their ions. Will (170) reports saturation current values for hydrogen adsorbed on the 100, 111 and 110 planes of a platinum crystal to be 0.51, 0.46 and 0.30 milli-coulombs per square centimeter for the respective planes. Thon and his co-workers (171) report that a deposit of nickel on iron with its 100-plane parallel to the base (this orientation is preferred when nickel is deposited from a solution at 60°C) is much less porous than a deposit with its 110-plane parallel to the base (this orientation is preferred when nickel is deposited from a solution at 20°C). Tingly (172) reports that there is a rapid exchange between a solution of radioactive silver isotopes and an inactive rod of silver when the rod of silver is first introduced into the solution, but the exchange rate decreases with time.
The exchange rate for extended times is close to that expected from grain boundary diffusion rates, and there is a variation in the activity found on the different planes of the silver. The uptake of radioactive isotopes along the 311 plane is the slowest, and the rates along the 110, 100 and 111 planes are 1.2, 2.4 and 7.2 times as fast as the rate along the 311 plane. The percents of activity released into distilled water after 50 hours from the different planes are 20, 15 and 10 percent for the 100, 110 and 111 planes, respectively.

Thon and co-workers (166) report that a 20 micron deposit of silver from a cyanide solution is porous enough to permit $7.2 \times 10^{-5}$ liters of a noncorrosive gas to pass per square centimeter of surface per minute. If this data can be related to the more extensive data on the porosity of electrolytically deposited iron, the atom ratio of the number of absorbed hydrogen atoms to the number metal atoms is in the range between 1:130 to 1:300.

An increase in the current efficiency for the reduction of silver by increasing the temperature can be explained by the reduction of hydrogen as the competing reaction. If the slow step in the reduction of silver (173) is the release of the water molecules, absorption of thermal energies by the silver ion and its associated molecules of water could cause increased vibrations between the ion and its water molecules. This should weaken the bonds between these molecules and the silver ion and cause the rate of reduction of silver ions to increase, relative to the rate of reduction of hydrogen ions. This would result in an increase in the current efficiency for the reduction of silver. This assumes that the equilibrium between the hydrated proton and the proton and water
molecule is much less influenced by heat than the corresponding equilibrium for the hydrated silver ion.

If a portion of the current was used to produce an atomic form of hydrogen with a half-life of five minutes as was observed by Uhlig and Krutenat, this species would be capable of reducing silver ions in the body of the solution and form a small amount of powdered silver.

In conclusion, the loss in current efficiency for the deposition of silver was observed to be due to the reduction of hydrogen for low concentrations of silver nitrate, and the reduction of hydrogen was proposed as the competing reaction at higher concentrations as an explanation of the effects of varying the electrical and chemical properties of the system, and as an explanation for the formation of the minute quantity of powdered silver. The mechanism for the reduction of hydrogen seems to involve the adsorption of a limited number of hydrogen ions which are reduced to an atomic form of hydrogen. The atomic form of hydrogen can be either absorbed into the metallic deposit as a tenaciously held species, or absorbed on the surface as a labile species which can undergo a combination reaction to form a gaseous molecule or form a soluble species in solution. The course of the reaction in which the atomic form of hydrogen is involved seems to be governed by the environment in which it is formed.
CHAPTER VII

DETERMINATION OF SILVER BY REVERSE ISOTOPE DILUTION
AND A CONSTANT CURRENT ELECTRODEPOSITION

Introduction

It was originally hoped that the current efficiency studies would lead to conditions under which 100 percent current efficiency could be obtained for the deposition of at least a fraction of the silver from solutions containing low silver-ion concentrations. Under these conditions the number of coulombs of electricity passed would directly give the number of moles of silver deposited and the isotope dilution method of analysis would permit the calculation of micro quantities of silver originally present in a sample from sub micro quantities of metal plated on an electrode. However, conditions were not found for plating silver at 100 percent current efficiency from solutions containing low concentrations of silver and large concentrations of other ions that frequently occur with silver.

The second possibility was the calculation of the current efficiency of a standard silver solution run in series with the unknown and the correction of the recorded coulombs to obtain the true weight of silver deposited from the unknown solution. However, the current efficiency for silver deposition is often not the same for a solution of just silver ions, and a solution of the same concentration of silver ions in the
presence of large quantities of other metallic ions. The preparation of a standard with the approximate concentrations of all the ions obtained from dissolution of a sample that contained a trace of silver would tend to decrease the difference in the current efficiencies between the standard and the unknown solutions, but the preparation of such a solution becomes more impractical as the complexity of the unknown increases.

In order to overcome these difficulties, the method suggested in the present work involves standard addition of silver to several aliquots of the unknown solution. The unknown sample is dissolved, the radioactivity is added, and the solution is divided into n equal parts. The first part is used as a reference solution, and increasing known quantities of inactive silver are added to each of the remaining parts. By treating both the current efficiency and unknown quantity of silver originally present as unknowns, a mathematical expression was derived to calculate the unknown amount of silver from two independent measurements. These measurements are the activity of silver electrolytically deposited from the solution with no added silver and the deposit from a solution with a known-quantity of added silver. The major assumption in the derivation is that the current efficiencies for each of the solutions are the same. This is reasonable since, except for some variation in the silver concentration, the type and concentration of all ions present are exactly the same for all the solutions. If the variation in current efficiency due to a variation in the silver-ion concentration caused a change in the current efficiency, it should be systematic. This variation should be at least largely eliminated by a graphical extrapolation of the
results to zero added silver by using a plot of the calculated unknown quantities of silver against the quantity of added known silver.

In order to test this method, known solutions were made from the same reagents which were used in the current efficiency studies and the same apparatus was used as in the current efficiency studies. The concentration of the supporting electrolyte was always 100-fold the silver-ion concentration, and the pH was approximately 2.

The procedure for the electrodeposition and the measurements of the activity deposited was the same as for the current efficiency studies. The current density was 0.306 milliamperes per square centimeter. The rate of stirring was 400 revolutions per minute, and the duration of the run was one minute.

**Derivation of the equations**

In order to derive an equation for the number of moles of silver in the unknown, the following symbols were defined:

- $M_o$: The moles of silver originally present
- $M_a$: The moles of silver added to that originally present
- $M_{p-o}$: The moles of silver plated from the solution with no added silver
- $M_{p-a}$: The moles of silver plated from the solution with added silver
- $M_e$: The moles of silver calculated in the original sample
- $A_t$: The total activity in each cell
- $A_a$: The activity plated from the solution with added silver
- $A_o$: The activity plated from the solution with no added silver
The activity plated from the solutions with no added silver and solutions with added silver were expressed by the following equations:

\[ A_o = \frac{(M_p-o)(A_t)}{(M_o)} \quad \text{(vi)} \]

\[ A_a = \frac{(M_p-a)(A_t)}{(M_o + M_a)} \quad \text{(vii)} \]

Rearrange (vi) and (vii)

\[ A_t = \frac{(A_o)(M_o)}{(M_p-o)} \quad \text{(viii)} \]

\[ A_t = \frac{(A_a)(M_o + M_a)}{(M_p-a)} \quad \text{(ix)} \]

