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Laboratory Division

QUANTITATIVE ELECTROPLATING OF URANIUM FOR ISOTOPIC ANALYSIS

using

NICKEL AND MONEL AS BASE METALS

Clayton McAuliffe

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QUANTITATIVE ELECTROPLATING OF URANIUM FOR ISOTOPIC ANALYSIS

using

NICKEL AND MONEL AS BASE METALS

The preparation of a quantitative, uniform, adherent film of uranium is one of the most important steps in the alpha and fission counting methods of isotopic analysis of uranium. When this research was undertaken a method making electroplated films with platinum as the base metal was in use. However, it was impossible to electroplate consistently a film of uranium thick enough to facilitate rapid counting and still be adherent. This report deals with the investigation of other metals and the conditions necessary to obtain heavy, uniform, adherent, quantitative films for the counting methods of isotopic analysis.

An efficient multiple plating unit was designed for electroplating films with ease and a minimum of attention, while maintaining the standards of constant area and position of film, temperature, current density and speed of stirring. The characteristics of a good electrodeposit were defined as well as the techniques for determining the quality of a film. Gold, silver, copper, aluminum, monel and nickel were investigated as a base metal to be substituted for platinum. Of these metals, monel and nickel proved far superior to the others and an investigation of the electroplating conditions was made for these metals. Although it was found that different surface roughnesses had a significant effect on the quality of the electrodeposit, the cold-rolled nickel and monel surfaces were satisfactory to give reproducible results. Various methods of

cleaning this cold-rolled nickel or monel surface, degreasing, electropolishing, alkaline cleaning, acid treatment, and use of abrasives were tried. Of these methods the simple degreasing technique proved to be the most satisfactory.

An entire series of ammonium salts of various concentrations was tried as electrolytes. Several proved satisfactory, but none was superior to ammonium oxalate, the electrolyte originally selected. The electrolysis variables of temperature, current density, speed of stirring and time of plating were studied. As a result a temperature of 80° C., a current of 3.0 amperes, a stirring speed of 500 r.p.m., and a 50 minute electrolysis were selected. After considering the electroplating solution variables, 6.0 millimoles of ammonium oxalate in a plating solution of 40 ml and an initial pH value from 2.0 to 9.0 were found to give good quality electrodeposits. The rate of resolution of the electrodeposit in the residual plating solution was negligible. The ignition of a series of films at different temperatures and for different lengths of time showed that a temperature from 425° to 525° C from 10 to 15 minutes to be satisfactory. The addition of relatively large amounts of a number of metallic impurities had little effect on the quality of the electrodeposit. Since only traces of these metals occur in our plating solutions, they have no significant effect.

Good precision by this electroplating method is obtained. A careful investigator is able to obtain a standard deviation of 0.15% or less as the error in the preparation of a single film. Films made by operators had a standard deviation of 0.25% for 1337 samples of normal uranium plated in duplicate from September through December, 1945. A similar number of films plated during the first 6 months of 1945 had a

standard deviation of 0.18%. The majority of this increase in error is probably due to error in pipetting the aliquot of uranium.

This report covers the rather extensive investigation of the quantitative electroplating method. The apparatus and procedure are given first followed by the characteristics of a good film. A section on the selection of the base metal along with effects of surface roughness and methods of cleaning follows. A comprehensive investigation of electrolytes, electrolysis and plating solution variables is then given. The last section deals with the ignition of the film and effect of metallic impurities.

APPARATUS AND PROCEDURE

The apparatus and procedure used in this investigation are in principle the same as reported by Cohen and Hull*. A multiple plating unit has been designed and certain changes and improvements have been made in the cell assembly to give greater precision and more rapid operation. Nickel and monel have been used as the base metal instead of platinum, and the electroplating conditions altered to give an excellent electrodeposit on these base metals.

The Multiple Plating Unit.

The multiple plating unit is shown in Plates 1, 2 and 3. The framework is constructed from duraluminum finished with black crackle paint. The motor drives the four pulleys by means of an endless dental belt. The shield which covers the pulleys and belt has been removed. These pulleys in turn drive the stainless steel shaft and platinum anode. When the shaft is in the lowered position as shown by the two cells on the right, the brass piece, A, serves to drive the shaft, a thin rubber gasket, B, furnishing the necessary friction. This brass piece can be moved along the stainless steel shaft permitting adjustment of the anode height. When the shaft is held in the raised position by the spring clip P, it is free from the pulley and does not turn. This arrangement permits the use of one or more cells without influence on the others, a definite advantage which will become apparent when the electroplating procedure is discussed.

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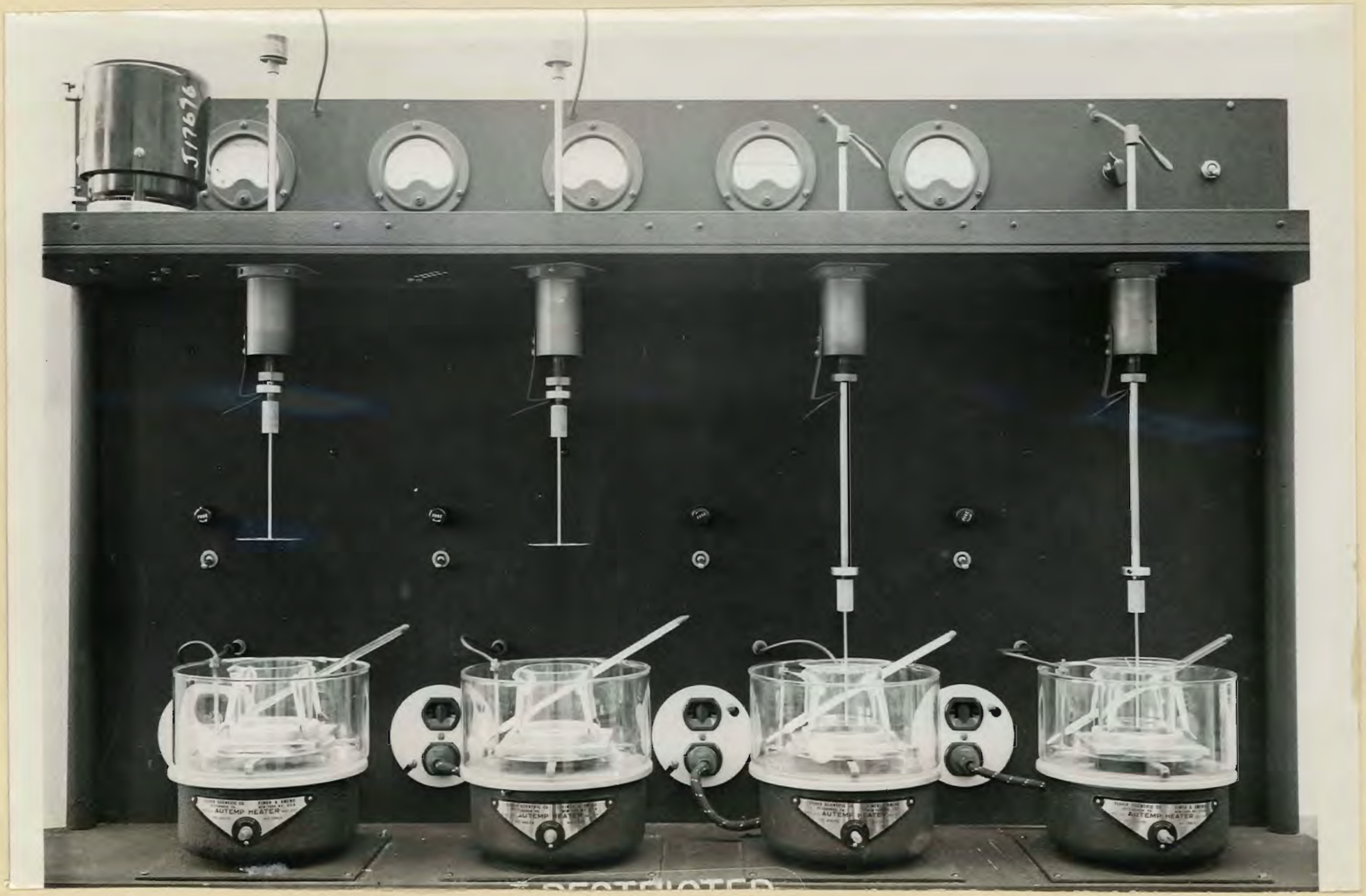
*Cohen, B. and Hull, D. E., The Counting Method of Isotopic Analysis of Uranium, Part II--Preparation of Films by Electroplating; A-1235: page 3 (1944).

Plate 1. Top-front View of Multiple Plating Unit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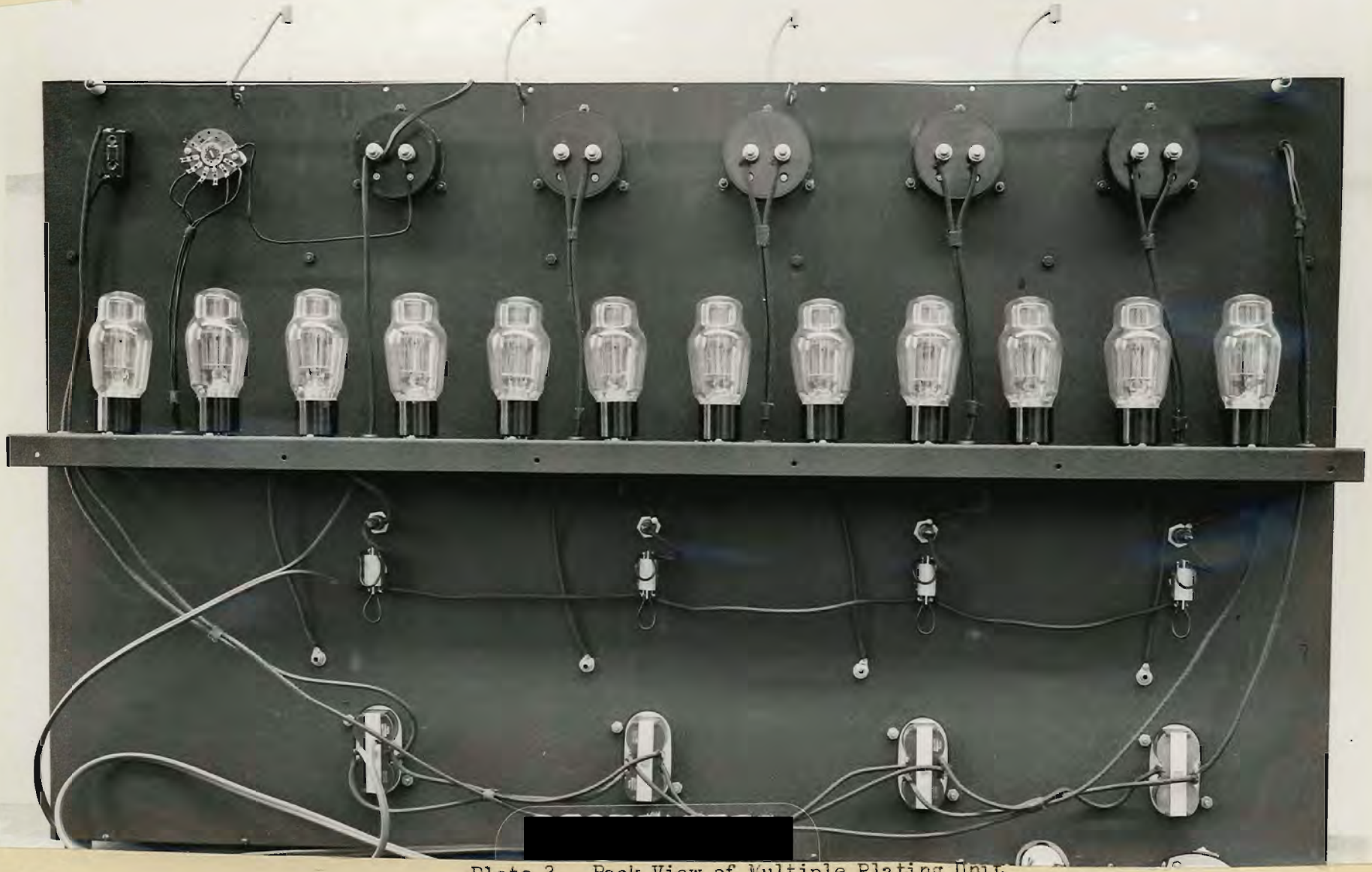

