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THE ELECTROLYTIC RECOVERY OF SILVER
FROM WASTE SILVER RESIDUES

BY

BAILEY WARREN HAGAR

A

THESIS

submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the
Degree of
MASTER OF SCIENCE, CHEMICAL ENGINEERING
Rolla, Missouri
1949

Approved by W. H. Schreiner
Chairman, Department of Chemical Engineering

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I wish to express my appreciation to Dr. W. T. Schrenk, Chairman of the Department of Chemical Engineering and Chemistry, for his suggestions and guidance throughout this investigation.

B. W. H.

CONTENTS

	Page
Acknowledgement	ii
List of illustrations	iv
List of tables	v
Introduction	1
Review of literature	3
Theory and chemical consideration of the electrolysis of silver-bearing solutions . . .	7
Reagents and solutions used	12
Description of electrolytic apparatus	13
Electrolytic precipitation of silver sulfide . . .	17
Electrolytic deposition of metallic silver	29
Conclusions	50
Summary	53
Bibliography	54
Index	55

LIST OF ILLUSTRATIONS

Figure	Page
1. Ratio of permissible current to silver content of bath	10
2. The individual parts of the electrolytic apparatus	15
3. The electrolytic apparatus assembled	15
4. Diagram of electrical circuit	16
5. Rate of silver recovery (Experiment XIV)	33
6. Rate of silver recovery (Experiment XIX)	43
7. Rate of silver recovery (Experiment XX)	47

LIST OF TABLES

Table	Page
1. Determination of amount of silver contained in the waste silver residue	18
Electrolytic precipitation of silver sulfide	
2. Experiment I	20
3. Experiments II-VIII	22
4. Experiments IX-XIII	25
5. Final distribution of silver after electro- lytic precipitation of silver sulfide . . .	27
6. Optimum temperature for maximum solubility of waste silver residue	30
7. Recovery of silver using platinum cathode and a carbon anode (Experiment XIV)	32
8. Recovery of silver using platinum cathode and a carbon anode (Experiment XV)	36
9. Recovery of silver using one steel cathode and a carbon anode (Experiment XVI)	38
10. Recovery of silver using two steel cathodes and a carbon anode (Experiment XVII) . . .	39
11. Recovery of silver using two steel cathodes and a steel anode (Experiment XVIII) . . .	41
12. Recovery of silver using two steel cathodes and a platinum anode (Experiment XIX) . . .	42
13. Recovery of silver using two steel cathodes and a platinum anode (Experiment XX) . . .	46
14. Recovery of silver from a used fixing bath . . .	49

INTRODUCTION

A considerable amount of silver is contained in the silver chloride-silver thiocyanate residue resulting from the use of silver nitrate and potassium thiocyanate by students of quantitative analysis in the volumetric determination of chlorine. The main objective of the work described in this paper, therefore, was to find a simple and efficient method for recovering the silver from this silver chloride-silver thiocyanate residue.

Of the various methods of silver recovery mentioned in the literature, the electrolytic process is the more efficient and yields a pure product. A great many methods for the electrolytic recovery of silver have been proposed but the majority of these methods are based on the electrolysis of a cyanide solution since the majority of the common silver compounds are soluble in potassium and sodium cyanide baths, the latter also being good electrolytes. Cyanide solutions, however, are quite toxic as well as expensive and to avoid these disadvantages, it was decided to experiment with the recovery of the silver from a sodium thiosulfate solution.

Although not as common as the cyanide process, the electrolytic recovery of silver from thiosulfate solutions is employed quite extensively in the photographic industry, particularly by the motion picture processing laboratories

where recovery of silver from used "hypo" or fixing baths is economically necessary. The expense of such equipment at the present time, however, makes its use by any but the larger laboratories impractical. Therefore, it was hoped that the experimentation described in this paper might also result in the design of inexpensive equipment which might be used by the small photographic shop.

REVIEW OF LITERATURE

A large amount of research has been performed and described in the literature on the recovery of metallic silver from solutions containing silver ions. A review of the literature has shown that electrolytic methods are in general preferable to purely chemical methods.

Weiner⁽¹⁾ cites a method for obtaining bright electrodeposits of silver from a bath containing 40 grams of silver (as silver chloride), 170 grams of sodium thiosulfate crystals, 20 grams of sodium bisulfite, and 50 grams of sodium sulfate per liter at a current density of 0.3 to 0.5 amperes per square decimeter. The sodium bisulfite prevents oxidative decomposition of the silver thiosulfate complexes, and the sodium sulfate facilitates solution of the anode.

Neblett⁽²⁾ mentions several methods by which the silver in a used fixing bath may be recovered:

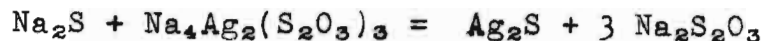
Silver Recovery with Sodium Sulfide

The silver is precipitated as silver sulfide by the addition of sodium sulfide to the used fixing bath. Acid fixing baths are first neutralized with caustic soda to prevent unpleasant fumes of hydrogen sulfide.

(1) Weiner, R., Zeitschrift fur elektrochemie, Vol. 45, pp. 757-759 (1939)

(2) Neblette, C. B., Photography-Its principles and practice. 4th ed. N. Y., Van Nostrand, 1942. pp. 361-364.

The chemistry of this reaction is as follows:



Silver Recovery with Zinc

The silver may also be precipitated from either acid or alkaline fixing baths by the addition of either zinc dust, granulated, or sheet zinc. Best results are obtained if the bath is acid. The rate of precipitation with granulated or sheet zinc is considerably slower than with zinc dust.

The chemistry of the foregoing process is:



The amount of silver recovered is less than with sulfide and precipitation is not as rapid, but no objectionable odors are produced.

Electrolytic Methods of Recovery

An electric current passing between electrodes immersed in the fixing bath will cause the silver to separate either as metallic silver or as a suspension of silver sulfide depending upon the difference in potential.

Silver recovery units of separated copper and zinc plates forming an electrolytic couple are available commercially. When placed in a discarded fixing bath containing silver, a current flows through the bath from the zinc to the copper; if the potential is about 0.7 volts, metallic silver is deposited on the copper plate. Since these units produce a sludge, they cannot

be placed in a fixing bath when in use.

In the motion picture processing laboratories,⁽³⁾ the silver is recovered as metallic silver and since the processes employed may be used to remove silver from a fixing bath while in use, it retains its fixing and hardening properties longer. The factor of expense, however, places such equipment beyond the resources of all but the larger laboratories.

Another article⁽⁴⁾ on the recovery of metallic silver by electrolysis on an industrial scale is found in Industrial and Engineering Chemistry, Vol. 25, 1933. The electrolytic regeneration of fixing baths involves the use of large cells containing 100 square feet of cathode surface through which a current of 300 amperes is passed at one to one and one-half volts. To secure good plating, vigorous agitation together with the presence of acid sulfite and certain promoting agents is essential. The electrodes in this cell consist of graphite anodes and stainless steel cathodes.

Herr⁽⁵⁾ gives a description of the process used by Metro-Goldwyn-Mayer motion picture studios for the electrolytic regeneration of their fixing baths. The electrolytic unit consists of eight cells (wooden boxes) 3 feet

(3) Hickman, K., Sanford, C. R., and Weyerts, W. J. Soc. Mot. Pict. Eng., Vol. 17, pp. 568-590 (1931)

(4) Hickman, K., Weyerts, W., and Goehler, O. E. Ind. Eng. Chem., Vol. 25, pp. 202-212 (1933)

(5) Herr, F. Metal Finishing, Vol. 39, pp. 427-428 (1941)

long, 2 feet wide, and 2.5 feet high, each containing eleven carbon anodes and ten stainless steel cathodes. Space is left at the top and bottom of the electrodes to provide for free circulation of the fixing bath. The silver is left in a soft mushy deposit which hardens when the cathodes are removed from the cell. The hardening deposits are dislodged by jarring the cathodes against a wooden bench. The recovered product contains 99 per cent silver and one per cent gelatin.

THEORY AND CHEMICAL CONSIDERATIONS OF THE ELECTROLYSIS OF
SILVER-BEARING SOLUTIONS

Upon passing an electric current between two uncorrodible electrodes (a carbon anode and a platinum cathode) immersed in a water solution of a metallic salt, (6) oxygen gas is generally evolved at the anode and the metal is deposited at the cathode. Depending on the conditions, the metal may be powdery, crystalline, dull or bright, loose or adherent. If, however, a current of normal plating density is passed through a thiosulfate solution containing silver, no gases are evolved, both the oxygen and hydrogen being absorbed by the solution. In general, tetrathionates are liberated at the anode and a black deposit of silver sulfide at the cathode.