Since the total amount of activity which was in the solution with no added silver was the same as in all the solutions with added silver, equate (viii) and (ix).

\[ \frac{(A_a)(M_o)}{(M_p-o)} = \frac{(A_a)(M_o + M_a)}{(M_p-a)} \quad \text{(x)} \]

Rearrange (x) so one can calculate \( M_o \).

\[ \frac{(M_p-a)(A_o)(M_o)}{(M_p-a)(A_o)(M_o)} = \frac{(M_p-o)(A_a)(M_o + M_a)}{(M_p-o)(A_a)(M_o + M_a)} \]

\[ \frac{(M_p-a)(A_o)(M_o)}{(M_p-a)(A_o)(M_o)} = \frac{(M_p-o)(A_a)(M_o + M_a)}{(M_p-o)(A_a)(M_o + M_a)} \]

\[ \frac{(M_p-o)(A_a)(M_o + M_a)}{(M_p-a)(A_o) - (M_p-o)(A_a)} \quad \text{(xi)} \]

Since the physical, electrical and chemical properties for all of the series electrodepositions were approximately the same, \( M_p-o \) should be close to \( M_p-a \). Assuming they were equal, permitted the cancelation of these terms from the numerator and denominator of (xi).

\[ (M_o) = \frac{(M_p)(A_a)}{(A_o) - (A_a)} \quad \text{(xii)} \]
Since this expression involves the above assumption of equal current efficiency, \( M_c \), the moles calculated, was substituted for \( M_0 \).

\[
(M_c) = \frac{(Na)(Aa)}{(Ao) - (Aa)}
\]  

(xiII)

From 3 to 5 electrodepositions were run in series. One of these contained only the unknown sample and the others contained the same quantity of unknown together with various known amounts of added silver. Equation (xiii) was used to calculate the number of moles of silver in the cell which contained the unknown quantity of silver or the lowest quantity of silver in any series run. One value for the unknown quantity of silver was calculated for each cell with a different known quantity of added silver. This meant there were \( n - 1 \) values for the unknown quantity of silver, where \( n \) was the number of cells in the series. Each of the calculated values were plotted as a function of the quantity of added silver, and a line was drawn between the points which extrapolated back to zero added silver.

In order to evaluate the error introduced in the calculated values of the unknown quantities of silver due to the difference in \( (M_p - c) \) and \( (M_p - a) \), an expression for the percent error in the calculated quantity of unknown silver was derived as a function of the ratio of added silver to the unknown silver, and the current efficiencies for the electrodepositions.

The percent error is defined as--

\[
\% \text{ Error} = \frac{100(M_c)}{(M_0)} - 100
\]  

(xIV)
The activity plated out on the electrode was

\[ A_o = \frac{(M_p-o)(A_t)}{(M_o)} \]  \hspace{1cm} (xv)

\[ A_a = \frac{(M_p-a)(A_t)}{(M_o + M_a)} \]  \hspace{1cm} (xvi)

Substitute (xv) and (xvi) into (xiii):

\[ M_o = \frac{(M_a) \left[ \frac{(M_p-a)(A_t)}{(M_o + M_a)} \right]}{\left[ \frac{(M_p-o)(A_t)}{(M_o)} - \frac{(M_p-a)(A_t)}{(M_o + M_a)} \right]} \]  \hspace{1cm} (xvii)

Since \( A_t \) was the same in all of the solutions from a particular series, it was factored out of the numerator and the denominator and canceled from the equation.

\[ M_o = \frac{(M_a) \left[ \frac{(M_p-a)}{(M_o + M_a)} \right]}{\left[ \frac{(M_p-o)(M_o) + (M_p-o)(M_a) - (M_p-a)(M_o)}{(M_o)(M_o + M_a)} \right]} \]  \hspace{1cm} (xviii)

Cancel \( (M_o + M_a) \) from the numerator and the denominator:

\[ M_o = \frac{(M_a)(M_p-a)(M_o)}{(M_p-o)(M_o) - (M_p-o)(M_a) - (M_p-a)(M_o)} \]  \hspace{1cm} (xix)

Substitute (xix) into (xiv):

\[ \% \text{ Error} = \frac{100(M_a)(M_p-a)(M_o)}{\left[ (M_o)(M_p-o)(M_o) - (M_p-o)(M_a) - (M_p-a)(M_o) \right]} - 100 \]  \hspace{1cm} (xx)

If \( M_p \) is the number of moles plated with 100 percent current efficiency, \( K_o \) is the current efficiency for the electrodeposition from the solution without added silver and \( K_a \) the current efficiency for the
electrodeposition from the solution with added silver, then the following was true:

\[(Mp-o) = (Ko)(Mp) \quad \text{(xxi)}\]
\[(Mp-a) = (Ka)(Mp) \quad \text{(xxii)}\]

Cancel \(Mo\) from denominator and numerator of (xv), substitute (xxi), and (xxii) into the resulting equation, and then factor \(Mp\) out of the denominator.

\[
\%\ Error = \frac{(100)(Ma)(Mp)(Ka)}{(Mp) \left[ (Mo)(Ko) + (Ma)(Ko) - (Mo)(Ka) \right]} - 100 \quad \text{(xxiii)}
\]

If \(R = Ma/Mo\), cancel \(Mp\) from the denominator and numerator,

\[R = \frac{Ma}{Mo} \quad \text{(xxiv)}\]

Cancel \(Mp\) from the numerator and denominator of (xxiii), divide the numerator and denominator by \(Mo\), and substitute (xxiv) into the resulting equation.

\[
\%\ Error = \frac{(100)(R)(Ka)}{Ko + (R)(Ko) - Ka} - 100 \quad \text{(xxv)}
\]

Some interesting results were obtained when values for \(Ka\) and \(Ko\) were substituted into Equation (xxv) and the \% Error was calculated as a function of \(R\) (see Figures XVI through XX).

a. When the fraction plated or current efficiency is the same for both electrodes, the \% Error is 0.0 for any value of \(R\).

b. When \(Ko\) is less than \(Ka\) and \(R\) increases from zero, the error goes to \(-\infty\), then abruptly to \(+\infty\), and then to less positive errors.

c. When \(Ko\) is less than \(Ka\) and the value of \(R\) is greater than the point of discontinuity, the positive \% Error decreases rapidly for small increases of \(R\) at first, then it decreases at a slower rate towards a limiting value of \((100)(Ka/Ko) - 100\).
FIGURE XVI

Error Analysis Showing the Region of Discontinuity

Values of Ko and Ka are indicated on the curves
FIGURE XVII

Error Analysis for Large Differences between $K_0$ and $K_a$

Values of $K_0$ and $K_a$ are indicated on the curves
FIGURE XVIII

Error Analysis for Small Differences between Ko and Ka

Ka is held constant
Figure XIX

Error Analysis for Small Differences between Ko and Ka

Ko is held constant
FIGURE XX

Error Analysis for Same Difference between Ko and Ka but Decreasing Values

Values of Ko and Ka are indicated on the curves
d. If Ko is greater than Ka, then the % Error is always negative. As R increases from zero, the negative error decreases rapidly, and it approaches a limiting value of \((100)(Ka/Ko) - 100\) for large values of R.

e. If the values of Ko and Ka were interchanged, the absolute value of the positive error was greater than the absolute value of the negative error.

f. When Ko was larger than Ka and the difference between them was kept constant while decreasing their values, the positive error increased.