Plate 3. Back View of Multiple Plating Unit

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Referring to Plate 2, the bearing housing, C, contains a ball bearing at the bottom and one at the top into which the pulley is press-fitted. Should a bearing fail, it is an easy matter to remove the bearing housing and pulley as a unit by unscrewing the collar, D, and substituting a different unit. This rapid change allows the defective bearing to be repaired at leisure without removing the entire multiple plating unit from service. This same quick change feature is present in the hot plates where removing 4 screws allows a defective hot plate to be removed and another substituted.

The wiring diagram shown in Figure 1 is a simple circuit consisting of three 10A12 amperite tubes wired in parallel, with switch, fuse, ammeter, and voltmeter. A single voltmeter with selector switch is used to determine the voltage drop across any one cell. The amperite tubes serve to maintain the current at 3 amperes during the course of the electrolysis while the resistance of the cell changes. Plate 3 shows the back of the multiple plating unit with the amperite tubes and wiring exposed. Two notable features concerning the electrical circuit are the method of making contact with the rotating anode and the insulation of the D. C. circuit. Contact with the rotating anode is accomplished by means of a mercury reservoir. A 1/8" hole drilled in the top of each stainless steel shaft to a depth of 3 inches is two-thirds filled with mercury, and the mercury in turn is covered with oil. A nickel wire, M, is inserted so that it rests on the bottom of the hole. A small brass collar is pressed into the top of the 1/8" hole and fits the nickel wire loosely. This collar serves to prevent the mercury from splashing out.

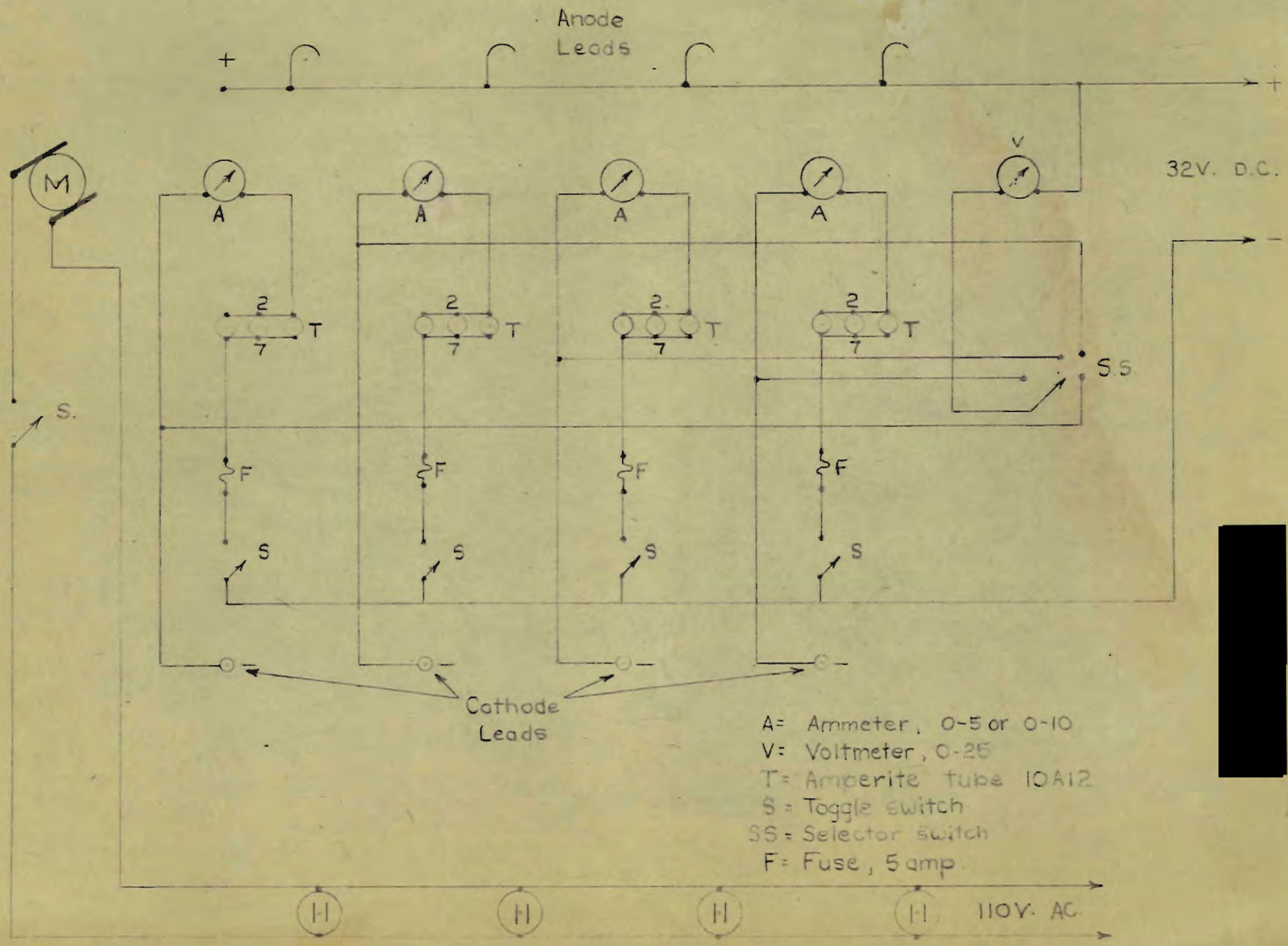


Figure 3. — Wiring Diagram for Multiple Plating Unit

LE-SK-55

The brass piece N, adds sufficient weight to keep the nickel wire seated firmly. Flexible test-lead wire joins the brass piece with the D.C. source. The D.C. circuit is completely insulated by separating the bearing housing and pulley from the frame of the unit with thin plastic. The lower piece of plastic O, can be seen in Plate 2.

From 6 to 8 of these multiple plating units have been in continuous service, 24 hours per day, for the past 10 months. The unit takes up little space; it is efficient, runs quietly, and requires relatively little maintenance.

The Electroplating Procedure.

To assemble the cell, Plate 4, a degreased nickel disk, E, is placed in the smaller recessed area of the stainless steel base plate F. The molded pure-gum rubber gasket G, rinsed in dilute nitric acid and dried with acetone, is fitted around the glass cylinder H, which has been previously cleaned with chromic acid. The cylinder and gasket are positioned in the larger recessed area of the base plate, the diameter of the recessed area being slightly larger than the outside diameter of the rubber gasket. The cylinder is then held firmly and securely in position with four strong rubber bands, I.

This arrangement gives a constant film area and centers the electrodeposit on the nickel disk. Since the range of alpha particles and fission particles is small in the electrodeposited film, 11 to 13 microns for alpha particles in U_3O_8 ; variation in thickness of the film will change the number of particles escaping to the outside to produce ionization in the air and therefore change the specific activity. Because of this self-absorption, it is

Plate 4. Plating Cell Disassembled and Assembled

necessary to define the area of the electrodeposit. This is accomplished in the above arrangement by selecting the glass cylinders so that each has a definite outside diameter, 60 mm $\pm$ 0.2 mm. The molded rubber gaskets all have the same lip, and when slightly stretched over the glass cylinder, they define the area exposed to electroplating which in this case is approximately 24 cm^2 $\pm$ 0.18 cm^2. A cross-section of the rubber gasket is shown by the small piece J.

The assembled cell is cleaned with chromic acid for a few seconds, followed by a thorough rinse with tap water and distilled water. Most of the experimental work employing nickel as the base metal was done without this chromic acid rinse. It was felt that it was not essential and indeed might be harmful, for chromium present tends to reduce the counting rate. Further the acid may stain the nickel surface, probably carbonaceous material, causing peeling of the electrodeposit on these stained areas.

Four millimoles of ammonium oxalate conveniently handled in the form of a 0.4 M solution is pipetted into the clean assembled cell. A known quantity of uranium in the form of a uranyl salt in aqueous solution is then pipetted or dispensed from a weight burette into the cell. Nitrate, sulfate, fluoride, and acetate solutions have been used. Sufficient water is added to the cell before the uranyl solution to adjust the total volume of the plating solution to 30 ml.

The assembled cell is placed in the water bath at 80°C., on the cell support K. The platinum anode L, is lowered until the disk is below the top of the glass cylinder. The cell is then covered with a set of split watch glasses, not shown in Plate 4 but shown in

Plates 1 and 2, and the anode lowered into the plating solution. The height of the anode disk is adjusted so that it is approximately 1 mm below the surface of the plating solution. The anode is rotated about 500 r.p.m. A current density of 3.0 amperes is used for a cell having a cross-sectional area of 24 cm^2.

The electrolysis is carried out for fifty minutes with the voltage drop across the cell varying from 6 to 8 volts at the start to 15 to 20 at the end, depending upon the temperature of the bath. The current is maintained at 3.0 amperes by the amperite tubes. The bath temperature is maintained between 75 and 85 degrees C.

When the electrolysis is completed, the watch glasses are removed and, if the plating solution is to be saved for determination of residual uranium, are rinsed with water and the washings collected in a beaker. Approximately 60 ml of methyl alcohol is added to the plating cell. The anode is raised and the contents of the cell immediately poured into a beaker. The solution is discarded unless a residue is to be determined. The methyl alcohol serves to dry the cell rapidly, particularly when the vapors are blown away.

The cell is disassembled and the nickel disk ignited for 10 minutes at 425° C. The resulting uranium film is ready for counting.

In the remainder of this report the above discussed procedure will be referred to as the "standard procedure", and any variation of conditions will be indicated.