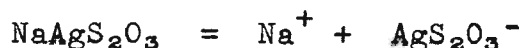
A study of Mellor's discussion of thionic acids (7) reveals that a simple thiosulfate solution exposed to the air may contain hydrogen sulfide, sulfur dioxide, thiosulfate, the four thionic acids, sulfite, hydrosulfurous and sulfoxylic acids. A result of this complex situation is the formation of colloidal silver sulfide at the cathode when a silver-bearing thiosulfate solution is electrolyzed under ordinary laboratory conditions.

(6) Allmand, A. J. The principles of applied electrochemistry. 2nd ed. N. Y., Longmans, 1924. p. 111.

(7) Mellor, J. W. A comprehensive treatise on inorganic and theoretical chemistry. Vol. X, London, Longmans, 1930. pp. 536-538.

Mellor also describes work performed by other scientists in determining the actual compounds formed when silver chloride is dissolved in sodium thiosulfate. J. W. Herschel reported crystals of sodium silver trithionate, $2 \text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Ag}_2\text{S}_2\text{O}_3 \cdot 2 \text{H}_2\text{O}$, to be formed by evaporating a solution of silver chloride in a solution of sodium thiosulfate. A. Rosenheim and G. Trewendt used the formula, $\text{Na}_4[\text{Ag}_2(\text{S}_2\text{O}_3)_3] \cdot 2 \text{H}_2\text{O}$. J. W. Herschel, A. Rosenheim, S. Steinhauser, and E. Cohen obtained sodium silver thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Ag}_2\text{S}_2\text{O}_3$, or NaAgS_2O_3 , or $\text{Na}[\text{Ag}(\text{S}_2\text{O}_3)]$ from a solution of silver chloride to a solution of sodium thiosulfate. In this paper, the simplest formula, NaAgS_2O_3 , will be used to designate the compound, sodium silver thiosulfate.

In the separation of the silver metal from silver thiosulfate, the salt yields ions as follows:



Since the silver is now in the negatively charged particle, it is driven away from the cathode toward the anode. When these particles reach the latter pole, the thiosulfate ions are oxidized and the silver remains in the solution. At the cathode the sodium ions are discharged as metallic sodium atoms and are so reactive that they decompose any ions in their vicinity yielding silver if there remains enough AgS_2O_3^- ions; otherwise water is reduced to hydrogen or the thiosulfate is reduced to a series of compounds which are detrimental to good silver plating.

It is necessary, therefore, to keep enough silver ions around the cathode to react with the electric charge or the sodium atoms so that the thiosulfate will not be attacked yielding such compounds as sodium sulfide which in turn precipitate silver sulfide.

This desired condition can be obtained by vigorously agitating the bath to renew the solution in the vicinity of the electrodes. As the agitation is increased, the current density may also be increased. Rates of flow from one to four feet per second have proved most economical.⁽⁸⁾

The silver content of the solution also affects the current density. The graph in figure 1 shows the ratio of permissible current to silver content of the bath.⁽⁸⁾

Hickman, Weyerts, and Goehler⁽⁹⁾ give an excellent discussion regarding the improvement of silver deposition by the addition of gelatin and certain promoters such as thiourea to the silver thiosulfate solution. When the cathode acquires silver from a silver thiosulfate solution containing no gelatin, a number of differently oriented crystal lattice areas will develop into crystals with faces growing at various speeds thus causing a rough deposit. If a small quantity of an amphoteric colloid such as gelatin is added to the solution, the colloid will migrate to the cathode and be deposited in a structure of sufficient strength

(8) Hickman, Sanford, and Wegerts, Op. Cit., p. 5.

(9) Hickman, Wegerts, and Goehler, Op. Cit., p. 5.

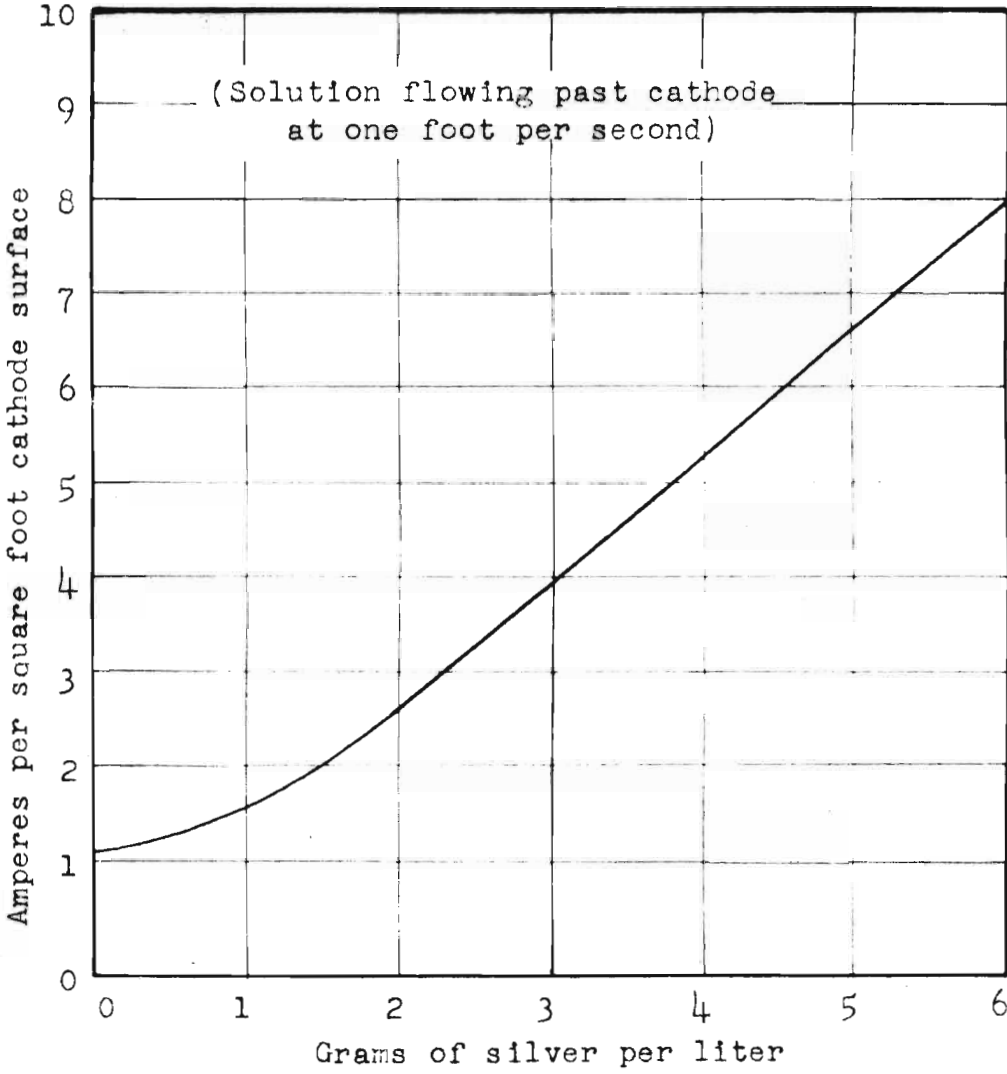


Figure 1. RATIO OF PERMISSABLE CURRENT TO SILVER CONTENT OF BATH

to interfere with the building of the silver crystal lattice. If there is only a small amount of gelatin (one part in a thousand), no loss of conductivity results and the fluidity in the immediate neighborhood of the cathode does not diminish; thus the plating proceeds smoothly.

The function of thiourea or other promoter is probably as follows: 1) as a polar molecule it can migrate to the cathode where it competes for position with the gelatin, and 2) as a substance having a great affinity for silver chloride, it can act as a carrier for silver, and forms a complex which migrates toward the cathode instead of in the opposite direction taken by the silver thiosulfate ions.

Sulfite ions are important in the solution to prevent the acidic decomposition of sodium thiosulfate and to destroy any hydrosulfite formed. There is always a small amount of silver sulfide formed and acid sulfite acts as a digesting agent for this precipitate.

REAGENTS AND SOLUTIONS USED

Standard solutions of potassium thiocyanate were prepared by standardization with silver nitrate solutions of known normality using ferric nitrate as an indicator.

Sodium thiosulfate solutions of various strengths were prepared by dissolving varying amounts of reagent grade sodium thiosulfate (fine crystals), $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$, in distilled water.

Alkaline fusions were made using reagent grade sodium carbonate and sodium peroxide.

Silver sulfide precipitations were made in the silver sodium thiosulfate solutions by the addition of normal sodium sulfide. This latter solution was prepared by dividing a measured volume of normal sodium hydroxide solution in equal parts, saturating one part with hydrogen sulfide, and then combining the two portions.

Quicking solution for amalgamating copper cathodes was prepared as follows:⁽¹⁰⁾ 14.6 grams of mercuric chloride were dissolved in about 300 milliliters of water and caustic soda solution added until there was no further precipitation. The precipitate was allowed to settle and the clear liquid poured away. After washing the precipitate with water, it was dissolved in about 250 milliliters of a cyanide solution containing 28.4 grams of potassium cyanide. This solution was then diluted to one liter.

(10) Field, S. The principles of electro-deposition. London, Longmans, 1911. 383 p.