**Development and testing of the method**

The method of analysis was developed and tested by treating known quantities of silver as the unknown. This permitted calculation of the current efficiencies for each of the solutions independently from the calculation of the unknown quantity of silver. Since the percent current efficiencies were calculated by an independent method, they could be used in Equation (xxv) to predict the error introduced in the unknown quantity of silver which resulted from the assumption that the current efficiency for the deposition of silver is the same in all of the solutions. The current efficiencies determined were used together with the predicted error and the actual error to evaluate which factors were most responsible for errors in the calculated unknown quantity of silver. The procedure was then modified to minimize the effect of these factors and the error in the unknown quantity.

Calculated percent errors given in Tables 30, 31, 32, 33, and 35 are obtained by using Equation (xxv), and the current efficiencies for Ko and Ka. These are compared with the percent errors in the quantity of silver calculated by means of Equation (xiii).
When the current efficiency was studied as a function of the concentration of silver, the current efficiency increased as the concentration of silver increased. This means there should be an increase in the error with an increase in R values because of the increased difference in current efficiencies. The error in the calculated values can either decrease with increasing R values as demonstrated in Figures XVI to XX, or increase due to a change in the current efficiency with increasing concentrations of silver ions.

The effect of R values on the calculated unknown quantity of silver.--The experimental conditions were chosen so the current efficiencies for the deposition of silver did not vary a large amount from one solution to another, and the effect of R values on the calculated quantity of silver could be evaluated.

A stock solution of $4.09 \times 10^{-4}$ molar silver nitrate containing 0.1 molar sodium nitrate and 0.01 molar nitric acid was prepared. The unknown solutions were 50 milliliters of this stock solution with an appropriate quantity of radioactive tracer. Solutions with added silver had R values which were 0.25 and 1.00, 0.50 and 1.50, and 1.00 and 3.00, and these were prepared by addition of the appropriate quantity of $0.1023$ molar silver nitrate and radioactive tracer. Each series of three solutions were electrolyzed at a current density of 0.306 milliamperes per square centimeter until 0.402 micro moles of electrons were passed through the solution. The moles of the unknown quantity silver calculated by means of Equation (xiii) is plotted against the number of moles of silver added in Figure XXI, and an error analysis is presented in Table 30.
FIGURE XXI

The Effect of Small Quantities of Added Silver on the Determination of the Unknown Quantity of Silver
The following observations were made from Figure XXI:

1. The error was positive, and this resulted from the fact that Ko was less than Ka.

2. The decrease in the difference between current efficiencies as Ha became smaller did not offset the error introduced by R values less than 1.

3. The extrapolated values produced a more positive error than any of the calculated values for combinations which had R values less than 1.

4. There was a smaller positive error for the set with the largest R values.

The exact quantity of silver in the unknown was indicated by an arrow in Figure XXI.

TABLE 30
An Error Analysis for Small Values of R

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Current Efficiency</th>
<th>R</th>
<th>Percent Error Calculated from the Equation</th>
<th>Quantity of Silver for Each Result</th>
<th>Extrapolated Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ko</td>
<td>Ka</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>190</td>
<td>0.926</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>191</td>
<td>0.963</td>
<td>0.50</td>
<td>13.0</td>
<td>12.7</td>
<td></td>
</tr>
<tr>
<td>192</td>
<td>0.955</td>
<td>1.50</td>
<td>5.3</td>
<td>-5.3</td>
<td>16.7</td>
</tr>
<tr>
<td>193</td>
<td>0.889</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>194</td>
<td>0.915</td>
<td>1.00</td>
<td>3.6</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>195</td>
<td>0.913</td>
<td>0.25</td>
<td>8.3</td>
<td>7.8</td>
<td>11.6</td>
</tr>
<tr>
<td>196</td>
<td>0.933</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>197</td>
<td>0.956</td>
<td>1.00</td>
<td>5.1</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>198</td>
<td>0.962</td>
<td>3.00</td>
<td>4.2</td>
<td>4.1</td>
<td>5.2</td>
</tr>
</tbody>
</table>

The agreement in Table 30 was very good between the percent error predicted using the current efficiency data in Equation (xxv), and the percent error in the quantity of silver calculated using Equation (xiii).
This demonstrates the high precision with which the radioactive techniques were applied. If the current efficiency, $K_a$, of experiment 195 was different by 2 percent, $K_a$ would change from 0.913 to 0.931 and the predicted error would change from 8.3 to 20.5 percent.

The fact which was not apparent in Table 30 or Figure XXI, and deserves mentioning, was that the predicted errors in the quantities of silver calculated using Equation (xxv) could only be calculated using the $K_o$ and $K_a$ values in the same series run. In some of the runs, the temperature variations in the room caused larger differences between $K_o$ and $K_a$ values than the silver concentration differences. The quantity of unknown silver must be calculated by only using the data from the same series electrodeposition for the same reason.

In the second series of runs, four instead of three electrodepositions were made in series. In this way three calculated values of the unknown quantity of silver in the sample could be obtained for each series. Thus a better defined curve was obtained for each series. In addition the values of $R$ were increased to 5, 10 and 15. The same concentration of silver and supporting electrolyte for the unknown was used in this series of runs as in the first series of runs. The results are shown in Figure XXIII and the error analysis is presented in Table 31.

The following observations were made from Figure XXIII:

1. The slopes of the lines for the two runs with the above $R$ values were very small in comparison to the slopes obtained with smaller $R$ values in Figure XXI.

2. The individual calculated values fell relatively close to the line.

3. The curve was better defined.
FIGURE XXII

The Effect of Large Quantities of Added Silver on the Determination of the Unknown Quantity of Silver
4. The extrapolated value for the quantity of silver in the solution treated as the unknown was in error by approximately 2 percent as compared to 10 percent when smaller values of $R$ were used.

### Table 31

An Error Analysis for Large Values of $R$

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Current Efficiency</th>
<th>$R$</th>
<th>Percent Error Calculated from the Quantity of Silver for Equation (xxv)</th>
<th>Each Result</th>
<th>Extrapolated Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>205</td>
<td>0.919</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>206</td>
<td>0.933 5</td>
<td></td>
<td>1.8</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>207</td>
<td>0.941 10</td>
<td></td>
<td>2.6</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>208</td>
<td>0.925 15</td>
<td></td>
<td>0.7</td>
<td>1.5</td>
<td>2.3</td>
</tr>
<tr>
<td>209</td>
<td>0.946</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>210</td>
<td>0.972 5</td>
<td></td>
<td>0.5</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>211</td>
<td>0.968 10</td>
<td></td>
<td>0.2</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>212</td>
<td>0.966 15</td>
<td></td>
<td>0.1</td>
<td>1.8</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Four experimental points are necessary in order to distinguish more rapidly any one point that involves a large indeterminate error.