[redacted]

METHODS EMPLOYED TO DETERMINE QUALITY OF ELECTROPLATED FILM

A good quality electroplated film has a bright metallic deposit characterized by brilliant interference colors. The film thickness is uniform over the entire area, and when viewed under 108 diameters the electrodeposit appears uniform and continuous. The deposit is adherent to the base metal to such an extent that it cannot be removed by rubbing hard with Kleenex. Since the fundamental problem is to obtain a film giving a reproduceable specific activity under the same conditions, the electrodeposit must possess the characteristics of adherence, quantitativeness, uniformity, composition, and possibly other properties necessary to fulfill the requirement.

To determine the quality of the electroplated film, visual observation with the unaided eye and with the 108 diameter binocular microscope, an exploring disk, photographs, rubbing of the film, determination of residual uranium in the plating solution, and specific activity of the film were used.

The degree of film uniformity can be determined by the regularity and brightness of the interference colors. This is a good indication of adherence too, for a film which does not possess interference colors but is brown or black most likely has a non-adherent deposit. With rotational stirring as used in this method, a lighter deposit is formed in the center of the film than over the remainder of the area. Since the speed of stirring is constant, the light area in the center remains quite constant. Because of this light center area, it is possible to estimate roughly the weight of the electrodeposit as well as the speed of stirring by the interference colors.

The 108 power binocular microscope is of value in closely examining the electrodeposits for uniformity and continuity. In most cases, however, visual observation gives sufficient detail.

Another method measuring uniformity consists of the use of an exploring disk. The disk covers the electrodeposit of uranium in the counter ion-chamber. Holes of uniform diameter are drilled in the disk and these fitted with covers. Uncovering one hole at a time and counting the emerging alpha or fission particles gives a measure of the quantity of uranium exposed.

Photographs and alpha-particle photographs give indications as to the smoothness and uniformity of the deposit, but are inferior methods to visual observation. Photographs appear to give better results than the alpha-particle photographs.

The adherence of the electrodeposit can be determined by rubbing the film hard with Kleenex. If the deposit is adherent, nothing visible appears on the white tissue. With decreasing adherence, larger and larger quantities of black oxide appear. A very non-adherent film will rub off easily, exposing the surface of the nickel or other base metal.

To determine if the procedure is quantitative, the residual uranium is determined at the end of electrolysis. The ratio of the number of counts from the remaining solution to the number on the film gives the approximate percentage of the uranium not plated.

To determine the reproducibility of any set of conditions, the films are counted. In this report the specific alpha- or fission-activity, the A- or F- value, or the number of counts per minute

will be used to indicate variation in the plating technique and the quality of the electrodeposit.

$$\text{Specific A- or F-Activity} = \text{No. of A- or F-Counts/min/mg } U_3O_8$$

$$\text{A- or F-Value} = \frac{\text{Specific Activity of Unknown}}{\text{Specific Activity of Normal Uranium}}$$

In other words, the specific alpha or fission activity is equal to the number of alpha or fission counts per minute per mg of U_3O_8. The A- or F-value is equal to the number of alpha or fission counts per minute per mg U_3O_8 obtained from a sample of uranium of unknown isotopic composition divided by the number of alpha or fission counts per minute per mg of U_3O_8 from a sample whose isotopic composition is that found in nature. The number of counts per minute has been used in some instances when the same quantity of uranium was plated and counted on the same amplifier. Specific activity would be obtained by merely dividing counts per minute by the mass.

In the remainder of the report, these methods of determining the quality of the electroplated film have been used.

SELECTION OF BASE METAL

The quantity of uranium which can be repeatedly deposited on a platinum disk giving an adherent uniform film is only about 4 mg of U_3O_8 per 24 sq. cm. Furthermore platinum disks require cleaning and counting between uses to insure the complete removal of the electrodeposited uranium. This means the use of valuable amplifier time which could be better utilized. For these two primary reasons, other base metals were investigated.

[redacted]

Polished disks of gold, silver, copper, aluminum, monel and nickel were obtained. Films of varying weight of U_3O_8 were plated on each metal using standard conditions. The films electroplated on gold were similar to platinum in that films heavier than 4 to 8 mg were non-adherent. Silver gave good adherence, but there was no convenient way of removing the electrodeposit and reusing the silver disk, silver being too expensive to discard after a single use. Copper gave better adherence than platinum. However, since it is necessary to ignite the film to obtain reproducible results for precise work, copper was not considered because of its excessive oxidation when heated at relatively low temperatures. Aluminum was entirely unsuited under the conditions used, for the aluminum reacted with the plating bath during electrolysis, filling the solution with a white flocculent aluminate precipitate. Of the metals investigated, nickel and monel gave the best results, nickel being superior to monel. Nickel gave the most uniform, adherent, and the heaviest deposit of the metals investigated.

The use of nickel and monel possesses a number of advantages over the use of platinum as a base metal on which to electroplate uranium.

1. Uniform adherent films as heavy as 16 to 18 mg of U_3O_8 per 24 sq. cm. can be consistently plated compared to 4 to 6 mg on platinum. Films of 22 mg have been plated which are quantitative but at this value show tendencies toward peeling, and slight amounts of the electrodeposit can be rubbed off with Kleenex.

[redacted]

2. Nickel and monel can be cold rolled and disks fabricated for a cost of roughly 4.4 and 4.0 cents each. The disks are thus economical enough to warrant using once and then discarding. When a sample has been counted on a platinum disk, it is then necessary to dissolve off the electrodeposit in concentrated nitric acid, carefully rinse and dry the disk. Sometimes a trace of uranium will be left on the disk after cleaning, and it is therefore necessary to count the blank disk before plating on it again. Discarding the nickel or monel disk does away with these extra operations, and the saving is far greater than the cost of the nickel disk.

3. In the case of certain research samples in which the quantity of uranium is small, the use of platinum has the advantage that the sample recovered from the platinum disk requires less purification to obtain pure uranium than a sample recovered from a nickel disk. The use of a mixture of sulfuric acid-hydrofluoric acid removes the uranium from the nickel disk plus a small amount of nickel which must be separated before the sample can be re-analyzed. However, in the analysis of routine samples or samples with a sufficient quantity of material, it is not necessary to recover the uranium from each individual nickel disk separately. If the uranium is to be recovered, it can be removed from a large number of disks at one time.

4. Nickel and monel can be cold rolled to a surface that is

[redacted]

sufficiently smooth to give excellent results. A large quantity of nickel or monel can be rolled and fabricated at the same time, giving a uniform surface. Platinum, after repeated use, becomes scratched and dented. This may lead to error in the analysis, and it does require the salvage of platinum and the purchase of additional expensive disks.

5. The nickel and monel disks are 0.025 inches in thickness and are fabricated so that they have a plane surface with no warping. A disk of this thickness of these metals can be handled quite roughly without being misshapen. The platinum disks previously used were 0.005 inches in thickness and required careful handling to prevent denting and bending, especially since in the plating procedure the disks must be handled with tongs. Platinum disks 0.025 inches in thickness would be very expensive and still would not possess the physical properties of nickel.

6. The use of 0.025 inch nickel disks greatly simplified the holder design and positioning of the film in the counter ion-chamber. In the chamber with horixontal plates as in the alpha counter ion-chamber used at the K-25 laboratories and S.A.M. Laboratories in New York City, the disk is placed in a recessed area 0.020 inches deep. The disk lies in this recessed area and has sufficient mass to prevent microphonics. The thin platinum disk has to be held in position by a thin

annular ring. Even with this arrangement it was difficult to prevent the disk from warping. In a vertical chamber such as the fission counter used at the K-25 laboratories, the disk is held in the recessed holder by a thin annular ring which snaps into position, catching the extreme circumference of the nickel disk.

7. Because of oxidation, nickel and monel cannot be ignited at temperatures as high as platinum. However, ignition at roughly 425°C., for ten minutes gives reproducible results and appears entirely satisfactory.

SURFACE ROUGHNESS OF BASE METAL

The cold rolling of one-half hard A-nickel results in a surface that is quite smooth and free from scratches and pits. During the subsequent fabrication of the nickel strip into disks and handling in shipment and in the laboratory, the surface of some of the disks is slightly scratched. To determine the significance of these scratches, a large number of disks was sorted and grouped according to the degree of scratching, with group 1 having essentially no scratches, and group 3 having the worst surface found. The same quantity of uranium from the same solution was plated on 12 disks from each group with the following results:

Group	Mean Alpha Counts/min.	± Std. Dev. of Mean
1	9050	6
2	9045	6
3	9046	8

These data show no significant difference between the groups. This indicates that the scratching incurred in the fabrication and handling

[redacted]

is not sufficient to alter the counting rate.

Since the surface roughness of the cold rolled nickel might vary from one shipment to another, disks from the first shipment of 30,000 were compared with those from the second shipment. Visual observation indicated little difference in surface roughness. To determine if an effect actually existed, 12 disks were electroplated from the first shipment and 12 from the second using the same uranyl nitrate solution under identical conditions.

	First Shipment	Second Shipment
Mean Alpha Counts	6469	6461
Std. Dev. of Single Measurement	12	19
Std. Dev. of Mean	4	6

To the precision of the measurements, no significant difference could be shown. This is further substantiated by the routine analysis of several thousand samples of normal material by the alpha method during the past year. The specific activity of these samples has not significantly changed from the standard calibration films.

To increase the quantity of scratching under controlled conditions four nickel disks were ruled with a carborundum-tipped pencil. The lines were spaced about 1/8" apart, both horizontally and vertically across the face of the disk. A cross-section of these scratches was roughly an equilateral triangle 0.1 mm. on a side, as determined under 100 diameters using a microscope with an eye piece calibrated with stage micrometer. The following data give a comparison of the number of counts obtained after plating the same quantity of uranium on the scratched surfaces and on unaltered nickel disks.

		Alpha Counts/min.	± Std. Dev. of Mean
Discs with no scratches		5762	7
Scratched disk	1	5636	
	2	5649	
	3	5587	
	4	5627	

Comparing disk 3 with the unaltered disks, the counting rate has been lowered roughly 3.1%. By considering the total length of scratches, the increased area caused by scratching and the number of alpha particles stopped by the scratches, a rough calculation indicated that the count should have been lowered by somewhat less than 4%. This agreement is as good as could be expected under the conditions of the experiment.

To determine the effect of various surfaces of the base metal, a series of disks were given the following treatments:

1. No treatment
2. Hand polished with crocus cloth
3. Electropolished using H_3PO_4-glycerol bath
4. Polished in metallographic wheel using 600 grade carborundum
5. Scratched with No. 80 grade carborundum cloth
6. Etched three minutes with concentrated nitric acid

Of these treatments, only the electropolishing needs explanation. A 40% phosphoric acid (85%) - 60% glycerol bath was used. The nickel disk to be polished was the anode, at a bath temperature of approximately 100°C., with a current density of 15-20 amperes/disk for a period of two to three minutes. Microphotographs of the cross-sections of these surfaces are shown in Plates 5, 6, 7, 8, 9, and 10.