DESCRIPTION OF ELECTROLYTIC APPARATUS

The electrolytic apparatus used throughout the research was primarily the same as that shown in figure 3. Individual parts of the apparatus are pictured in figure 2.

Electrolysis took place in the glass battery jar (A) which was 9 centimeters wide, 11.25 centimeters long, and 5 centimeters high. The anode chamber consisted of a porous cup (B), 5 centimeters in diameter and 11 centimeters high, in which was suspended an arc lamp carbon (C) which served as the anode. The porous cup served to prevent oxidation anodic products from reacting with the cathodic products to form an undesirable sludge.

Four different types of cathodes were used in order to determine the characteristic plating action of each. These cathodes were: an arc lamp carbon (D), sheet copper (E), platinum foil (F), and stainless steel plate (G). The metal cathodes were constructed so as to present a cathode surface of one square decimeter each.

The solution was agitated by a portable motor stirrer (H) to give a surface velocity of approximately two feet per second.

Alternating current was converted to direct current by a Westinghouse Rectox Rectifier, T-7 (J) designed to operate on 115-volt, 60 cycle alternating current. This current was reduced further by a Powerstat Variable Transformer, Type 116 (K) which was capable of providing a current density as low

as 0.01 ampere per square decimeter.

The direct current was measured by installing a Weston milliammeter (L) connected in series along the positive lead between the transformer and the cell anode. Voltage across the electrodes was measured by a Weston millivoltmeter (M).

A diagram of the electrical circuit is given in figure 4.

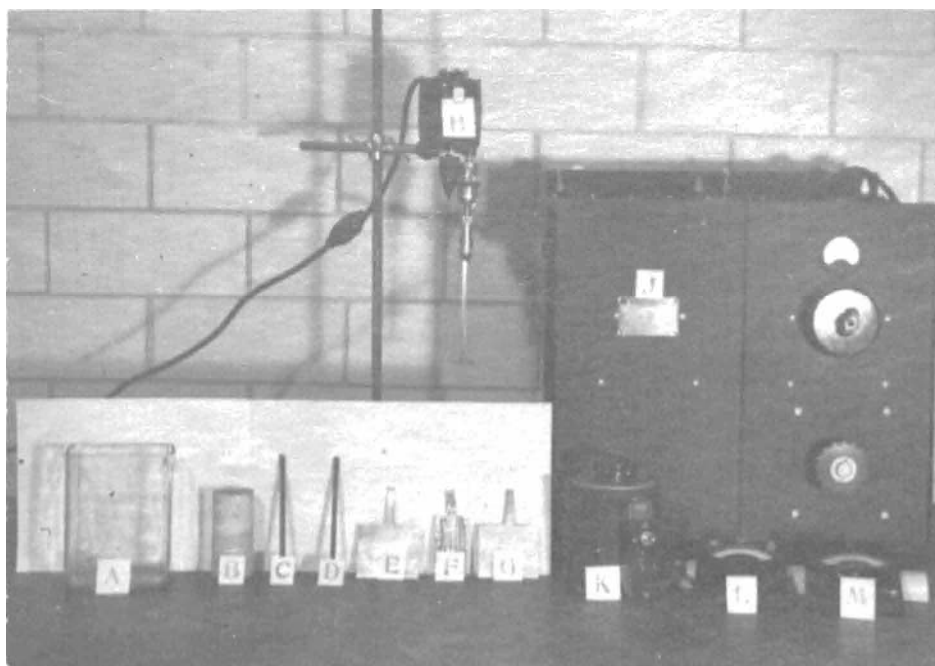


Figure 2. THE INDIVIDUAL PARTS OF THE ELECTROLYTIC APPARATUS

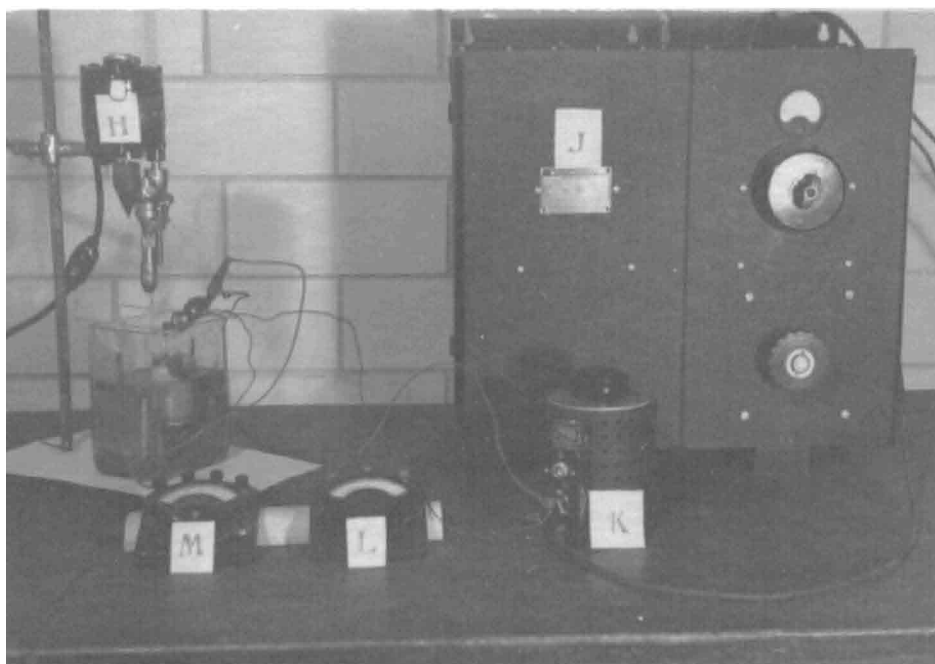


Figure 3. THE ELECTROLYTIC APPARATUS ASSEMBLED

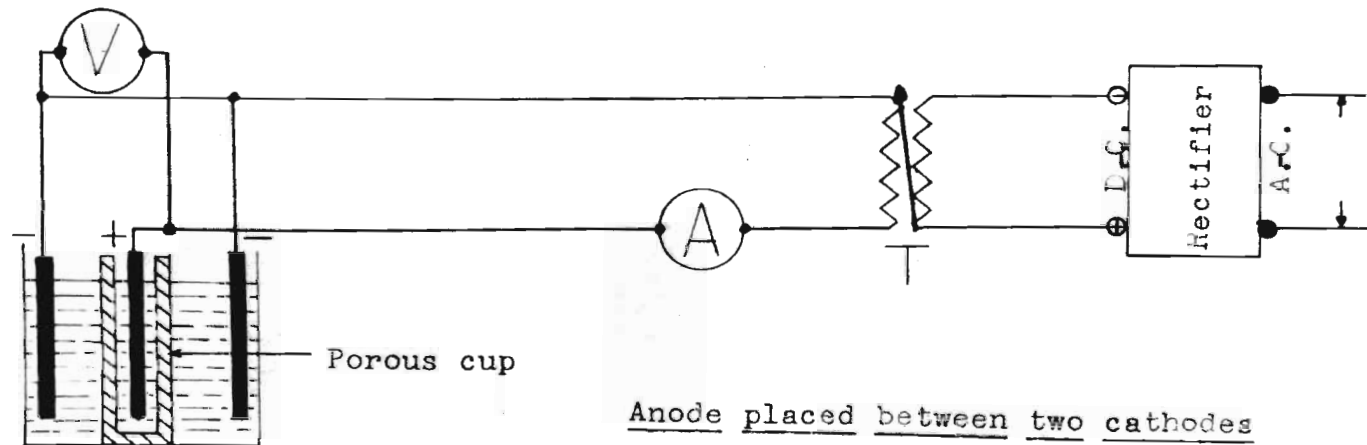
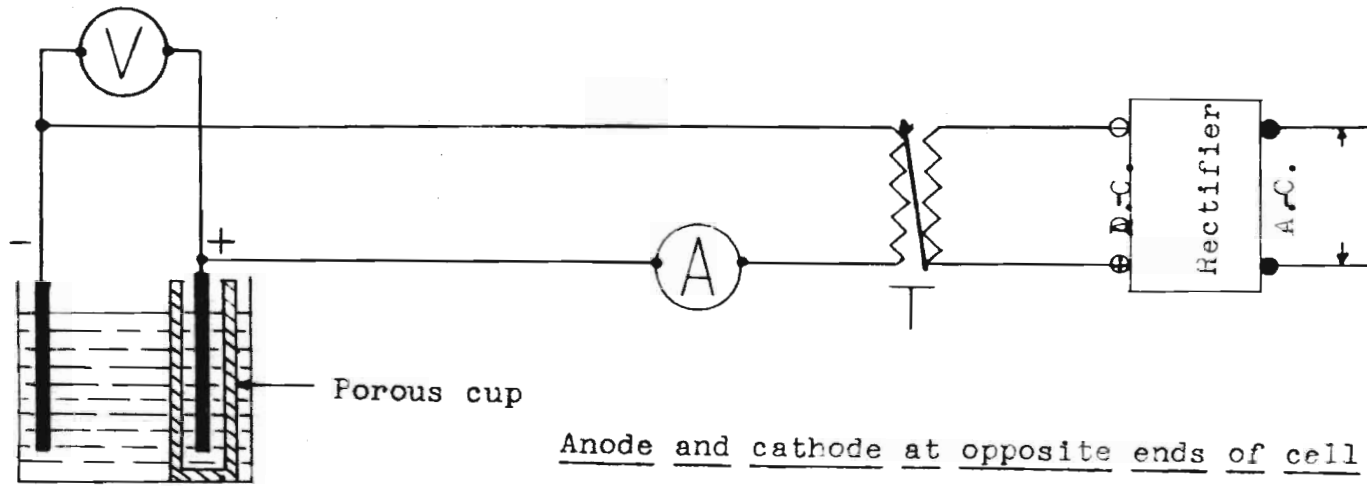