The potential drop across an operating cell was measured to assure that the addition of a fifth cell in series would not require an output potential of the coulometer in excess of six volts. This was the output potential limit which the manufacturer of the coulometer suggested should not be exceeded for maximum accuracy with the 0.643 milliampere output current. There was an added advantage of increasing the number of cells in series from three to five. The time required to obtain four values of the unknown quantity of silver was cut in half.
The effect of increasing current efficiencies with increasing R values on the calculated unknown quantity of silver.--The experimental conditions were chosen so there would be a noticeable increase in the current efficiency with increasing concentrations of silver ions, and the largest increase would be between the unknown solution and solution with the smallest amount of added silver.

A stock solution of $1.023 \times 10^{-4}$ molar silver nitrate containing 1.0 molar cupric nitrate was prepared. No sodium nitrate or nitric acid was added because the cupric nitrate acted as the supporting electrolyte and the pH of the solution was slightly above 3. The preparation of the other solutions and conditions of electrolysis were the same as in the investigations of the effect of R values on the calculated unknown quantity of silver. The results were plotted in Figure XXIII, and an error analysis was given in Table 32.

Observations from Figure XXIII and Table 32 are--

1. The values for the calculated unknown quantities of silver from the first run fell very close to the line drawn between them, and the line had a very low positive slope.

2. The large differences in current efficiencies between the unknown solution and the solutions with added silver caused a large positive error in the calculated unknown quantity of silver.

3. The effect of increasing current efficiencies on the calculated quantity of unknown silver between the solutions with added silver was compensated to a greater or lesser degree by the increasing R values.

4. When the solutions from the first run were electrolyzed a second time, the values for the calculated unknown quantities of silver were more scattered, and had a greater positive error.

5. The increased positive error in the second run is attributed to larger differences in the current efficiency between the electrodeposition of silver from unknown solutions and solutions with added silver.
FIGURE XXIII

The Effect of Increasing Current Efficiencies on the Determination of the Unknown Quantity of Silver
Moles of Ag calculated $\times 10^{-6}$ vs. Moles of Ag added $\times 10^{-5}$
TABLE 32

An Error Analysis for the Calculated Unknown Quantity of Silver with Large Variations in the Current Efficiencies between Solutions

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Ko</th>
<th>Ka</th>
<th>R</th>
<th>Equation (xxv)</th>
<th>Quantity of Silver for Each Result</th>
<th>Extrapolated Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>371</td>
<td>0.544</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>372</td>
<td>0.782</td>
<td>4.0</td>
<td></td>
<td>61.4</td>
<td>61.1</td>
<td></td>
</tr>
<tr>
<td>373</td>
<td>0.829</td>
<td>9.0</td>
<td></td>
<td>61.8</td>
<td>61.5</td>
<td></td>
</tr>
<tr>
<td>374</td>
<td>0.864</td>
<td>14.0</td>
<td></td>
<td>65.8</td>
<td>65.4</td>
<td></td>
</tr>
<tr>
<td>375</td>
<td>0.338</td>
<td>19.0</td>
<td></td>
<td>58.6</td>
<td>58.4</td>
<td>61.1</td>
</tr>
<tr>
<td>376</td>
<td>0.515</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>377</td>
<td>0.819</td>
<td>4.0</td>
<td></td>
<td>86.6</td>
<td>86.0</td>
<td></td>
</tr>
<tr>
<td>378</td>
<td>0.824</td>
<td>9.0</td>
<td></td>
<td>71.1</td>
<td>70.9</td>
<td></td>
</tr>
<tr>
<td>379</td>
<td>0.892</td>
<td>14.0</td>
<td></td>
<td>82.7</td>
<td>82.2</td>
<td></td>
</tr>
<tr>
<td>380</td>
<td>0.819</td>
<td>19.0</td>
<td></td>
<td>64.0</td>
<td>63.3</td>
<td>83.6</td>
</tr>
</tbody>
</table>

Evaluation of the results.—The calculated quantity of silver in the unknown is plotted as a function of the added quantity of silver. This curve is extrapolated to zero added silver to obtain the quantity of silver in the unknown. If a line with a pronounced negative slope is obtained, this generally does not give accurate extrapolated values. A line with a slope more nearly approaching zero can be obtained by increasing the R values, although results from a line with a slope approaching zero does not assure accurate results: see Figures XXII and XXIII and Tables 31 and 32.

A modified method of calculating the quantity of silver in the unknown has been used. This method was based on the relatively constant current efficiencies of silver depositions from the solutions with added
silver. Since these current efficiencies were relatively constant, the quantity of silver in the solution with the lowest amount of added silver was treated as the unknown and its silver content was determined with a fair amount of accuracy. The unknown quantity of silver was obtained by subtraction of the accurately known quantity of added silver from the total quantity calculated. Although this indirect method of calculation is more subject to experimental error than the direct method, it has been used effectively as a check. If calculated values by the two methods check within about six percent, the results by the direct method are used. If there is a large discrepancy between the two, this is an indication of difficulty. This may be caused by an unusually large determinate error. In this case, repeating the determination usually leads to accurate results. It may also be the result of an unknown solution that contains too low a concentration of silver. This can be remedied by rerunning the determination with a larger sample.

The data from Tables 31 and 32 are used in an error analysis for the silver calculated by the indirect method in Table 33 and a comparison of the percent error introduced into the calculated values by the direct and indirect methods of calculation in Table 34.

The error analysis presented in Table 33 demonstrated the following points:

1. There was a close agreement between the predicted error and the actual error in the calculated quantity of silver.

2. The small differences between $K_0$ and $K_a$ values support the assumption that the current efficiencies change less as the concentration of the silver increases.
TABLE 33

An Error Analysis for the Silver Calculated by the Indirect Method

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Current Efficiency</th>
<th>R</th>
<th>Percent Error of the Total Silver Determined in the Solution with the Smallest Quantity of Added Silver</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ko&lt;sup&gt;(a)&lt;/sup&gt;</td>
<td>Ka</td>
<td>Calculated by Equation (xxv)</td>
</tr>
<tr>
<td>206</td>
<td>0.933</td>
<td>0.941</td>
<td>0.833</td>
</tr>
<tr>
<td>207</td>
<td>0.933</td>
<td>1.666</td>
<td>-0.09</td>
</tr>
<tr>
<td>208</td>
<td>0.966</td>
<td>0.968</td>
<td>0.833</td>
</tr>
<tr>
<td>209</td>
<td>0.970</td>
<td>1.666</td>
<td>0.7</td>
</tr>
<tr>
<td>372</td>
<td>0.782</td>
<td>0.829</td>
<td>1.00</td>
</tr>
<tr>
<td>373</td>
<td>0.829</td>
<td>0.864</td>
<td>2.00</td>
</tr>
<tr>
<td>374</td>
<td>0.838</td>
<td>3.00</td>
<td>9.8</td>
</tr>
<tr>
<td>375</td>
<td>0.819</td>
<td>0.824</td>
<td>1.00</td>
</tr>
<tr>
<td>377</td>
<td>0.824</td>
<td>0.892</td>
<td>2.00</td>
</tr>
<tr>
<td>378</td>
<td>0.819</td>
<td>3.00</td>
<td>-0.2</td>
</tr>
</tbody>
</table>