These types of surfaces were then electroplated with various weight

films of uranium under standard conditions to determine the effect on the counting rate. The results from this investigation are given in Table 1. It is apparent that the type of surface has an appreciable effect on the counting rate. Polishing the surface with crocus cloth, metallographic wheel, and electropolishing increased the counting rate by roughly 1%, while the acid etching and scratching lowered the count from 2 to 4%. The photomicrographs of the surface finish indicate the same order of roughness as obtained by counting. It is felt that with experience, visual observation of the surface is almost as good a guide to surface roughness as is the photomicrograph.

When considering the information obtained from these surface roughness investigations, it is apparent that the surface of the base metal has an important effect on the specific activity. However, the surface in any one shipment of nickel disks apparently is reproducible, and even different shipments of nickel may have the same surface roughness.

[redacted]

Plate 5. Cross-section of Normal Nickel disk. 1000 x

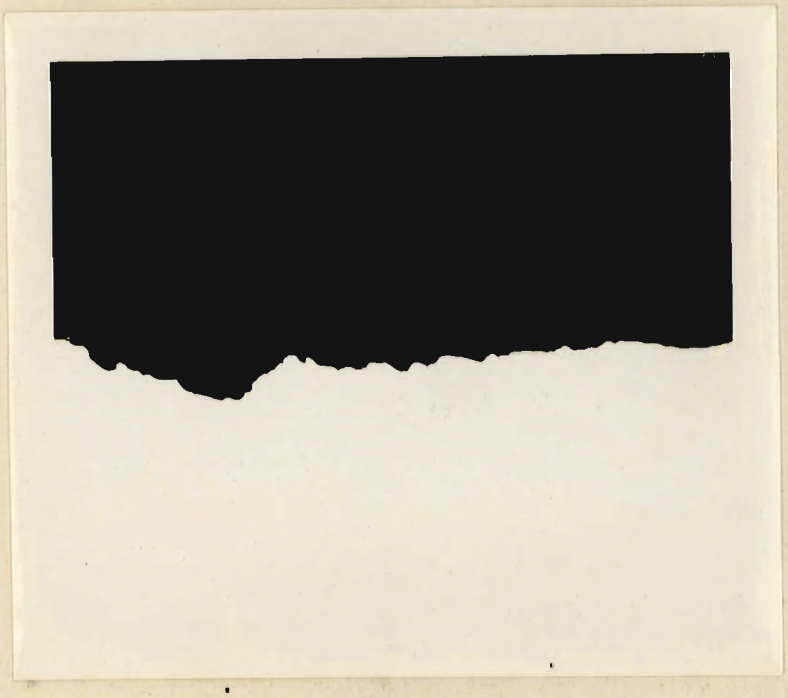


Plate 6. Cross-section of Nickel Disk polished by 80 grade carborundum Cloth. 1000 x

[redacted]

Plate 7. Cross-section of Electropolished Nickel disk 1000 x

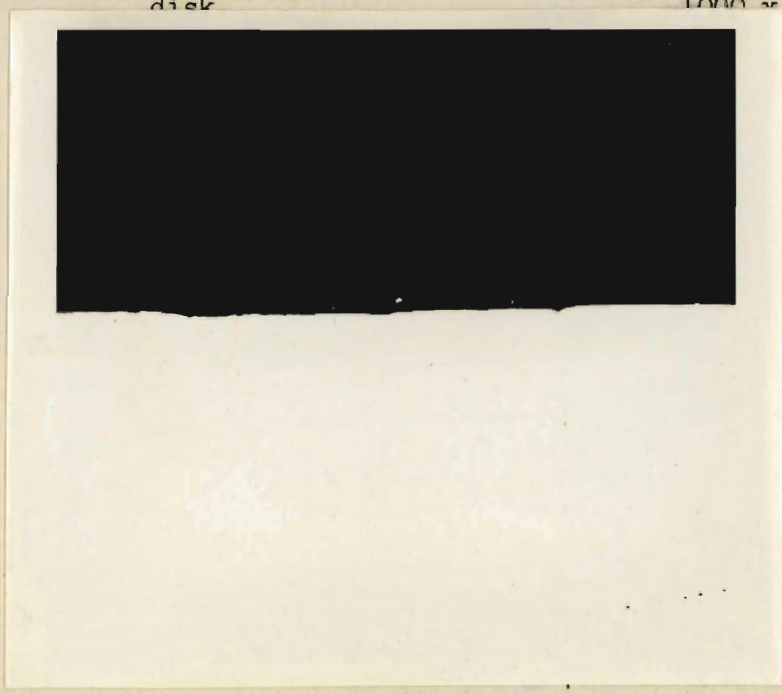


Plate 8. Cross-section of Nickel Disk polished on metallographic Wheel using 600 grade carborundum. 1000 x

[redacted]

Plate 9. Cross-section of Nickel Disk Polished by Crocus Cloth. 1000 x

Plate 10. Cross-section of Nickel Disk etched with Concentrated Nitric Acid 1000 x

[redacted]

Table 1. The Effect of Surface Roughness on the Electrodeposit.

Treatment of nickel disk	Appearance of nickel disk	Film[a] weight mg[b]	Mean alpha counts/minute	± Percent std. dev. of mean	Mean fission counts/minute	± Percent std. dev. of mean
1. Degreased	Normal	0.4	8281	0.13	2098	0.33
2. Polished crocus cloth	bright, fine scratches	0.4	8318	0.07	2101	0.33
3. Electro-polished	mirror-like	0.4	8325	0.13	2103	0.28
4. Polished on metallo-graphic wheel	Very highly polished	0.4	8330	0.07	2109	0.14
5. Scratched with No.80 carborundum	Scored with deep scratches	0.4	7941	0.25	1941	0.21
6. Conc. HNO_3 for 3 min.	Rough, crystal-line	0.4	8022	0.30	1997	0.40
1	As 1 above	11	8178	0.07	927	0.32
4	As 4 above	11	8317	0.06	959	0.31
6	As 6 above	11	8057	0.09	926	0.32
1	As 1 above	7.4			7910	0.10
4	As 4 above	7.4			7984	0.08
6	As 6 above	7.4			7650	0.18

[a]Four films were plated in each case.
[b]Throughout this report, the film weight is given as the number of mg. of U_3O_8.

CLEANING OF BASE METAL PRIOR TO ELECTROLYSIS

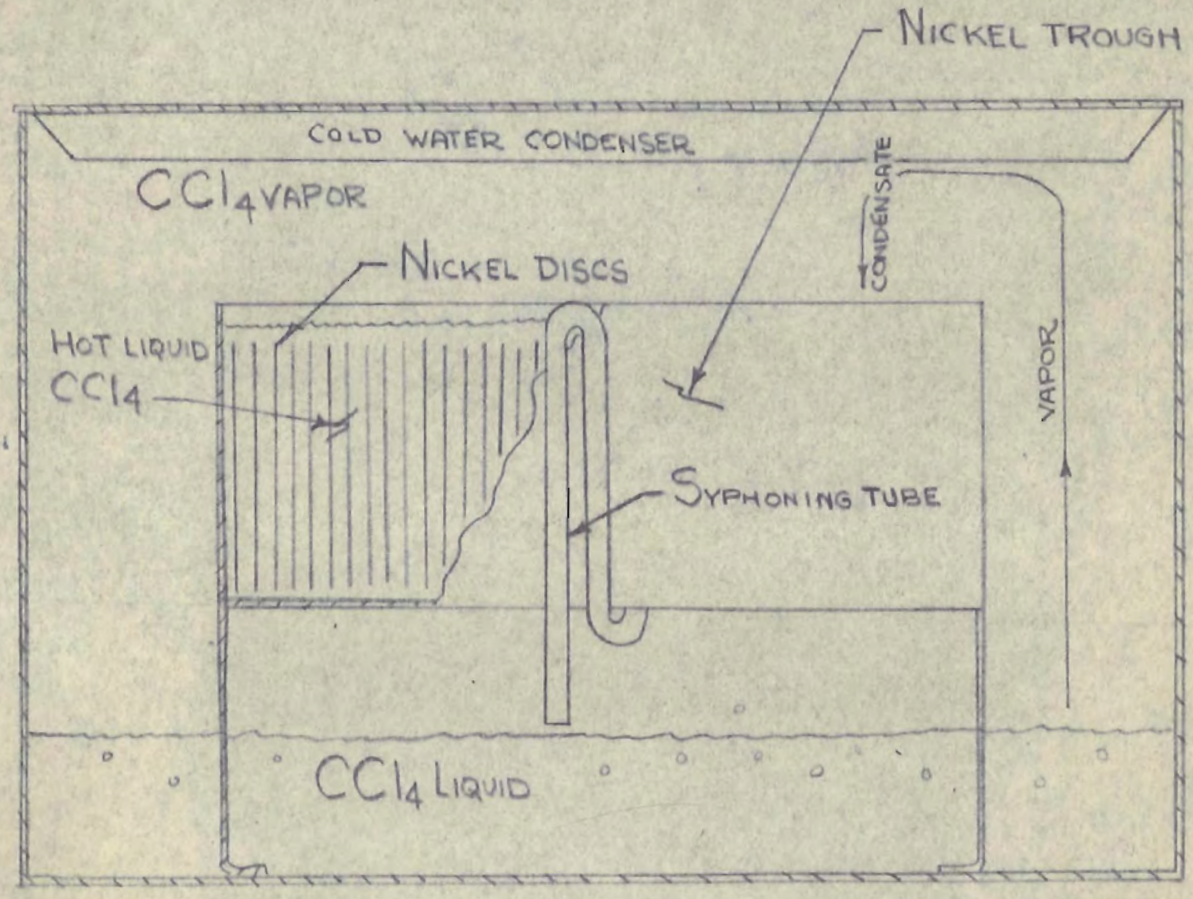
As is generally true with electroplating, the cleaning of the base metal prior to electrolysis is important. In the case of electroplating uranium on nickel or monel, the best procedure appears to be a simple degreasing rather than the more elaborate techniques of acid dips, alkaline dips, electrolysis and others. A number of cleaning techniques was investigated and will be discussed in this section of the report.

Degreasing

The nickel or monel disks as received from the manufacturer are covered with a light cutting oil used in the fabrication process. The metal disks are degreased in a modified Soxhlet extractor, Figure 1a. This apparatus consists of a nickel trough in which the disks are held vertically in a rack and spaced approximately 3/16" apart. The trough is supported on legs in a bath of carbon Tetrachloride or trichloroethylene. As the solution boils, the vapors are collected on a cold water condenser, and the condensate drips into the trough. The level of the collected condensate rises in the trough until the disks are completely covered. The solvent then is discharged back into the boiling bath by means of a syphoning tube. Rapid boiling of the solvent allows the Soxhlet to make a cycle in roughly fifteen minutes using a trough of such length that it holds about 25 disks.

This method of degreasing has proved very efficient and appears to be the only cleaning needed to obtain an excellent electrodeposit of uranium meeting the requirements as set forth in the previous

[redacted]


NICKEL TROUGH
COLD WATER CONDENSER
CCl_4 VAPOR
CONDENSATE
NICKEL DISCS
HOT LIQUID
CCl_4
VAPOR
SYPHONING TUBE
CCl_4 LIQUID

section, Determination of Quality of Electroplated Films, on page 14.