Figure 4. DIAGRAM OF ELECTRICAL CIRCUIT

ELECTROLYTIC PRECIPITATION OF SILVER SULFIDE

The silver chloride-silver thiocyanate residue from which the silver was to be recovered resulted from the use of silver nitrate and potassium thiocyanate by students of quantitative analysis in the volumetric determination of chlorine. This residue was washed and dried in an oven at approximately 100° C. The dried residue was then ground in a mortar to pass a 100-mesh sieve.

An approximate 0.5 gram sample of this powdered residue was then accurately weighed and transferred to a porcelain crucible containing two grams of sodium carbonate. Approximately two grams of sodium peroxide were then added to the crucible followed by five additional grams of sodium carbonate. This mixture was then fused over the flame of a Fischer burner for one-half hour. The crucible was then cooled and transferred to a 200 milliliter beaker containing 75 milliliters of boiling water. After boiling for five minutes, the crucible was removed and thoroughly washed with hot water. The solution was then filtered by decantation through medium filter paper and thoroughly washed with hot water to remove all soluble salts. The rinsed crucible was then placed back in the beaker along with the fused silver compound. Twenty milliliters of 1:1 nitric acid were added and the resulting solution brought to boiling. After all of the silver was dissolved, the crucible was removed and thoroughly rinsed with hot dilute nitric acid. Any of the

silver compound remaining on the filter paper was dissolved in hot nitric acid solution and transferred to the beaker containing the dissolved silver. This solution was then diluted to 100 milliliters and titrated with 0.1 N potassium thiocyanate.

Results of this silver determination are given in table 1.

TABLE 1
SILVER CONTENT OF THE WASTE SILVER RESIDUE

Sample number	1	2	3
Weight of sample (grams)	0.7604	1.2833	0.6687
Weight of silver in sample (grams)	0.5220	0.8850	0.4585
Percentage of silver in sample (per cent)	68.50	68.80	68.65
Average percentage composition - 68.65 per cent silver			

In experiment I (see table 2), approximately 10 grams of the silver residue was accurately weighed and placed in the battery jar. This residue was then dissolved in a solution containing 50 grams of sodium thiosulfate, 500 milliliters distilled water, and one milliliter of sodium hydroxide (6 N) to insure a basic solution. A small amount of the residue remained undissolved. A direct current of one ampere and six volts was then passed through the solution for 105 minutes. (No porous cup was used in this experiment.) A black precipitate formed at the arc lamp carbon cathode and settled to the bottom of the cell. Analysis of this precipitate proved it to be silver sulfide. The electrolyzed solution was then filtered and the precipitate was dissolved in 1:1 nitric acid and brought to the boiling point. All of the silver sulfide was dissolved but a gray yellow precipitate, previously obscured by the black silver sulfide, remained undissolved. This solution was then filtered into a 400 milliliter beaker and the insoluble precipitate thoroughly washed with hot dilute nitric acid. The filtrate was then diluted to exactly 500 milliliters and a ten milliliter aliquot was titrated with potassium thiocyanate. The weight of silver contained in the solution was then determined and the percentage of silver recovered as silver sulfide was calculated.

Although a small amount of the original silver residue remained undissolved in the sodium thiosulfate solution, a larger quantity of insoluble material remained after

solution of the silver sulfide in nitric acid. This increase in insoluble material indicated that some additional compound had been precipitated during electrolysis.

TABLE 2
ELECTROLYTIC PRECIPITATION OF SILVER SULFIDE

Experiment I

500 ml. electrolyte 1 ampere 6 volts

Weight of silver in residue sample	(grams)	6.40
Duration of electrolysis	(minutes)	105.00
Weight of silver recovered as Ag_2S	(grams)	5.15
Percentage of silver recovered as Ag_2S	(per cent)	85.40

Procedure used in experiments II-VIII (see table 3) differed from that used in experiment I as follows:

The weight of the residue samples was reduced to approximately five grams. The portion of the residue which remained undissolved in the thiosulfate solution was filtered off and analyzed for silver content. A porous cup was placed around the arc lamp carbon anode to prevent anodic products from reacting with the cathodic products. All other conditions were held constant and the time of electrolysis was varied in order to establish a minimum time of electrolysis for maximum recovery of silver.

Several experiments were conducted using the thio-sulfate solution from previous silver sulfide filtrations to determine whether the electrolyte could be used more than once.

TABLE 3

ELECTROLYTIC PRECIPITATION OF SILVER SULFIDE

Experiments II-VIII

50 grams $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ 500 ml. water 1 ampere 6 volts

Experiment number		II	III	IV	V	VI	VII	VIII
Weight of silver in residue sample	(grams)	3.02	3.05	3.05	3.05	3.05	1.40	0.67
Duration of electrolysis	(minutes)	60.00	45.00	40.00	30.00	45.00	45.00	45.00
Weight of silver recovered	(grams)	2.33	2.62	2.55	2.21	2.15	1.69	0.95
Percentage silver recovered	(per cent)	85.63	85.82	83.80	72.50	68.92	121.00	142.00
Percentage silver in insoluble silver residue	(per cent)	0.01	0.06	0.08	0.05	0.80	1.00	1.20

Analysis of the waste silver residue remaining undissolved in the sodium thiosulfate solution showed that the silver content of this residue was very low and could be considered negligible.

Percentage of silver recovered in experiments IV and V was somewhat less than that recovered in other experiments because of the shorter time allowed for electrolysis. Data from table 2 when compared with experiments II-V of table 3 showed that the most efficient time of electrolysis was 45 minutes.

The electrolyzed solution from experiment V was used to dissolve the silver residue sample in experiment VI. The low percentage of silver recovery obtained in this latter experiment was due to a loss of current resulting from the corrosion of the electrodes. For most efficient operation, the electrodes and their electrical connections should be cleaned after each electrolysis.

The volume of solution from experiment VI had increased to about 900 milliliters because of accumulated washings from previous filtrations. This volume, therefore, was divided in half and used in experiments VII and VIII. Since these divided portions contained only one half of the original sodium thiosulfate salt, only half as much silver was dissolved in each of the solutions. The resulting recovery of more than 100 per cent of the silver was due to the amount of dissolved silver contained in the solution which had not been precipitated in experiments V and VI.

The quantity of insoluble material precipitated during the formation of silver sulfide was not lessened by the presence of the porous cup surrounding the anode. Therefore, it was concluded that this insoluble precipitate resulted from the electrolytic decomposition of compounds contained in the electrolyte.

Procedure followed in experiments II-VIII was modified in experiments IX-XIII as shown below:

The portion of the original silver residue which remained undissolved in the thiosulfate solution was not filtered off prior to electrolysis. The cathode surface was doubled by the addition of another arc lamp carbon. Electrolyte of experiments XI-XIII had been used in previous experiments.

As a result of the larger cathode surface used in experiments IX-XIII and the continued use of the electrolyte, it was found that the amount of silver recovered was increased almost ten per cent.

Experiment IX was made allowing only 22.5 minutes for electrolysis and resulted in only 65.25 per cent of the silver being removed.

The amount of silver recovered in experiment X seemed unusually large. Experiment Xa was made under conditions identical to those under which experiment X was made and although the percentage of recovery was less, it was still better than that obtained in experiments II-VIII.

Experiments XI-XIII confirmed previous observations that the continued use of used electrolyte solutions was

TABLE 4
ELECTROLYTIC PRECIPITATION OF SILVER SULFIDE
Experiments IX-XIII

3.02 grams silver 50 grams $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ 500 ml. water 1 ampere 6 volts

Experiment numbers	IX	X	Xa ¹	XI	XII	XIII
Duration of electrolysis (minutes)	22.50	45.00	45.00	45.00	45.00	45.00
Weight of silver recovered (grams)	1.97	2.81	2.71	2.66	2.78	2.83
Percentage silver recovered (per cent)	65.25	92.70	89.80	88.10	92.00	93.70

Note: ¹Experiment Xa made under conditions identical to those of experiment X.

feasible. Besides the ability of the used electrolyte to dissolve additional residue, much of the silver not removed from solution in previous experiments was removed in subsequent experiments.