*Ko<sup>a</sup> is the current efficiency for the solution with the lowest added quantity of silver which is treated as the unknown in the indirect method.*
TABLE 34
Comparison of the Percent Error Introduced into the Calculated Quantity of Unknown Silver by the Direct and Indirect Method of Calculation

<table>
<thead>
<tr>
<th>Experiment</th>
<th>The Direct Method</th>
<th>The Indirect Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Individual Results</td>
<td>Average of Run</td>
</tr>
<tr>
<td>206</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>207</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>208</td>
<td>1.5</td>
<td>1.9</td>
</tr>
<tr>
<td>210</td>
<td>1.8</td>
<td>1.9</td>
</tr>
<tr>
<td>372</td>
<td>61.1</td>
<td></td>
</tr>
<tr>
<td>373</td>
<td>61.5</td>
<td></td>
</tr>
<tr>
<td>374</td>
<td>65.4</td>
<td></td>
</tr>
<tr>
<td>375</td>
<td>58.4</td>
<td>61.6</td>
</tr>
<tr>
<td>377</td>
<td>86.0</td>
<td></td>
</tr>
<tr>
<td>378</td>
<td>70.9</td>
<td></td>
</tr>
<tr>
<td>379</td>
<td>82.2</td>
<td></td>
</tr>
<tr>
<td>380</td>
<td>63.3</td>
<td>75.6</td>
</tr>
</tbody>
</table>
3. The error was small in the calculation of the sum quantity of unknown and the lowest quantity of added silver, and the R values as low as one did not cause the calculated error to be large.

4. The error in the unknown quantity, which was obtained by subtracting the accurately known added quantity of silver from the calculated sum quantity, was approximately five to six times the error in the sum quantity.

The National Bureau of Standards alloys

The next step in the investigation of the method of internal standard addition with isotope dilution was to apply it to the determination of the quantity of silver present in an alloy. The alloys available from the National Bureau of Standards had either macro amounts or micro amounts of silver present. This method was applied most advantageously to the determination of micro amounts of silver in the presence of macro amounts of other metals. Macro amounts of other metals were most likely to interfere in the analysis of silver by other methods.

Two types of alloys were chosen for this investigation. Alloy 127A was a solder which contained the following metals: lead (69%), tin (30%), antimony (0.8%), arsenic (0.1%), bismuth (0.004%), copper (0.004%), silver (0.004%), and nickel (0.002%). Alloy 54D was a tin base bearing metal which contained the following metals: tin (88%), antimony (7%), copper (4%), lead (0.6%), arsenic (0.1%), bismuth (0.04%), iron (0.03%), silver (0.003%), and nickel (0.002%). The National Bureau of Standards reported that the silver in alloy 127A was analysed by a dithione-photometric method and photometrically as AgCl after an internal electrolysis separation. The quantity of silver was reported to be 0.003 percent and 0.004 percent by weight for the respective analyses. The National Bureau of Standards reported that the silver in alloy 54D was
analyzed by internal electrolysis using a copper wire, the weight of electrolytically deposited silver on a platinum electrode, a dithizone-photometric method, turbidimetrically after dissolving the sample in HNO₃-HF and precipitation as the chloride, spectrochemically, a rhodanine-photometric method, and a fire assay method. Their results ranged from 0.001 percent to 0.004 percent by weight and 0.003 percent was given as the most likely value.

During the preparation of the alloys for the electrolytic deposition, the alloys had to be oxidized with an excess of oxidizing reagent, and the insoluble products along with the excess oxidizing agent were then removed. Before removing the insoluble products, the radioactive isotope was added so there would be complete isotopic exchange with all the silver present, and not with just the quantity of silver washed off the precipitate.

In the previous investigations of the method, there were no precipitates formed that could adsorb or entrap silver ions. If the silver ions were just adsorbed on the surface of the very fine precipitate, the ions would be in equilibrium with those in the solution and complete isotopic exchange could be effected upon the addition of the radioactive isotope. If the silver ions are entrapped in the crystal structure of the precipitate, those ions would not be in equilibrium with the ions in the solution and complete isotopic exchange could not take place upon addition of the radioactive isotope.

In order to determine whether silver ions were entrapped in the crystalline structure of the insoluble material, two types of experiments
were conducted. The one type of experiment was done to find how much activity or silver would be lost due to adsorption. This was performed by oxidizing a sample of the alloy and adding the active tracer to the mixture of insoluble materials and the resulting solution. The mixture was digested for a period, and the insoluble material was separated by centrifugation. It was then washed a number of times until the blue copper color was completely discharged. The percent activity not washed off the precipitate was noted to be approximately 1 percent of the original amount. The other type of experiment was designed to cause maximum entrapment. This was done by mixing a basic solution which contained the basic soluble salts and an acid solution containing radioactive silver and the acid soluble salts in an amount which was comparable to dissolving 10 grams of the alloy in 50 milliliters of solution. The precipitate which formed was extremely fine, and was more difficult to centrifuge than the precipitate from the alloy. The mixture was digested, washed and counted in the same manner as the alloy. A number of such precipitations were performed in this manner, and the digestion times were altered to find out what effect it had on the quantity of silver retained by the precipitate. The following results were observed by measuring the activity of the precipitate:

1. The percentage of activity decreased with the number of washings.

2. The percentage of activity left on the precipitate according to the above procedure ranged from 2 to 6 percent.

3. The percentage of activity left on the precipitate decreased with increasing times of digestion.

4. The percentage of activity left on the precipitate increased slightly when the density of the precipitate decreased (e.g., 2.41 percent on 3.05 ml, 3.18 percent on 5.55 ml for the same weight).
The results indicate that silver ions were adsorbed instead of entrapped. Adsorption of silver was indicated by the ease of rinsing the radioactivity from the insoluble materials.

The time and conditions necessary for the exchange of the radioactive silver ions and the adsorbed inactive silver ions were determined by dissolving a one-gram sample of the alloy in an excess of nitric acid, and adding a quantity of radioactive silver at a time designated as zero time. Subsequent treatments of the mixture before one milliliter portions were removed by counting were noted in Table 35.

**TABLE 35**

Isotope Exchange Rate Study

<table>
<thead>
<tr>
<th>Time of Removal</th>
<th>Activity</th>
<th>Prior Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 min</td>
<td>16,600</td>
<td>one minute of stirring, five minutes of centrifuging</td>
</tr>
<tr>
<td>21 min</td>
<td>9,650</td>
<td>ten minutes of stirring, five minutes of centrifuging</td>
</tr>
<tr>
<td>36 min</td>
<td>9,604</td>
<td>ten minutes of stirring, five minutes of centrifuging</td>
</tr>
<tr>
<td>141 min</td>
<td>9,595</td>
<td>ten minutes of centrifuging</td>
</tr>
<tr>
<td>171 min</td>
<td>9,531</td>
<td>twenty-five minutes of stirring, 80°C, five minutes of centrifuging</td>
</tr>
</tbody>
</table>

The rate of exchange between the silver isotopes was fairly rapid. The aliquot removed after 21 minutes was only stirred for ten minutes at room temperature, and the activity of the subsequent aliquots changed less than one percent.
In order to permit dissolution of the smaller particles and growth of the larger particles, a digestion time of 30 minutes at 80°C with stirring was used after the introduction of the radioactive isotope. This procedure was long enough to cause complete isotopic exchange, and it aided the separation of the insoluble materials much easier.