This method of degreasing the metal disks has been used in the laboratories for all routine analyses for the past year. Occasionally a series of bad electrodeposits has been made, and in most cases has been attributed to improper degreasing of the base metal. Trichloroethylene was the solvent used for a number of months, but the poor grades available tended to break down rapidly, especially when water would get into the bath from the condenser. This resulted in the bath accumulating a sticky black material, and disks cleaned under these conditions gave inferior electroplated films. Carbon tetrachloride has been substituted with better results. However, a good grade of trichloroethylene or carbon tetrachloride is satisfactory.

Since the possible breakdown of carbon tetrachloride with the formation of HCl and the resultant etching of the nickel disks had been mentioned as a means of lowering the specific activity, the following experiment was undertaken. A series of disks was degreased for different lengths of time in the carbon tetrachloride Soxhlet. This investigation also revealed the length of time necessary for sufficient degreasing. Chromic acid cleaning solution was not used in the assembled cell as stated in the standard procedure.

The results are summarized in Table 2. These data indicated that sufficient degreasing was obtained after only 15 minutes in the Soxhlet extractor. Even disks degreased by merely rubbing with Kleenex have a quantitative electrodeposit, although they turned brown after ignition. However, other work has shown the specific

[redacted]

Table 2. The Effect of Time of Degreasing upon the Specific Activity and the Quality of the Electrodeposit.

Time nickel disk in Soxhlet extractor, CCl_4 as solvent	No. of 10 mg films	Mean A-Value	± Per cent[a] std. dev. of mean	Appearance of film
2-1/2 days	4	1.0005	0.13	
8 hours	4	1.0010	0.11	
2-1/2 hours	4	1.0038	0.18	excellent
1/2 hour	4	1.0025	0.09	
1/4 hour	4	1.0023	0.20	
Dipped in hot vapors 4 times	4	1.0013	0.13	streaks of brown after ignition.
Rubbed with only Kleenex	4	1.0023	0.16	dull brown color after ignition

[a] Throughout this report, the "t"-test* has been used to determine the significance between two means. The 0.05 level of probability in Student's table of t has been used to determine if a difference is significant. The statement "no significant difference" has been used, but it should be realized that this means no significant difference was found to the precision to which the measurements were made. Obviously, more precise measurements may prove a difference to be significant.

*Freeman, H.A., Industrial Statistics, Second Edition, John Wiley and Sons, New York (1944). Chapter I

[redacted]

activity of these brown films to be as much as 2 to 3% low. The amount of etching of the nickel disks after 2 1/2 days in the extractor did not sufficiently roughen the surface to lower the specific activity significantly.

In order to determine if more elaborate cleaning methods might produce an even better electrodeposit, several other methods of cleaning the metal disks were investigated. Light films with bright interference colors show non-uniformity better than heavier films. Films plated under standard conditions at less than one mg U_3O_8 per 24 sq. cm., show localized non-uniformity, evidenced by multicolored streaks curving from the center toward the outer edge of the film, indicating different thicknesses of deposit. In this report such a deposit will be referred to as "pinwheel." Films from one to eighteen mg plated under standard conditions do not show this pinwheel effect nearly as often. For this reason, light films were plated using different cleaning techniques, with visual observation as a test of the success of the cleaning method.

Electropolishing.

The disks were electropolished by immersing the previously degreased nickel disk in a 40% phosphoric acid--60% glycerol bath at 100° C. A current from 15 to 20 amperes was allowed to flow for 2 minutes, with the disk to be cleaned as the anode. The polished disk, after removal from the bath was washed thoroughly with water and then placed in boiling isopropyl alcohol for 2 minutes

to remove comtaminants from the phosphoric acid--glycerol bath. Nickel disks cleaned by this technique have a bright mirror-like surface.

Four 4.0 and four 0.4 mg films were plated on these electropolished disks. Two of the 4.0 mg films were quite uniform, while the other two had a pinwheel appearance. Three of the 0.4 mg films were pinwheel and only one gave a uniform deposit. In other respects the films were normal, having good adherence.

Alkaline Cleaners

Two nickel disks were degreased with carbon tetrachloride and then immersed in 10% NaOH solution at 50° C. for one hour. The disks were washed with water, placed in 20% acetic acid for ten minutes and again washed thoroughly with water. The 0.4 mg films plated on these disks were adherent, but were pinwheeled.

Four disks were placed in a 10% $Na_2S_2O_3$ solution for ten minutes. Each disk was washed thoroughly with water. Following this, one disk was plated with a 0.4 mg film without further treatment, a second disk was dipped into 6 n HCl, washed with water and plated, and the remaining two were dipped into 20% acetic acid, washed with water, and plated. These films were all non-uniform with a spotty appearance instead of pinwheels. The electrodeposit was adherent.

Nickel disks were anodically and cathodically cleaned for one minute, three minutes, six minutes and twelve minutes in an alkaline bath composed of 30 g Na_2CO_3, 15 g Na_3PO_4, and 7.5 g NaOH per liter of solution. The temperature of the bath was 80 C with a current of 5 to 6 amperes and 6 volts. After the electrolysis, the

[redacted]

disks were washed with water, dipped into 20% H_2SO_4 at room temperature, and again washed thoroughly with water. The 0.4 mg films plated on the disks cleaned anodically were adherent but pinwheeled. The 0.4 mg films plated on the disks cleaned cathodically were non-adherent as well as being pinwheeled.

When alkaline cleaners were used, none of the resulting films possessed the quality obtained by merely degreasing the nickel disks.

Acid Treatment

Nickel disks were dipped from two to three seconds in an acid mixture consisting of 400 ml of concentrated sulfuric acid, 143 ml of concentrated nitric acid, 10 ml of concentrated hydrochloric acid, and 400 ml of water. The disks were thoroughly washed with water and 0.45 mg films plated on eight disks. When these films were compared visually with eight films of the same weight plated under standard conditions, no apparent difference was observed in uniformity of the electrodeposit or in the over-all quality of the film. Four 5.0 mg films, acid dipped, gave an A-value of 1.759 $\pm$ 0.08% (standard deviation of mean), and four 5.0 mg films plated under a standard conditions gave a corresponding A-value of 1.750 $\pm$ 0.12%. This short acid treatment does not roughen the nickel surface sufficiently to lower the A-value. If the acid treatment is prolonged, the specific activity will be lowered by the rough surface (c.f. page 27).

The section, Surface Roughness of Base Metal, indicates that nitric acid etching of the nickel surface does no apparent good. As

mentioned under the section on Apparatus and Procedure, the use of chromic acid cleaning solution was discontinued for the same reason. The above data indicate no apparent benefit from the acid treatment.

Use of Abrasives.

In Table 3 are summarized the results of polishing the nickel surface with various abrasive cloths. Inferior results were obtained using abrasives, with one notable exception. Hand polishing the disks with crocus cloth, using rotating motion, gave an electrodeposit which was as good or possibly superior to that obtained by merely degreasing. Referring to the section on Surface Roughness of Base Metal, page 27, it will be noted that altering the surface changes the specific activity by several percent. Thus polishing with the crocus cloth requires that the degree of roughness be the same from one nickel disk to another. It is felt that the possible slight advantage to be gained does not warrant the additional cost of this added operation.

When considering all the above methods of cleaning the base metal prior to electrolysis, only the use of crocus cloth and the acid treatment following degreasing gave results comparable to those obtained by the simple degreasing. Because of the small number of man-hours consumed by this simple technique, other methods requiring more work should show notable advantage over the degreasing before their use is adopted.

[redacted]

Table 3. The Effect of Hand Polishing the Nickel Disk upon the Uniformity of the Electrodeposit.

Treatment		Number of films	Film weight mg	Appearance of film
Crocus cloth	1500 rev.	2	4.0	very uniform, excellent adherence
	1500 rev.	3	0.4	
	300 rev.	4	0.4	
	300 straight strokes	4	0.4	slight pinwheel
Carborundum cloth (grade 120)	150 rev.	1	0.4	pinwheel, good adherence
	300 rev.	1	0.4	
	500 rev.	1	0.4	
	800 rev.	1	0.4	
Carborundum cloth (grade 362)	150 rev.	1	0.4	pinwheel, good adherence
	300 rev.	1	0.4	
	500 rev.	1	0.4	
	800 rev.	1	0.4	
Carborundum paper (grade 471)	150 rev.	1	0.4	slight pinwheel, good adherence
	200 rev.	1	0.4	
	500 rev.	1	0.4	
	800 rev.	1	0.4	

INVESTIGATION OF ELECTROLYTES

After the selection of nickel and monel as base metal substitutes for platinum, it was thought desirable to investigate other electrolytes in an effort to find one which might be superior to ammonium oxalate. During these experiments, all other variables which might affect the quality of the films were maintained as nearly as possible at the values specified by the standard plating procedure.

It will be noted in the following list that attempts to find a new electrolyte were confined to the ammonium salt of the various acids tried. This is the result of the previous demonstration by Pierle' * that metallic ions, such as sodium, co-deposit with the uranium, and since they are not removed by the ignition which follows the plating, they lower the counting rate of the films. In general, 0.4 molar solutions of the electrolytes were used. These solutions were made up either directly by weighing the required amount of the salt, or by mixing equivalent amounts of ammonia and the acid.

The results of these investigations summarized according to the electrolyte are as follows:

Single Electrolytes.

1. Ammonium acetate: No adherent films could be made in the range of electrolyte concentration from two to eight millimoles. All films were black and amorphous in appearance.

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*Pierle', J. Phys. Chem., 23: 517 (1919)

[redacted]

2. Ammonium benzoate: This electrolyte was used in an alkaline solution of pH 9. During the course of electrolyses employing ammonium benzoate, the plating solution became a deep brown, and a considerable amount of foaming was observed. The dark material was soluble in methanol and was probably impure diphenyl formed by electrolytic decomposition of the benzoate. When removed from the plating solution, the films showed brilliant colors in erratic patterns, not concentric rings, but this appearance was lost on ignition. Counts made on the same films before and after ignition to determine the effect of this volatile organic material presumably responsible for the colors showed that its presence lowered the counting rate by about 1%. Plating was not quantitative in the range where from 1.2 to 8.0 millimoles of electrolyte was used. The completeness of deposition varied from 63% to 22% respectively between these two limits, Table 4, Figure 2.

3. Ammonium borate: This solution, made by passing ammonia gas into a suspension of boric acid until it dissolved, was quite alkaline with a pH of about 10. Deposition was incomplete with large quantities of electrolyte; only about 40% of the uranium plated when 8.0 millemols were used. In quantities of 4.0 millimols and less, deposition was generally complete, but erratic low results were obtained and the electrolyte was not reliable.

[redacted]

Table 4. The Effect of Different Electrolytes on the Electrodeposit.