A separate experiment was performed to determine the silver content of the precipitate which occurred along with the precipitation of the silver sulfide but which did not dissolve in nitric acid as did the silver sulfide. See table 5 for data concerning this experiment.

After the silver sulfide had been dissolved, the remaining precipitate was filtered by suction through a fritted crucible previously dried at 110° C. to a constant weight. This precipitate was then dried to constant weight. Care was taken so that the temperature did not rise above 110° C. since the precipitate began to decompose around 130° C.

The dried precipitate was transferred to a porcelain crucible of known weight and analyzed for silver content as described on page 17. The percentage of original silver contained in the insoluble precipitate was found to be 3.50 per cent.

TABLE 5

FINAL DISTRIBUTION OF SILVER AFTER ELECTROLYTIC PRECIPITATION
OF SILVER SULFIDE50 grams $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$, 500 ml. water, 1 ampere, 6 volts

Weight of silver in original residue sample	(grams)	3.43
Weight of insoluble precipitate after drying	(grams)	0.87
Weight of silver in insoluble precipitate	(grams)	0.12
Percentage of silver in insoluble precipitate	(per cent)	13.80
Percentage of original silver contained in insoluble precipitate	(per cent)	3.50
Percentage original silver recovered as Ag_2S	(per cent)	88.10
Percentage original silver remaining in electrolyte	(per cent)	8.40

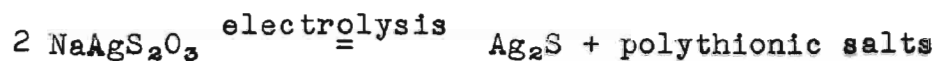
The silver sulfide precipitated as described in the foregoing experiments was converted into a silver nitrate solution suitable for use by students of quantitative analysis for use in both the volumetric and the gravimetric methods for the determination of chlorine.

Since the amount of silver thiocyanate in the original silver residue was found to be negligible, the chemical reactions leading to the formation of a silver nitrate solution may be shown as follows:

- a) Dissolving residue in thiosulfate solution



- b) Electrolytic precipitation of silver sulfide



- c) Dissolving of silver sulfide in nitric acid



ELECTROLYTIC DEPOSITION OF METALLIC SILVER

Because of the large volumes of solution which had to be filtered to recover the silver as silver sulfide, it was decided to experiment with the recovery of metallic silver on metal cathodes. It was reasoned that if metallic silver could be recovered efficiently, it could then be converted into a usable form (silver nitrate solution) by merely dissolving the metallic silver in nitric acid. Several different metals were used as cathodes to determine which would give the most efficient recovery of silver.

The electrolyte was prepared by dissolving approximately 60 grams of the waste silver residue in 800 milliliters of a 25 per cent by weight thiosulfate solution and heating this mixture to 60° C. to insure maximum solubility. (See table 6.) This solution was then filtered by suction through a Buchner funnel using medium filter paper. The residue was discarded and approximately 20 grams of sodium bisulfite were added to the filtrate which was then ready for electrolysis. Electrolysis was conducted for varying periods of time and at varying current densities using cathodes of the different metals.

To determine the optimum temperature for maximum solubility of the silver residue, the thiosulfate solution containing the residue was heated to various temperatures and the silver content in solution at each temperature was determined as follows:

The solid matter was allowed to settle and 5 milliliters of the clear solution was transferred to a 250 milliliter beaker by means of a pipette. This aliquot was then diluted to 100 milliliters and normal sodium sulfide solution was added in sufficient quantity to precipitate all of the silver as silver sulfide. This precipitate was then allowed to settle and was filtered through medium filter paper. The precipitate was dissolved in hot 1:1 nitric acid solution, the resulting solution diluted to 100 milliliters and titrated with potassium thiocyanate solution. The amount of silver contained in five milliliters of the thiosulfate solution was then calculated.

TABLE 6

OPTIMUM TEMPERATURE FOR MAXIMUM SOLUBILITY OF
WASTE SILVER RESIDUE

200 grams $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$, 800 ml. water

Temperature	Silver contained per 5 ml. solution
(°C.)	(grams)
25	0.1655
30	0.1682
40	0.1716
50	0.1735
60	0.1748
70	0.1746

At 70° C. the thiosulfate solution containing the silver residue began to decompose to yield a black precipitate of silver sulfide. Therefore, the solution was heated to a maximum of 60° C. before starting electrolysis. Maximum solubility of the silver residue was thus obtained without precipitating silver sulfide.

The first metal to be used as a cathode was sheet copper. It was soon found that this copper cathode went into solution by simple immersion replacing the silver from the solution. The silver that was deposited on the cathode was not recoverable since the copper also dissolved in the nitric acid thus contaminating the desired silver nitrate solution. Amalgamated copper cathodes were also tried but even though loss of copper in solution by simple immersion was lessened, the problem of contaminating the silver nitrate solution still existed.

Because of the difficulties encountered in using the copper cathode, it was replaced with an uncorrodible cathode of medium weight platinum foil. Data obtained using the latter type of cathode is given in table 7.

Experiment XIV took place over a period of 34 hours in order to determine minimum amount of silver required in solution to provide efficient recovery as well as to determine the effect of lengthy electrolysis on the sodium thiosulfate contained in solution. In order to maintain the thiosulfate ion concentration as constant as possible, a total of approximately ten additional grams of potassium

TABLE 7
RECOVERY OF SILVER USING PLATINUM CATHODE AND CARBON ANODE
Experiment XIV

Duration of electrolysis	Current density	Voltage	Amount silver deposited	Total silver accumulated
(hours)	(amperes per sq.dm.)	(volts)	(grams)	(grams)
2	0.50	2.0	2.13	2.13
4*	0.50	2.0	2.16	4.29
6	0.50	2.0	1.60	5.89
10	1.00	2.5	7.96	13.85
14	1.00	2.5	7.00	20.85
16*	1.00	2.5	4.65	25.50
18	0.50	2.0	1.67	27.17
20*	0.50	2.0	3.12	30.29
23	0.50	2.0	2.31	32.60
27	0.25	1.5	0.39	32.99
30*	0.25	1.5	0.08	33.07
34	0.25	1.5	0.04	33.11
Total silver in solution prior to electrolysis:				41.65
Total silver removed as metallic deposit:				33.11
Total silver remaining in solution:				1.67
Total silver in anodic deposit of Ag_2S :				6.66
* Cathode removed and stripped of silver deposit.				