In order to provide a silver-ion concentration above $7 \times 10^{-5}$ molar in the solution without added inactive silver ions, large quantities of the unknown alloy had to be dissolved. The radioactive tracer of silver was added after the alloy was completely oxidized. The extra digestion time was desirable, and the silver did not have a chance to be reduced by foreign materials before complete isotopic exchange took place.

The procedure for oxidation of the alloy and addition of the active silver tracer was as follows:

1. Fifty grams of the sample was weighed out in a 50-milliliter beaker. (The weighing was performed on a Metler Analytical Balance.)

2. The sample was transferred to a 600-milliliter electrolytic beaker fitted with a five-inch watch glass.

3. Fifty milliliters of DDD $\text{H}_2\text{O}$ (Demineralized Doubly Distilled water) was added to the alloy.

4. Five milliliter portions of 1:3 HNO$_3$ were added to the alloy until fifty milliliters of this mixture were added.

5. Five milliliter portions of 1:2 HNO$_3$ were added to the alloy until fifty milliliters of this mixture were added.

6. One milliliter portions of concentrated nitric acid were added until no more bubbles formed upon addition of the concentrated nitric acid.

7. Twenty milliliters of concentrated nitric acid were added in excess and the solution was allowed to reflux for thirty minutes.

8. The radioactive tracer of Ag 110 was added to the mixture, and it was allowed to reflux for thirty minutes.
The excess of nitric acid and insoluble materials were removed by evaporation, centrifugation, and filtration. The insoluble material was removed because of its abrasive action on the soft silver deposit, and the decrease in the concentration of silver in the solution due to adsorption of silver ions on its large surface.

In order to remove the nitric acid, a roto evaporator was used. A diagram of the roto evaporator is shown in Figure XXIV, but the evaporation flask and the steam bath which heated the evaporation flask were not shown. The evaporation flask was a round bottom one-liter flask with a female 24/40 standard tapered joint. The pressure in the flask was adjusted by means of an aspirator and stopcock so that the evaporation would proceed at a rapid rate, but slow enough so the contents would not be transferred from the evaporation flask into the acid receiving flask. The first evaporation did not remove enough of the acid to raise the pH of a resulting solution above 1, and in some samples a syrup formed instead of crystalline salts. Crystalline salts formed after solution of the residue of the first evaporation and a second evaporation to dryness. The solution formed by dissolution of the salts of the second evaporation had a pH above 1.

The filtration assembly shown in Figure XXV was to assure that no precipitate would be transferred from the centrifuged solution to the 250 milliliter volumetric flask. A fiber glass mat was used in the bottom of the Gooch Funnel instead of other materials which might cause the reduction of silver.
FIGURE XXIV

Roto-Evaporator

List of parts:

1. Ringstand, 1/2-in rod
2. Cork ring
3. Flask, f-28/15 ball joint, vacuum outlet, f-28/15 ball joint, f-14/20 joint
4. Condenser
5. Teflon piece, m-28/15 ball joint, m-24/40 joint, 15 mm hole
6. Feeder, m-14/20 joint, Teflon stopcock with 2 mm hole, and not shown: polyethylene tubing (200 mm long, 3 mm I.D.)
7. Adapter, m-34/45 joint concentric with f-24/45 joint, m-24/40 joint, 2 hooks
8. Aluminum block, 90 x 90 x 20 mm with hole for bearing
9. Fafnir bearing, No. 993L08 or 9108P
10. Brass pulley, to fit bearing, outer adapter joint, and belt
11. Support rod, 1/2 in
12. Condenser holder, 1 mm sheet metal (exact length depends on glass parts)
13. Rubber belt, Truflex 0200 (20 in long)
14. Motor, No. 5X203, cover No. 2 x 929; 1/35 M.P., 36 R.P.M.
15. Aluminum wheel, 100 mm O.D. 20 mm thick, to fit on motor axle
16. Screw clamp
FIGURE XXV

Filtration Assembly

List of parts:

1. Ringstand
2. Round bottom flask with 24/40 female joint
3. Clamp
4. Vacuum hose
5. Glass vacuum connector
6. Rubber stopper
7. Porous glass filter funnel
8. Gooch Funnel
9. Gooch rubber
10. Fiber glass mat
The procedure for removal of the excess nitric acid and the deposit of insoluble oxidation products was as follows:

1. The mixture was transferred from the 600-milliliter electrolytic beaker to a one-liter round bottom 24/40 standard tapered flask (evaporation flask). A couple of rinses aided in the transfer of the insoluble material.

2. The evaporation flask was attached to the roto evaporator and the nitric acid water mixture was evaporated until a crystalline material was obtained or a very viscous mass was formed.

3. The roto evaporator was disconnected at the teflon and glass ball and socket joint and rinsed with a stream of demineralised double distilled water so the rinse water drained into the evaporation flask. The larger portion of the deposit was dissolved in the rinse water by continued rotation of the flask over the steam bath.

4. The excess nitric acid in the acid receiver was disposed of and the apparatus was reassembled for the second evaporation.

5. The evaporation was continued until a crystalline mass appeared.

6. Approximately 75 milliliters of demineralised doubly distilled water was added to the evaporation flask to dissolve the soluble salts, and help transfer the resultant mixture to two 190-milliliter Boston round bottles.

7. The weights of the Boston round bottles with the solution and part of the precipitate were adjusted to the same mass on a trip balance with small additions of water, and the poly seal caps were affixed.

8. The mixtures were centrifuged, and an apparently clear solution was passed through the filtration apparatus into a 500-milliliter round bottom 24/40 standard tapered flask under a vacuum.

9. Steps 6 through 8 were repeated three times using fresh 50-milliliter portions of demineralised doubly distilled water.

10. The solution from the 500-milliliter round bottom flask was transferred to a 250-milliliter volumetric flask and this was followed by a few rinses of the filtering apparatus with demineralized double distilled water.

11. The solution was diluted to volume with demineralized doubly distilled water.
The resulting solution in the 250-milliliter volumetric flask was ready to be divided among the electrolytic beakers and adjusted with added quantities of inactive silver in amounts of 0, 5, 10, 15 and 20 times the approximated quantity of silver present in each portion of the unknown solution. The procedure that follows was the same as on pages 36-38.

The number of moles of silver calculated for ten-gram samples of the National Bureau of Standards samples 127A and 54D are plotted as a function of the added known quantities of silver in Figures XXVI and XXVII, respectfully. The extrapolated values for each series of electrodepositions are summarized in Table 36, and the standard deviations are given.