Single Electrolytes

Electrolyte	Millimols of Electrolyte	No. of[a] 8 mg films	Range of[b] A-value	Appearance of film
Ammonium acetate	2.0 - 8.0	8	-	black, amorphous, non-adherent
Ammonium benzoate	0.8 - 1.2	4	0.70 - 0.66	highly colored in erratic patterns, color fades on ignition; plating solution foams and turns brown.
	2.0 - 3.2	10	0.65 - 0.35	
	4.0 - 8.0	6	0.30 - 0.21	
Ammonium borate	2.0 - 4.0	8	0.98 - 0.99	normal
	6.0 - 8.0	4	0.36 - 0.42	normal, not plated
Ammonium carbonate	2.0 - 4.0	4	-	black, amorphous
	6.0 - 8.0	8	0.99 - 1.01	unevenly colored, pinwheel
Ammonium citrate	0.4 - 0.8	6	0.23 - 0.08)	normal but very light
	1.0 - 2.0	8	0.06 - 0.009)	
	4.0 - 8.0	6	0.006 - 0.005)	
Ammonium fluoride	0.0 - 2.5	14	-	black, amorphous
	2.5 - 4.0	12	0.99 - 1.00)	metallic silver color,
	6.0 - 8.0	10	0.86 - 0.48)	disappears on ignition
Ammonium formate(pH 4)	4.0 - 8.0	8	-	black, amorphous, non-adherent
Ammonium formate(pH 8)	0.0 - 4.0	10	-	black, amorphous
	4.0 - 20.0	46	0.99 - 1.01	normal as with ammonium oxalate
Ammonium tartrate	0.0 - 0.5	4	-	peeling
	0.5 - 1.5	8	0.33 - 0.17)	normal appearance for
	2.0 - 8.0	8	0.07 - 0.02)	light film

[a]The number of films indicated is for the range of electrolyte covered. For example, in the case of ammonium acetate, two films were plated at 2.0, 4.0, 6.0, and 8.0 millimols.

[b]The first A-value corresponds to the first quantity of electrolyte, the second to the second quantity of electrolyte.

Table 4. (continued) [redacted]

Mixed Electrolytes

Electrolyte	Millimols of electrolyte	No. of 8 mg. films	Range of A-value	Appearance of films
50% amm fluoride 50% amm benzoate	4.0	4	0.75 - 0.90	brightly colored before ignition
50% amm oxalate 50% amm benzoate	4.0	4	0.50 - 0.60	brightly colored before ignition
90% amm oxalate 10% amm fluoride	4.0	4	1.04 - 1.05	same as if ammonium oxalate were used alone
80% amm oxalate 20% amm fluoride	4.0	4	1.03 - 1.04	
70% amm oxalate 30% amm fluoride	4.0	4	1.03 - 1.04	
60% amm oxalate 40% amm fluoride	4.0	4	1.038 - 1.044	same as if ammonium fluoride were used alone
50% amm oxalate 50% amm fluoride	4.0	4	1.009 - 1.010	

[redacted]

Figure 2

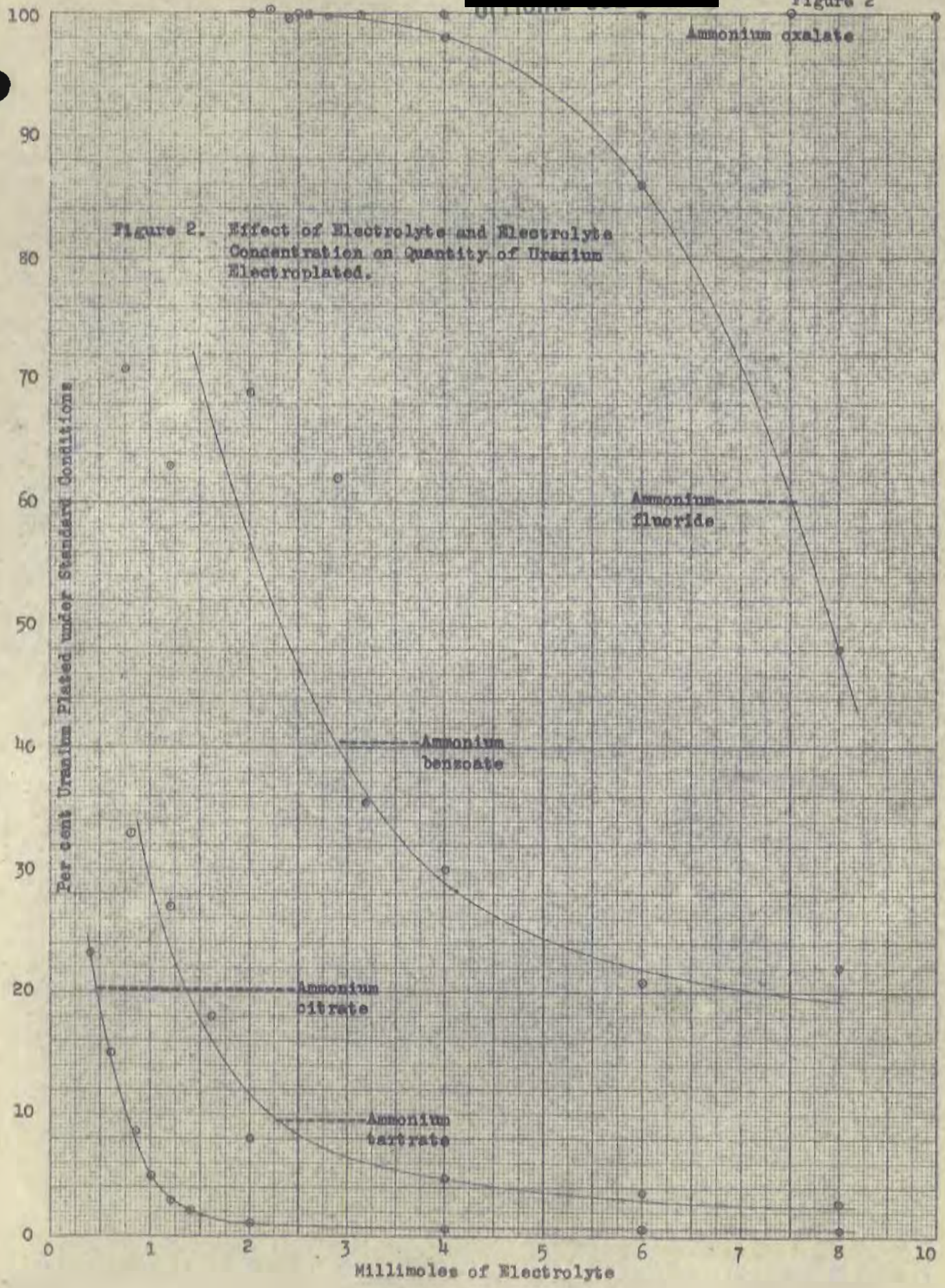

Figure 2. Effect of Electrolyte and Electrolyte Concentration on Quantity of Uranium Electroplated.

4. Ammonium carbonate: The films obtained when less than 4.0 millimoles of electrolyte was used were non-adherent, black and amorphous in appearance. When more electrolyte was used results improved and deposition could be made quantitative to 0.3%, but some films still proved non-adherent.

5. Ammonium citrate: This solution was slightly alkaline with a pH of about 8. Upon addition of the uranyl nitrate solution to this electrolyte, a deep yellow color was produced. That this color was produced by a fairly stable complex-ion was indicated by the very incomplete deposition of U_3O_8 when employing ammonium citrate as an electrolyte. With even as little as 0.4 millimoles of the electrolyte, only 23% of the uranium was plated, Figure 2. The marked difference shown in the curve between the amounts of uranium plated on either side of an electrolyte concentration of two millimoles was interesting in light of the fact that there was about one millimole of uranium present in the solution. This suggests one millimole of uranium complexing with two millimoles of electrolyte.

6. Ammonium fluoride: This solution was made slightly basic by additions of some excess ammonia to prevent attack on the glass cell. The films were silvery and metallic in appearance. Deposition was not quantitative when 4.0 or more millimoles of electrolyte were used. The completeness of deposition fell off rapidly past this point, and when 8.0 millimoles was used

only about 50% of the uranium plated, Figure 2. When 4.0 millimols was used, 98% of the uranium was deposited, and in the range from 2.0 to 4.0 millimols, plating may be considered quantitative. However, as the amount of electrolyte was diminished, the rate of deposition increased and the films became less and less adherent. With smaller quantities of electrolyte many non-adherent films were obtained.

7. Ammonium formate: When the solution of this electrolyte was made with ammonia and a slight excess of formic acid to give a pH of 4, the resulting films were amorphous and uneven. They were non-adherent and could be removed from the base metal with gentle rubbing.

   When enough excess ammonia was added to bring the pH of the solution up to 8, the results improved. Quantitative results were obtained when anywhere from 5.0 to 20.0 millimols of electrolyte were used. However, even these films had areas of varying surface textures so that parts of the films looked dull when compared with the rest. The use of less than 5.0 millimols of electrolyte gave films of amorphous appearance which, when counted, were not quantitative.

8. Ammonium tartrate: The solution was slightly alkaline, with a pH of 8. As with ammonium citrate (c.f. page 41), a fairly stable complex with uranium appeared to be formed in the plating solution. Here it appeared to be somewhat less resistant to electrolytic decomposition since the amount of

U_3O_8 deposited varied from 33% when 0.8 millimols of electrolyte was used to 0.3% when 8.0 millimols was used. Here again the amount deposited began to increase sharply only when less than two millimols of electrolyte was used for a one millimol sample.

Mixed Electrolytes

1. Ammonium fluoride - ammonium benzoate: The bright colors associated with ammonium benzoate as an electrolyte were apparent on the films which were plated using an equimolar mixture of these two electrolytes totaling four millimols. However, on ignition the color was lost, and the films acquired an uneven appearance showing dull amorphous areas.
2. Ammonium oxalate - ammonium benzoate: When an equimolar mixture totaling four millimols was employed, the films had the bright colors associated with ammonium benzoate as an electrolyte, but none of the color was retained on ignition. However, deposition was only 50 - 55% complete.
3. Ammonium oxalate - ammonium fluoride: Using a mixture of the two electrolytes totaling four millimols, the films looked like those using only fluoride whenever 35% or more was fluoride. However, while the films were adherent, the deposition became less quantitative as more fluoride was used, and was already 3% below theoretical when the mixture was composed of equal quantities of each electrolyte.

None of these salts has given any indication of being superior to ammonium oxalate for use as the electrolyte in the plating procedure.

It must be kept in mind that they were tried using optimum conditions for ammonium oxalate, and it may be possible that some of these electrolytes would prove very valuable if other conditions of the plating procedure were altered at the same time.

ELECTROLYSIS VARIABLES

As the different electroplating variables are considered, the data at times will be somewhat sketchy, for it is difficult to investigate a variable and then definitely state that a certain value is the best one. This value would be true only under the conditions used for the particular investigation, for the reason that a change in other variables may appreciably change the one under investigation, and thereby alter the conclusions drawn. Since the number of plating variables is quite large, it can be seen that a complete study of the effect of one on another would be almost an endless task and not justifiable considering the results obtained by present techniques.