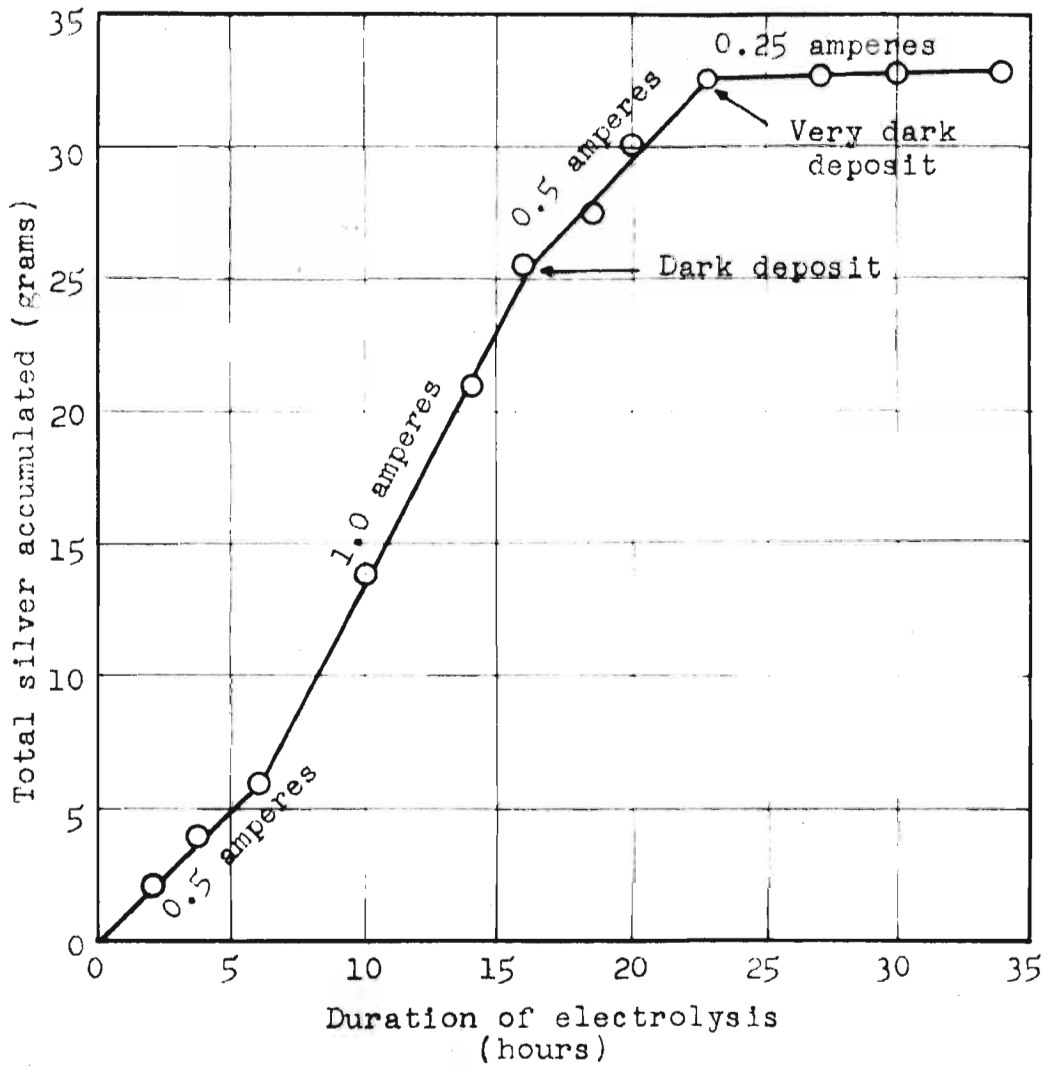


Figure 5. RATE OF SILVER RECOVERY (Experiment XIV)

bisulfite were added in small portions at varying intervals in addition to the initial 20 grams added prior to electrolysis.

Although the solution in the cell remained clear throughout the electrolysis, the porous cup surrounding the anode was found to contain a substantial amount of a black precipitate, presumably silver sulfide. To determine the silver content of this anodic precipitate, it was filtered, dried, and weighed. A weighed portion of this dried precipitate was then analyzed and found to contain 32 per cent silver. The total amount of silver contained in the anodic precipitate was then calculated to be 6.66 grams.

It was found that 33.11 grams of silver were recovered as metallic silver and the final electrolyte analysis showed a total content of 1.68 grams of silver. A total of 41.44 grams of silver was thus accounted for as compared to the 41.65 grams of silver that was contained in the solution prior to electrolysis.

At various intervals, electrolysis was stopped and the cathode was removed, rinsed, dried, and weighed thus obtaining the amount of silver deposited in a specific time. (See graph, figure 5.)

The current density was purposely varied to determine the most efficient operating conditions.

The rough deposit of silver was removed from the cathode at the end of 4 hours, 16 hours, 20 hours, and 30 hours. Before dissolving the silver in nitric acid, an attempt

was made to remove the silver metal from the cathode by peeling. At the end of 4 hours, the cathode was removed and a small portion of the deposit peeled off. This revealed a very bright deposit of silver next to the platinum surface. Much care had to be taken, however, since the platinum foil tended to tear as the silver was peeled from its surface. Solution in nitric acid, therefore, was found to be the most logical method of stripping the silver from the cathode.

For experiment XV, the electrolyte remaining from experiment XIV was treated with approximately 40 grams of the silver residue and 25 grams of sodium thiosulfate crystals. This solution was then heated to 60° C., cooled, filtered, and permitted to stand for twenty-four hours. Thick needle shaped crystals were found to have crystallized from solution. Further examination of the crystals revealed that they were insoluble in cold water, slightly soluble in hot water, and soluble in fresh thiosulfate solution. The crystals were analyzed and found to contain 42 per cent silver and 26 per cent sulfur which closely approximated the composition of sodium silver thiosulfate, NaAgS_2O_3 .⁽¹¹⁾

Analysis of the electrolyte, after removing the crystals by decantation, showed a total silver content of 10.20 grams. Twenty grams of potassium bisulfite were then added and subsequent electrolysis using the platinum cathode removed

(11) Mellor, J. W., Op. Cit., p. 7.

TABLE 8
 RECOVERY OF SILVER USING PLATINUM CATHODE AND CARBON ANODE
 Experiment XV

Duration of electrolysis (hours)	Current density (amperes per sq. dm.)	Voltage (volts)	Amount silver deposited (grams)	Total silver accumulated (grams)
3	1.0	2.5	4.84	4.84
6	1.0	2.5	4.48	9.32
Total silver in solution prior to electrolysis:				10.20
Total silver removed as metallic deposit:				9.32
Total silver remaining in solution:				0.55
Total silver in anodic deposit of Ag_2S :				0.33

9.32 grams of metallic silver. Final analysis of the solution showed a total silver content of 0.55 gram. Only 0.33 gram of silver, therefore, was precipitated as silver sulfide by anodic decomposition.

Because of the expense and fragility of the platinum cathode, it was decided to experiment with more sturdy cathodes of stainless steel. These steel cathodes were cleaned by first scouring with a cleansing powder and then boiling in a saturated caustic potash solution for one hour.

Experiment XVI (see table 9) was performed using an electrolyte containing agar-agar in an attempt to obtain a deposit which could be stripped from the steel cathode by mechanical means. Although good silver recovery was obtained, the silver was firmly deposited on the cathode along with the agar-agar and had to be removed by dissolving in nitric acid.

Experiment XVII (see table 10) was the first of the experiments conducted with two steel cathodes, each having a surface area of one square decimeter. The carbon anode was placed in the center of the cell and one cathode was placed at each end of the cell (see figure 4). This arrangement shortened the distance between electrodes to five centimeters. A more rapid rate of silver recovery was obtained even though the deposit was not evenly distributed on the cathodes; the majority of it was deposited on the cathode surface facing the anode. In order to obtain a more evenly distributed deposit of silver, the cathodes

TABLE 9
RECOVERY OF SILVER USING ONE STEEL CATHODE AND
A CARBON ANODE

Experiment XVI

Duration of electrolysis	Current density	Voltage	Amount silver deposited	Total silver accumulated
(hours)	(amperes per sq. dm.)	(volts)	(grams)	(grams)
3	1.0	4.5	6.44	6.44
5	0.9	4.3	4.33	10.77
8	0.8	4.0	3.46	14.23
Total silver in solution prior to electrolysis:				15.29
Total silver removed as metallic deposit:				14.23
Total silver remaining in solution:				0.66
Total silver in anodic deposit of Ag_2S :				0.40

TABLE 10
RECOVERY OF SILVER USING TWO STEEL CATHODES AND
A CARBON ANODE

Experiment XVII

Duration of electrolysis (hours)	Current density (amperes per sq. dm.)	Voltage (volts)	Amount silver deposited (grams)	Total silver accumulated (grams)
2.5	1.0	4.5	9.81	9.81
4.0	1.0	4.5	8.06	17.87
5.0	1.0	4.5	4.66	22.53
9.0	1.0	4.5	5.32	27.85
Total silver in solution prior to electrolysis:				28.80
Total silver removed as metallic deposit:				27.85
Total silver remaining in solution:				0.60
Total silver in anodic deposit of Ag_2S :				0.35

were turned at each cessation of electrolysis.

The carbon anode began to deteriorate after long use and this led to a study of other possible types of anodes.

Experiment XVIII (see table 11) was conducted using a stainless steel anode placed at one end of the cell and the two steel cathodes placed at the opposite end of the cell. This arrangement of the electrodes resulted in a rate of silver recovery less than that obtained in experiment XVII. Electrode arrangement in all subsequent experiments, therefore, was identical to that used in experiment XVII.

After electrolysis, the steel anode was found to be heavily corroded. Because of this corrosion, no further experiments were performed using this type of anode.

Experiment XIX (see table 12) was performed using a platinum anode placed midway between the two steel cathodes. This anode remained bright throughout electrolysis and showed no signs of corrosion.

The electrolyte in all previous experiments had been prepared using distilled water. Ordinary tap water was used in experiment XIX, however, since this type of water is less expensive and is used in most photographer's fixing baths. Results were gratifying as efficient silver recovery was maintained.