**TABLE 36**

<table>
<thead>
<tr>
<th>National Bureau of Standards Sample</th>
<th>Sample</th>
<th>Extrapolated Values (micro moles)</th>
<th>Average of First Runs</th>
<th>Average of All Runs</th>
</tr>
</thead>
<tbody>
<tr>
<td>127A</td>
<td>A</td>
<td>5.12</td>
<td>4.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>4.55</td>
<td>4.57</td>
<td>4.78</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>4.69</td>
<td>4.62</td>
<td>4.49</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.79 ±0.30</td>
</tr>
<tr>
<td>54D</td>
<td>A</td>
<td>3.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>3.98</td>
<td>4.06</td>
<td>3.55 ±0.44</td>
</tr>
</tbody>
</table>
FIGURE XXVI

National Bureau of Standards 127A

Samples A, B, and C
FIGURE XXVII

National Bureau of Standards 54D

Samples A and B
Moles of Silver calculated $\times 10^{-6}$

Moles of Silver added $\times 10^{-5}$

Sample A

Sample B
Observations from Figures XXVI and XXVII are—

1. The lines have a small positive slope which was expected because of the increased current efficiencies with increased concentrations of silver.

2. There is a small variation of the extrapolated values with the number of runs, but this variation is not consistent from sample to sample. It was probably due to temperature variations in the room.

3. There are some values which were disregarded in drawing the lines because they were more than three times the average deviation of the other values from the line. The large deviations were observed to be associated with the reduction of the silver by a foreign material or dislodging of the deposit.

Examination of Table 36 indicated that the averages of the extrapolated results for silver in the National Bureau of Standards sample 127A did not vary greatly from the other results for the same sample or from the average of all of the extrapolated results. In the first sample of 54D only one electrodeposition was possible before the calculated values increased rapidly due to a decrease in the current efficiency of the solution without added silver. Two runs were possible on the second sample, and doubling the number of determinations in the second run increased the significance of the extrapolated results for this sample to cause the average of all the results to increase 5 percent over the average of the first results.

Since the extrapolated results from the first series of electrodepositions were representative of the results obtained from additional electrodepositions, the average of the extrapolated results from the first series of electrodepositions of each sample was used to calculate the percent of silver in the alloy. In this manner, the average of all the extrapolated results would not be influenced to a greater extent by
the sample with the greater number of extrapolated results. The percentage of silver found in each of the alloys was listed in Table 37, and they were compared with the percentages reported by the National Bureau of Standards.

**TABLE 37**

Comparison of the Quantity of Silver Determined by the National Bureau of Standards with the Quantity Determined by the Standard Addition-Isotope Dilution Method

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percent Reported by NBS</th>
<th>Selected Representative Value</th>
<th>Percent Determined</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Determined Percents</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NBS 127A</td>
<td>0.003</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.004</td>
<td>0.004</td>
<td>0.0052 ±0.0003</td>
</tr>
<tr>
<td>NBS 54D</td>
<td>0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.003</td>
<td>0.003</td>
<td>0.0038 ±0.0003</td>
</tr>
</tbody>
</table>

Interferences with the determination of silver in the unknown were minimized because the effect of the interference on the electrodeposition was constant in each of the cells. The only interference which was noticed was the reduction of silver in the electrolytic solutions by foreign materials. If pieces of cork which held the electrodes fell into the solution with no added silver and the solutions were
allowed to remain in contact with the cork over night, the silver concentration sometimes decreased enough to decrease the current efficiency and cause erratically high calculated unknown quantities of silver when this solution was used in another series electrodeposition. If the concentrated nitric acid which was used to clean the electrolytic cells and cell holders came in contact with the cork stoppers, the cork would be partially oxidized. The partially oxidized cork was slightly soluble in aqueous solutions, and it reduced silver ions rapidly. If this material was solvated by the spray of the electrolytic solution from the nitrogen flowing through it, the partially oxidized cork would run down the stem of the electrode into the solution. When the silver was reduced by the partially oxidized cork on the stem of the electrode, the reduced silver was included in the electrolytically deposited silver and the current efficiency was very high. If the concentration of the silver was decreased sufficiently in the electrolytic solution, the current efficiency for the electrolytic deposition would decrease. The oxidation products of the cork were a deep yellow in color, and corks which had any discoloration were replaced after this interference was identified.

The first indication of this interference was noticed during the electrolysis of sample B of the National Bureau of Standards sample 127A. The experimental values of the results 271 and 276 were much higher than the other values of the series indicated they should be. Replacement of the corks in the solution with the lowest amount of added silver and the highest added amount of silver permitted the solution with the highest added amount of silver to recover from the reduction by the oxidation products of the work so result 286 had the value indicated it should have
by two other values with smaller quantities of added silver. The solution with the lowest amount of added silver did not recover (273, 278, 283), and all of the results except the first result were higher than they should have been.

A summary of the advantages of the method of standard addition with isotope dilution and electrodeposition are as follows:

1. After the addition of tracer, some loss of sample does not influence the results, as long as the concentration of silver is above the concentration range where the current efficiency decreases rapidly.

2. The method is specific for silver.

3. It is not necessary to calculate the current efficiency for the electrodeposition.

4. Decreases in the current efficiency for the deposition of silver from interfering ions do not affect the determination of the unknown quantity of silver as long as the effect on the electrodeposition is the same in each of the solutions and the silver is not removed from the solution.

5. Quantities of silver as low as 38 parts per million in an alloy have been determined.

6. The electrodeposition only takes a minute.

7. Only 0.4 micro equivalents of the silver present need to be deposited for a determination.

8. The deposited silver is easily removed from the solution for activity measurements.

The recommended procedure:

1. Add 50 grams of unknown alloy to a 600-milliliter electrolytic beaker fitted with a watch-glass (Note 1). Add 50 milliliters of water and in 5 milliliter portions a total of 50 milliliters of 1:3 nitric acid, 50 milliliters of 1:2 nitric acid and 50 milliliters of concentrated nitric acid. Continue to add 5 milliliter portions of concentrated nitric acid until the alloy appears to be dissolved, then add an excess of 20 milliliters of concentrated nitric acid and digest at approximately 80°C for 30 minutes (Note 2 and 3).

2. Add carrier free radioactive silver to the mixture and digest for another 30 minutes at approximately 80°C (Note 4).
3. Transfer the mixture to a liter round bottom 24/40 standard tapered flask, and evaporate to dryness on the roto evaporator. Add approximately 75 milliliters of water to the syrup or crystalline material and evaporate a second time to dryness (Note 5).

4. Dissolve the crystalline material with 75 milliliters of water and transfer the mixture to two 190-milliliter Boston round bottles. Adjust the mass of the lighter bottle to the same mass as the heavier bottle by addition of water, affix poly seal caps, and centrifuge them (Note 6).

5. Filter the clear solutions through a Gooch Funnel fitted with a fiberglass mat into a 500-milliliter round bottom 24/40 standard tapered flask connected to the filtration assembly (Note 7). Add fifty milliliters of water to the residue, affix the cap, mix, centrifuge, and filter the clear rinse solution. Repeat with two more 50 milliliter rinses.

6. Transfer the solution to a 250-milliliter volumetric flask, and dilute to volume.

7. Pipet 50 milliliter portions of the unknown solution into five 180-milliliter electrolytic beakers, and add known amounts of inactive silver which are approximately 5, 10, 15 and 20 times the amount of silver in the electrolytic beakers to those numbered 2, 3, 4 and 5, respectively.

8. Transfer the solutions to the cells for electrodeposition, assemble the apparatus for the electrodeposition, deaerate with nitrogen for 15 minutes, and electrodeposit approximately 0.40 microequivalents of silver on the micro-gauze platinum electrodes at a current density of 0.306 milliamperes per square centimeter from the cells connected in a series circuit.