In certain instances, films were not actually alpha counted for the reason that counter time was not available under the urgency of sample analyses. Determination of the quantity of uranium remaining in the plating solution after electrolysis, the residue, was not always made. In some instances the residue was determined when it was not possible to count the film. When the film was counted the residue was often neglected with only an occasional check made. When noting the residues in the accompanying tables it should be realized that the method used of evaporating the solution on a thin foil for counting may be low by 2 or 3 fold. The uneven deposition may reduce the count considerably by absorption of the alpha particles in the solids. Only when the residue is small, of the order of 0.2 per cent of the count of the film or less, should any great faith be placed in that count. All residues should be considered as a minimum value.

This section of the report will discuss the effects of temperature, current density, speed of stirring and time of plating.

Temperature.

As would be expected, the temperature of the plating bath has a marked effect on the rate of plating, Tables 5 and 6. The temperature in all cases is the temperature of the water bath surrounding the electroplating cell. The temperature of the plating solution is practically the same at the start of the electrolysis, but the resistance of the cell to the passage of current rapidly raises the plating solution to a temperature 5 to 10 degrees higher than the water bath.

The results obtained using monel indicate that the temperature of the water bath must be at least 70° C in order to obtain quantitative deposition of the uranium in 50 minutes. The films plated at the lower temperatures have good adherence and look normal in every way except that the uranium is just not plated quantitatively. Films made at the boiling point of the plating solution appear slightly dull and less uniform than those made at 75° to 85° C. Increasing the quantity of electrolyte and volume of the plating solution slows somewhat the rate of plating.

Nickel behaves as does monel with the notable exception that films plated at boiling temperature are radically changed in appearance. Instead of having characteristic shiny-black color of films greater than 12 mgs and the bright interference colors of lighter films, the deposit looks silvery-white and metallic. After ignition, the deposit assumes normal appearance. However the count is not as reproducible. This is based on the comparison of 28 films plated at 80° and 28 plated at 100° C.

Table 5. The Effect of Temperature of Plating Bath on the Quality of the Electrodeposit using 2.0 millimoles Ammonium Oxalate, 30 ml Plating Solution, with Monel as Base Metal.

Temp. of water bath °C	No. of 9 mg films	Residue %	Mean A-value	± Per cent std. dev. of mean	Appearance of film
30	1	18.0	------	----	
40	1	20.0	------	----	good--not counted
50	1	8.3	------	----	
60	2	0.6	0.9975	0.08	
70	2	0.9	0.9985	0.27	
80	2	0.04	1.0008	0.14	excellent
90	2	0.04	0.9990	0.09	

Table 6. The Effect of Temperature of Plating Bath on the Quality of the Electrodeposit using 4.0 millimoles Ammonium Oxalate, 40 ml Plating Solution, with Monel as Base Metal.

Temp. of water bath °C	No. of 10 mg films	Residue %	Mean A-value	± Per Cent std. dev. of mean	Appearance of film
40	1	----	------	----	excellent, just not
50	1	----	------	----	plated in 50 min.
60	2	4.8	------	----	
70	2	0.08	1.0018	0.10	
80	2	0.07	1.0024	0.08	excellent, slight
90	2	0.03	1.0009	0.16	quantity removed when rubbed hard with Kleenex.

on nickel.

	Mean A-value of 28 films	± Per cent std. dev. of mean
80° C	1.001	0.12
100° C	1.000	0.35

Application of the F-test* gives a ratio of 8.2. If the precisions were the same at the 1 per cent level of probability, this ratio should be no greater than 2.88. This indicates that the precisions obtained under these two conditions are significantly different.

Since films are not quantitative if the bath temperature is less than 70°, and at 100° the specific activity is not reproducible, a temperature of 80° ± 5° C is recommended for the electroplating of uranium on either nickel or monel as the base metal.

Current Density.

The effect of current density is shown in Tables 7 and 8, where two concentrations of electrolyte were used, monel being the base metal. It is apparent that a current density from 2 to 5 amperes during a 50 minute plating period is satisfactory to obtain quantitative, adherent films. When only 2.0 millimoles of ammonium oxalate is used, the deposit is not adherent if the current density is less than 2.0 amperes. At 4.5 amperes, the film using 2.0 millimoles of ammonium oxalate was streaked with black, but this was probably due to the fact that the quantity of electrolyte being used was near the minimum required for satisfactory plating.

When nickel was used as the base metal and the electrolysis was carried out for 50 minutes, there was no noticeable difference in either

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* Freeman, H. A., Industrial Statistics, Second Edition, John Wiley and Sons, New York (1944). Chapter II.

Table 7. The Effect of Current Density on the Quality of the Electrodeposit using 2.0 millimoles Ammonium Oxalate, 30 ml Plating Solution, with Monel as Base Metal.

Current density amperes/24 cm.^{2}	No. of 10 mg films	Residue %	Mean A-value	± Per cent std. dev. of mean	Appearance of film
0.6	1	0.23	------	----	)black and amorphous,
1.0	1	0.06	------	----	)not counted.
1.5	1	0.03	0.9956	----	non-adherent.
2.0	2	0.02	1.0025	0.03	)
2.5	2	0.03	0.9998	0.22	)good, slightly non-
3.0	4	0.03	1.0010	0.07	)adherent at edge.
3.5	2	0.10	0.9989	0.02	good
4.0	2	0.05	1.0000	0.09	good
4.5	1	0.05	1.0027	----	streaked with black, cell boiled vigorously.

Table 8. The Effect of Current Density on the Quality of the Electrodeposit using 4.0 millimoles Ammonium Oxalate, 40 ml Plating Solution, with Monel as Base Metal.

Current density amperes/24 cm^2	No. of 10 mg films	Residue %	Mean A-value	± Per cent std. dev. of mean	Appearance of film
2.0	2	0.03	1.0004	0.09	)
2.5	2	0.08	1.0020	0.07	)
3.0	2	0.05	1.0015	0.10	)
3.5	2	0.11	1.0012	0.17	)excellent
4.0	2	0.07	1.0019	0.30	)
4.5	2	0.04	1.0025	0.08	)
5.0	2	0.07	1.0021	0.11	)

the appearance of the films or in the completeness of plating for current densities of 2, 3, 4 and 5 amperes, Table 9. With a current density of 4.5 to 5.0 amperes, the plating solution boiled vigorously. This limits the practical current density to a maximum of 4.0 amperes unless a cooling bath is used.

Figure 3 shows the amount of uranium plated at various time intervals using 3.0 amperes at 80° C. Figure 4 shows the logarithm of the percentage uranium left in solution vs. the time of plating for a current density of 2.0 and 3.0 amperes at 100° C., as well as 3.0 amperes at 80°. Since a straight line is produced a first-order reaction rate is clearly indicated. An initial divergence is due to a slower rate of plating caused by the lower temperature and/or a lower pH. As the electrolysis progresses, the passage of current heats the plating solution above the bath temperature, and a rise in pH accompanies the decomposition of electrolyte (c.f. page 70, <u>pH of Plating Solution</u>). After the first 2 to 4 minutes, the reaction becomes first-order with the rate constants indicated in Figure 4. The constant for 2.0 amperes, 0.22 min^{-1}, is two-thirds the constant for 3.0 amperes, 0.34 min^{-1}, showing that the efficiency of plating is about the same under these two conditions. Table 10 lists the data that were plotted in Figures 3, 4, and 5.

Because of the limitations imposed below 2.0 amperes and above 4.0 amperes/24 cm^2, the midpoint, 3.0 amperes, is recommended as the current density at which to electroplate uranium on nickel or monel as the base metal.

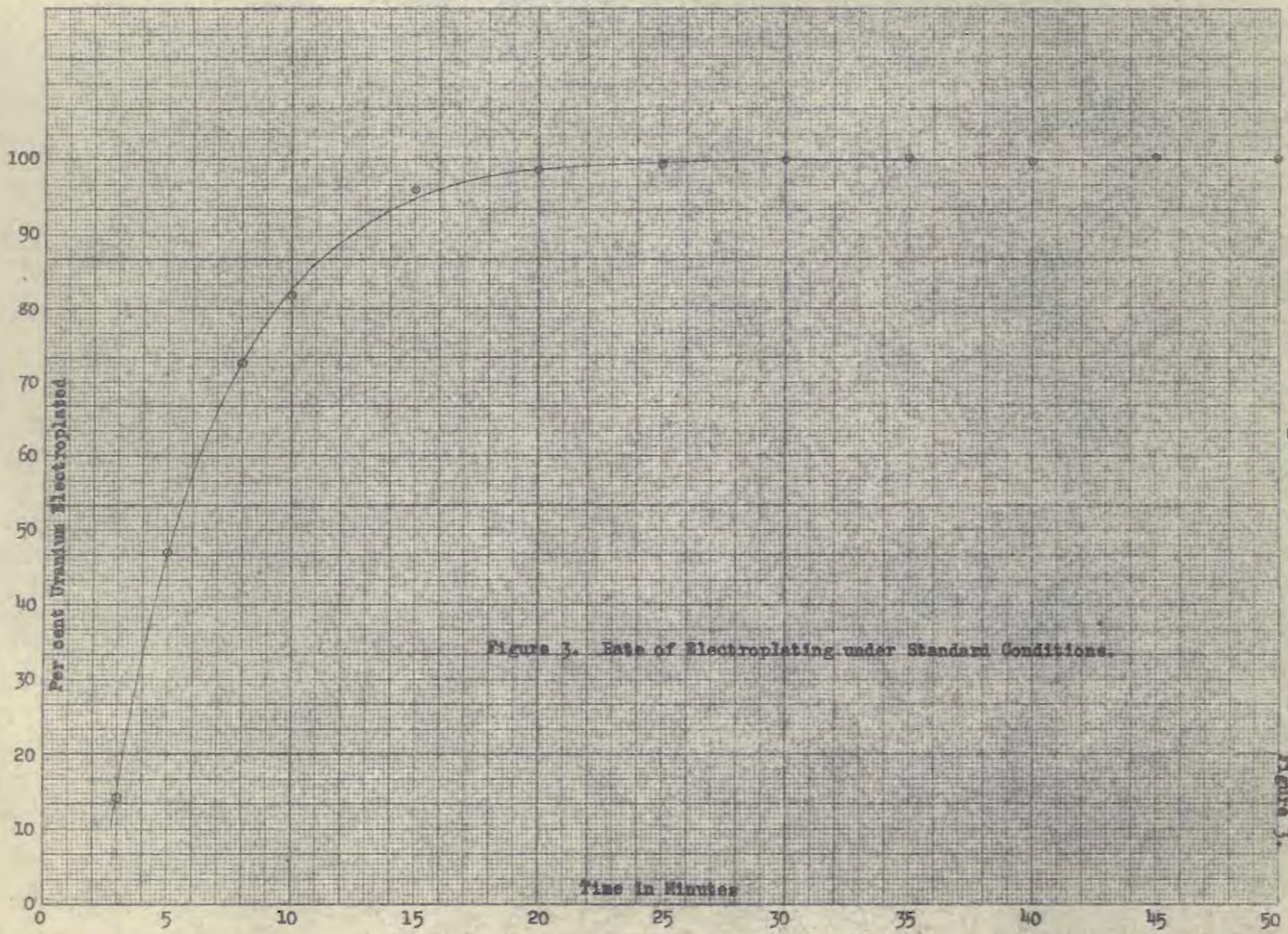

Figure 3. Rate of Electroplating under Standard Conditions.