To avoid cessation of electrolysis at different intervals to weigh the cathode deposit, a five milliliter aliquot of the electrolyte was analyzed at specified time intervals

TABLE 11
RECOVERY OF SILVER USING TWO STEEL CATHODES AND
A STEEL ANODE

Experiment XVIII

Duration of electrolysis	Current density	Voltage	Amount silver deposited	Total silver accumulated
(hours)	(amperes per sq. dm.)	(volts)	(grams)	(grams)
5	1.0	4.5	18.06	18.06
9	1.0	4.5	3.24	21.30
Total silver in solution prior to electrolysis:				23.02
Total silver removed as metallic deposit:				21.30
Total silver remaining in solution:				1.12
Total silver in anodic deposit of Ag_2S :				0.60

TABLE 12
RECOVERY OF SILVER USING TWO STEEL CATHODES AND
A PLATINUM ANODE

Experiment XIX

0.5 amperes per sq. dm. 4.5 volts 800 ml. solution

Duration of electrolysis	Total silver remaining in solution	Amount silver deposited	Total silver accumulated
(hours)	(grams)	(grams)	(grams)
0	29.44	-----	-----
2	20.48	8.96	8.96
3	16.68	3.80	12.76
6	8.96	7.72	20.48
7	4.91	4.05	24.53
8	0.96	3.95	28.48
10	0.08	0.88	29.36
13	negligible	negligible	29.36
Total weight of cathode deposit:			28.83
Total silver in cathode deposit:			27.97
Silver content of deposit			- 96.90 per cent

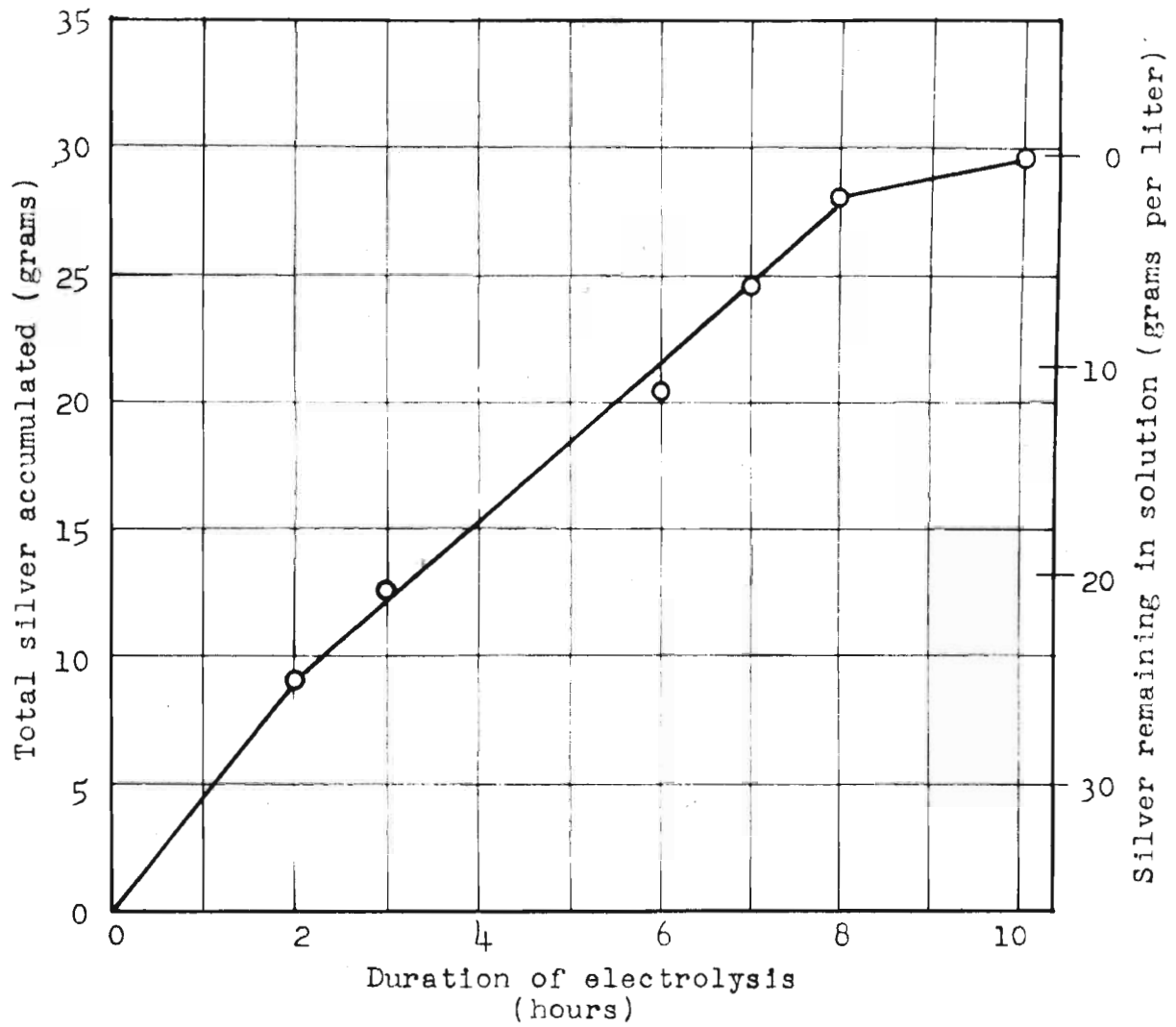


Figure 6. RATE OF SILVER RECOVERY (Experiment XIX)

thus enabling the experimenter to determine the rate of silver recovery with a minimum loss of time. This analysis showed a total recovery of 29.36 grams and weighing of the dried cathodes after electrolysis was completed showed 28.83 grams of silver actually deposited.

The silver deposited on the cathode was dissolved in 1:1 nitric acid and the resulting solution was diluted to exactly 500 milliliters. Subsequent analysis of an aliquot of this solution by titration with potassium thiocyanate revealed a silver content of 27.97 grams thus showing the deposit to contain 96.90 per cent silver.

Assuming 27.97 grams of silver recovered, calculation of the per cent of original silver in solution actually removed as metallic silver showed a 95 per cent recovery.

A graph showing the rate of silver recovery in experiment XIX is given in figure 6. It was observed from this graph that maximum rate of silver recovery was obtained at a current density of 0.5 ampere per square decimeter when the silver content of the electrolyte did not fall below 25 grams per liter.

Experiment XX (see table 13) was conducted using a current density of one ampere per square decimeter. The rate of silver recovery was found to be about twice that using a current density of 0.5 ampere per square decimeter. After three hours of electrolysis, however, a very dark deposit began to form on the cathodes. Electrolysis, therefore, was stopped and the cathodes were removed, washed,

dried, and weighed. The silver deposit was then dissolved in nitric acid and the quantity of silver present in the deposit was determined. This deposit was found to contain 26.70 grams of silver or a percentage composition of 98.50 per cent.

The clean cathodes were then returned to the cell and electrolysis was conducted for an additional one-half hour. A black deposit still occurred, however, and the rate of recovery was noticeably less.

TABLE 13

RECOVERY OF SILVER USING TWO STEEL CATHODES AND
A PLATINUM ANODE

Experiment XX

1.0 ampere per sq. dm. 8.5 volts 800 ml. solution

Duration of electrolysis	Total silver remaining in solution	Amount silver deposited	Total silver accumulated
(hours)	(grams)	(grams)	(grams)
0.0	37.28	-----	-----
0.5	31.20	6.08	6.08
1.0	26.72	4.48	10.56
1.5	22.56	4.16	14.72
2.0	18.50	4.06	18.78
2.5	14.25	4.25	23.03
3.0	10.40	3.85	26.88
3.5	7.40	3.00	29.88

After 3 hours of electrolysis:

Total weight of cathode deposit: 27.15

Total silver in cathode deposit: 26.70

Silver content of deposit - 98.50 per cent

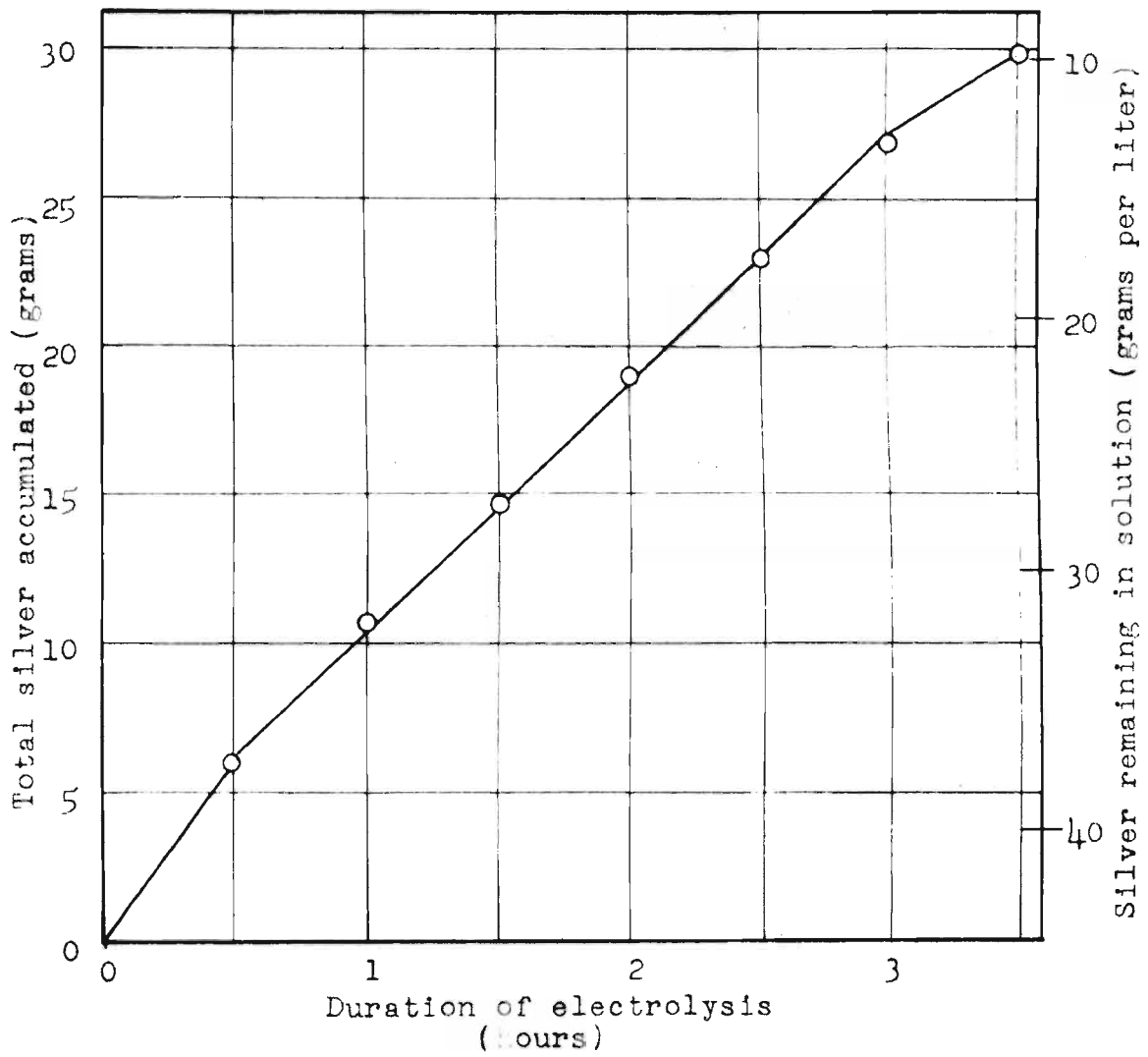


Figure 7. RATE OF SILVER RECOVERY (Experiment XX)

Experiment XXI (see table 14) was performed in the cell described in experiment XIX with an electrolyte made up of a used fixing bath solution obtained from a local photographic shop. This thiosulfate bath was found to contain only 4.06 grams of silver per 800 milliliters of solution. After subjecting this bath to electrolysis for two and one-half hours, only 2.54 grams of the silver were recovered. The deposit also became very dark after two hours of electrolysis.

Separation from a bath with such a low silver content therefore, was found to be impractical with the apparatus used. If desired, however, the solution could be used as a solvent for the waste silver residue since it contained 25 per cent by weight of sodium thiosulfate.

TABLE 14

RECOVERY OF SILVER FROM A USED FIXING BATH

Experiment XXI

1.0 ampere per sq. dm. 8.5 volts 800 ml. solution

Duration of electrolysis	Total silver remaining in solution	Amount silver deposited	Total silver accumulated
(hours)	(grams)	(grams)	(grams)
0.0	4.06	----	----
1.0	2.83	1.23	1.23
2.0*	1.65	1.18	2.41
2.5	1.52	0.13	2.54

* Deposit became very dark after 2 hours of electrolysis.

CONCLUSIONS

Sodium thiosulfate solution was found to be a very satisfactory solvent for the waste silver residue.

Recovery of the silver by the electrolytic precipitation of silver sulfide was proved to be feasible but was not as efficient as the electrolytic deposition of the metallic silver. The metallic silver deposit was found to be 98.50 per cent pure. Solution of the metallic silver in dilute nitric acid resulted in a satisfactory silver nitrate solution.

Of the various types of cathodes studied, the steel cathodes were found to be the most practical. The observed deterioration of the carbon anode in one of the experiments does not preclude the possible use of graphite anodes in a large cell. Obviously platinum anodes in larger cells would be economically impractical.

Installation of a porous cup around the anode proved effective in preventing anodic decomposition products from entering the main body of the electrolyte and contaminating the cathode deposit.

The most suitable electrolyte was a 25 per cent by weight of sodium thiosulfate solution containing 20 grams of sodium bisulfite and a maximum of 50 grams of silver per liter. Ordinary tap water was proved to be a suitable solvent for the soluble salts and continued use of the electrolyte was made possible by replenishing one liter of the used electrolyte with 30 grams of sodium thiosulfate

and ten grams of sodium bisulfite after each ten hours of electrolysis.

Because of the small concentration of silver in a used fixing bath, recovery of the silver therein was not feasible by the process developed in the foregoing experimentation.

For a cell of the type used in this experimentation, the optimum current density was determined to be one ampere per square decimeter as long as the silver content of the electrolyte remained above 12.5 grams per liter.

A larger cell, capable of recovering silver at a rate of 40 grams per hour, could be constructed by substituting an old storage battery case for the glass battery jar. The average sized battery case is about 17 centimeters wide, 20 centimeters deep, and 25 centimeters long. A battery case of this size could accommodate five steel cathodes and six graphite anodes. Each of the cathodes would consist of two steel plates (each plate having a surface area of one square decimeter) placed side by side two centimeters apart. Two or more arc lamp carbons, each surrounded by a porous cup or cloth filter bags, would comprise each anode.

Agitation of the solution could be provided by installing three air operated stirrers, one placed in the center of the cell and one at each end. The space left between the cathode plates would facilitate circulation of the solution.

This cell arrangement would enable a current of ten amperes to pass to an aggregate of ten square decimeters

of cathode surface.

The battery case would have a seven liter capacity and with a silver concentration of 50 grams per liter, electrolysis could be conducted without interruption for an eight hour period.

Based upon the direct current output consumption, the power cost per gram of silver recovered at a current density of one ampere per square decimeter was found to be more than twice the power cost per gram recovered at a density of 0.5 ampere per square decimeter. A true power cost, however, should be calculated on the basis of the alternating current input into the rectifier. This power input was measured and found to be 90 watts.

Since the average rate of silver recovery at the larger current density was eight grams per hour (see figure 7), 40.86 kilowatt-hours would be required to recover one pound of silver. The present cost of electrical power is two cents per kilowatt-hour and the cost of silver nitrate crystals is \$7.32 per pound. One pound of silver is equivalent to 1.575 pounds of silver nitrate. Therefore, silver nitrate solution containing \$14.06 worth of silver nitrate could be prepared at a power cost of one dollar by the electrolytic method of silver recovery used in the foregoing experimentation. The cost of chemicals used in this silver recovery was negligible when compared to the power cost.

SUMMARY

A simple and economical electrolytic process of recovering silver in a usable form from waste silver residues accumulated by students of quantitative analysis has been discussed.

This process involves the solution of the silver residue in a 25 per cent by weight sodium thiosulfate solution and subsequent electrolytic deposition of metallic silver on steel cathodes at a low current density (one ampere per square decimeter). The metallic silver is then dissolved in dilute nitric acid. The resulting silver nitrate solution is suitable for use in the quantitative determination of chlorine by both the volumetric and the gravimetric methods.

Suggestions have been set forth from which a working cell may be constructed of sufficient capacity to recover all silver accumulated in the quantitative analysis laboratories.

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INDEX

	Page
Agar-agar	37
Agitation of electrolyte	9
Effect on current density	9
Methods of	13, 51
Anode	
Carbon	13, 50
Deterioration of	40, 50
Platinum	40
Steel	40
Cathode	
Carbon	13
Copper	13, 31
Platinum	13, 31
Preparation of	12, 31, 37
Stainless steel	13, 37, 50
Surface area of	13, 37, 50
Current density	9
Optimum	9, 29
Cyanide solutions	1
Electrodes, arrangement of	16
Electrolyte	
Composition of	19, 29, 40, 50
Continued use of	24, 50
Optimum silver content	44, 51

	Page
Electrolyte (cont'd)	
Preparation of	29, 40, 50
Temperature of, maximum	29
Electrolytic apparatus	13, 15, 16
Diagram of	16
Gelatin in fixing baths	9
Porous cup, use of	21, 50
Preparation of electrolyte	29, 40
Promoters	9, 11
Quicking solution	12
Reagents	12
Silver	
Content	
In insoluble electrolytic precipitate	22, 26
Metallic deposit on steel cathode	42, 44
Residue insoluble in sodium thiosulfate	23
Cost of recovery as silver nitrate solution	52
Metallic, electrolytic recovery of	29, 50
Optimum content in electrolyte	44, 51
Effect on current density	9
Quantitative analysis of	17
Recovery as silver sulfide	17, 28, 50
Solution in nitric acid	29, 50
Thiosulfate compounds of	8

	Page
Silver recovery	
Fixing baths, from	3
Electrolytic methods	4
Sodium sulfide method	3
Zinc method	4
Sodium thiosulfate solutions, from	3
Bright electrodeposits	3
Electrolytic precipitation of silver sulfide	17, 28, 50
Rough deposits	9, 34
Silver sulfide	
Electrolytic precipitation of	17, 28, 50
Sodium sulfide precipitation of	3, 12, 30
Sodium bisulfite, purpose of	11
Sodium silver trithionate	8
Sodium silver thiosulfate	8
Sodium sulfide	
Preparation of	12
Use of	3, 30