9. Remove the electrolyte from the cell, rinse the cell and contents with water, transfer the micro-gauze platinum electrodes to counting tubes, add enough water to cover the deposited silver, and then transfer the electrodes to a second tube for measurement.

10. Measure the activity on each of the electrodes, and calculate the unknown quantity of silver according to Equation (xiii). Plot the calculated quantities of silver as a function of the quantity of added inactive silver, and extrapolate back to zero added silver for the unknown quantity of silver in the unknown aliquot.

11. Clean off the electrolytically deposited silver with two portions of hot concentrated nitric acid, a water rinse, a portion of hot ammonium hydroxide-potassium cyanide solution, a rinse of water, a rinse of acidified water, and another rinse of water.

12. The activity left on the electrode should not exceed 10 percent of the background activity.
Note 1. The size of the unknown sample should provide enough silver to make the concentration of the final solution $1 \times 10^{-4}$ molar or higher.

Note 2. Large quantities of heat are given off during the dissolution of the sample, and slow addition of nitric acid to the sample in a 600-milliliter electrolytic beaker should prevent loss of sample.

Note 3. Digestion of the sample helps to complete the oxidation of the sample, and the insoluble residue which forms becomes denser and easier to separate.

Note 4. The quantity of active silver added should correspond to the amount needed to produce a count rate of about 50,000 counts per minute for the deposit obtained from the solution without added inactive silver.

Note 5. Two evaporations are needed to increase the pH of the resulting solutions to above 2.

Note 6. The centrifuge cup must have a flat rubber bottom.

Note 7. The glass-filter mat eliminates the possibility of transferring any precipitate that may cause abrasion of the deposited silver. Organic filter will reduce some of the silver.

Ruzicka (39) used constant current and Ruzicka and Bemes (40) used controlled potential methods of electrodeposition for separation of a measurable quantity of silver, and they used a form of the direct isotope dilution equation, Equation (xxvi), to calculate the amount of unknown silver.

\[
\text{Amount of unknown silver} = \frac{\text{Activity separated from tracer}}{\text{Mass separated from tracer}} - 1
\]

\[
\frac{\text{Activity separated from unknown solution}}{\text{Mass separated from unknown solution}}
\]

Total silver in the tracer solution added to the unknown solution

(XXVI)
Two solutions were electrolyzed in series. The first solution contained a known quantity of silver with a known specific activity; and the second solution contained a measured amount of inactive silver which was treated as the unknown, and the same quantity of tracer as in the first solution. Both solutions were diluted to the same volumes, and they had the same supporting electrolyte. The assumption was made that the current efficiency was the same in both of the solutions, and the same quantity of mass would be deposited. Therefore, the mass terms were canceled, and the resulting expression which Rusicka and Bemes used (Equation xxvii) only had the activity terms and the known amount of silver in the tracer added to the unknown solution. Since the measurement of mass was

\[
\frac{\text{Amount of unknown silver}}{\text{Activity separated from tracer}} - \frac{\text{Activity separated from unknown solution}}{\text{Total silver in the tracer solution added to the unknown solution}} = 1
\]

eliminated from the direct isotope dilution equation, the limitation of the accuracy of mass measurements in the determination of small quantities of unknown electrodepositable materials was removed. The ratio of the concentration of silver between the known solution and the unknown solution was maintained between 1:1 to 1:3 for the best results (40).

In the method suggested in this work a constant current electrodeposition was used to separate a measurable quantity of the silver in the solution, and a form of the inverse isotope dilution equation, Equation (xxviii), was used to calculate the amount of unknown silver.
The solutions were run in a series electrodeposition and it was assumed that the current efficiencies were the same for each deposition, that is to say that the masses deposited from each of the solutions were the same. Since each of the solutions in series contained the same amount of unknown sample, this maintained constant conditions in the solutions with respect to the kind and concentration of foreign ions. Cancellation of the masses from the above equation results in the following equation which was used in this method.

\[
\text{Amount of unknown silver in the solution} = \text{Known added amount of inactive silver} \quad \frac{\text{Activity separated from the solution with added silver}}{\text{Mass separated from the solution with added silver}} - \frac{\text{Activity separated from the solution with no added silver}}{\text{Mass separated from the solution with no added silver}}.
\]

Elimination of the mass terms again removed the limitation of the accuracy of mass measurements in the determination of the small masses of deposited silver. The depositions were made in series with different
added amounts of silver and the calculated values were extrapolated back to zero added silver. This tends to eliminate errors due to differences in current efficiencies caused by concentration differences of the silver.
CHAPTER VIII

SUMMARY

The effect of varying the physical, electrical and chemical properties on the current efficiency for the constant current electrodeposition of silver was studied. The current efficiency for the electrodeposition of silver was determined by a constant current coulometric electrodeposition and radioactivity measurements. Silver-110m was used as the tracer.

Increased stirring, concentration of silver ions, or temperature of silver nitrate solutions resulted in an increase in the current efficiency. Increasing the size of the stirring bar had a marked effect, but increasing the stirring rate above 300 revolutions per minute had no significant effect.

An increase in the current efficiency was caused by adsorption of silver salts, entrapment of silver salts, the presence of high concentrations of sodium nitrate, and the presence of low concentrations of copper nitrate.

A decrease in the current efficiency was caused by dissolution of deposited silver by the rinses, high concentration of cations with oxidation states of (II) and (III), and possibly some reduction of platinum oxides on the electrode and production of powdered silver in the electrolyte. A small quantity of silver was found to dissolve with each
Rinse, but the total quantity of silver lost was estimated to be less than a percent of the deposit.

Increasing the current density and the duration of the run also caused the current efficiency for the deposition of silver to decrease. The decrease in the current efficiency was small until the current density exceeded a limiting current. There was approximately a 0.4 percent decrease in the current efficiency per minute of running time.

Separation of the anode from the cathode compartment and variation of the pH from 6 to 0.5 had a negligible effect on the current efficiency for the electrodeposition of silver.

An entrapment mechanism was used to explain why the addition of sodium nitrate to a silver nitrate solution decreased erratic changes in the current efficiency, and why the current efficiency was above 100 percent under certain conditions and below 100 percent under other conditions. The mechanism of entrapment depends on the concentration of silver ions adsorbed at the platinum surface, and whether a fresh supply of silver ions is supplied by diffusion or migration.

Some of the observed decrease in the current efficiency was attributed to reduction of hydrogen ions. The reduced forms of hydrogen could be adsorbed in the deposit of silver, released as a hydrogen molecule, or be solvated as a reducing agent.

A reverse isotope dilution method of analysis using a constant current electrodeposition for the separation of the silver was developed. An alloy was dissolved, carrier free radioactive silver was added, and the resulting solution was divided into five equal portions. Known quantities of silver were added to only four of the portions, and the
five solutions were electrolyzed in a series circuit. One value for the quantity of silver in the unknown was calculated for each solution with added silver. The activities of the deposits and the known quantities of added silver were used in these calculations. Alloys containing silver as low as 0.004 percent were analyzed.
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