Figure 3.

[redacted]

[redacted]

Figure 4

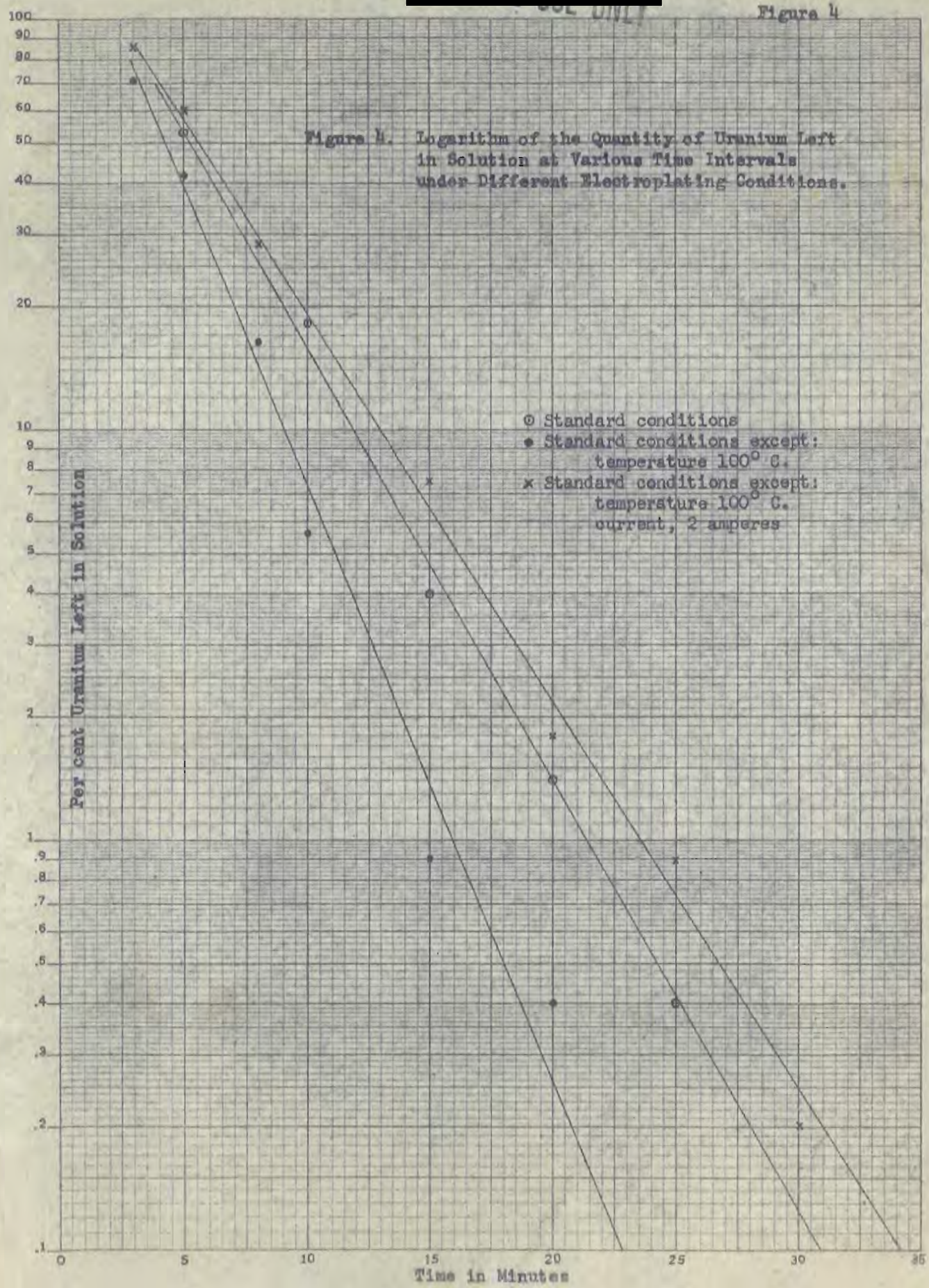

Figure 4. Logarithm of the Quantity of Uranium Left in Solution at Various Time Intervals under Different Electroplating Conditions.

Figure 5

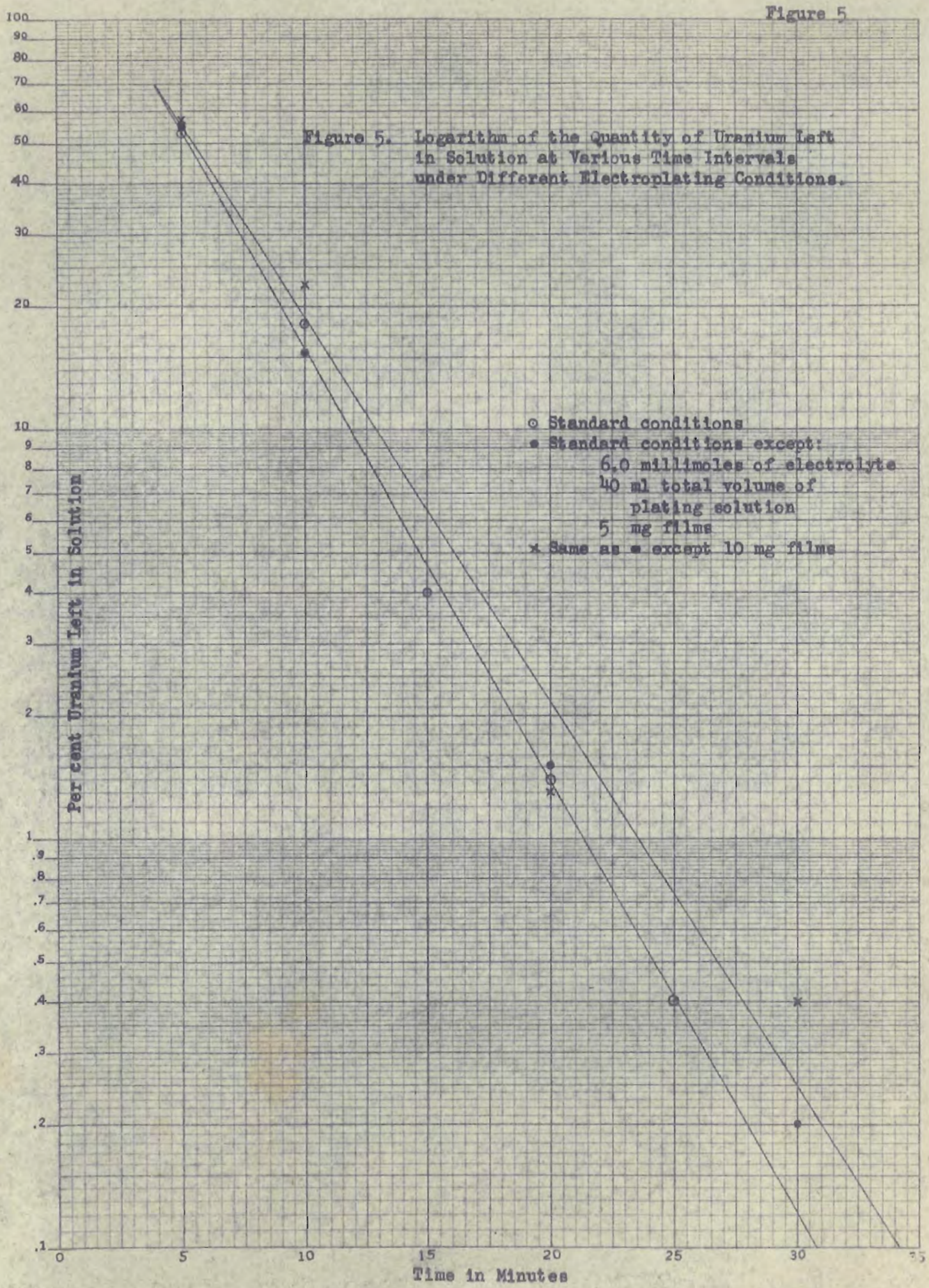

Figure 5. Logarithm of the Quantity of Uranium Left in Solution at Various Time Intervals under Different Electroplating Conditions.

KEUFFEL & ESSER CO., N.Y. NO. 359-11G
Semi-Logarithmic, 3 Cycles X 10 to the inch, 5th line accented
MADE IN U.S.A.

[redacted]

Table 9. The Effect of Current Density on the Quality of the Electrodeposit using Standard Conditions with Nickel as Base Metal.

Current density amperes/ 24 cm^2	No. of 8 mg films	Mean A-value	± Per cent[a] std. dev. of mean	Appearance of film
2.0	2	1.000	0.18	excellent
3.0	4	0.998	0.14	
4.0	1	0.995	----	
5.0	1	1.002	----	

[a] Theoretical std. dev. of count for single film was 0.22%.

Table 10. Quantity of Uranium Plated at the End of Various Time Intervals under Various Plating Conditions.

Time of Plating	Mean per cent[a] uranium plated ± std. dev. of mean.									
	Standard conditions 10 mg films		100° C. 10 mg films		100° C. 2 amperes 10 mg films		40 ml total volume, 6.0 millimoles of Ammonium oxalate. 4 mg films		10 mg films	
minutes										
3	14.2	± 7.8	28.7	± 9.7	14.1	± 7.8				
5	46.8	3.2	58.5	3.3	40.1	3.7	45.3	± 5.7	43.4	± 4.0
8	72.3	2.4	83.6	3.6	71.6	2.6				
10	81.7	1.3	96.4	0.52	82.5	2.3	84.7	1.6	77.3	4.7
15	95.8	0.73	99.0	0.20	95.9	0.63				
20	98.6	0.10	99.6	0.25	99.0	0.02	98.5	0.12	98.7	0.16
25	99.6	0.16	99.9	0.30	99.1	0.18				
30	99.9	0.10	100.0	0.37	99.8	0.23	99.8	0.02	99.6	0.12
35	100.1	0.12	100.1	0.32	100.0	0.16				
40	99.8	0.10	100.2	0.48	99.9	0.10			100.0	0.10
45	100.2	0.16	100.0	0.29	100.0	0.12				
50	99.9	0.09	99.9	0.35	100.0	0.14	100.0	0.10	100.0	0.09

[a] Each value in table represents the mean of 4 electroplated films

Speed of Stirring.

The rate of stirring affects the rate of plating as shown in Tables 11 and 12 where two different concentrations of ammonium oxalate were used employing monel as the base metal. The electroplating apparently was less quantitative below 400 r.p.m. with 2.0 millimoles of electrolyte than it was with 4.0 millimoles. The electrodeposit was not quantitative at speeds of less than 400 r.p.m., and from 100 to 200, the entire deposit became black and amorphous.

Nickel, as the base metal, gave similar results, Table 13, although the plating appeared to be quantitative from 300 r.p.m. to 700 plus. The upper limit is set by the centrifugal effect on the solution. If the rotation is too rapid, the solution is apt to be thrown from the cell. In addition, increased speeds result in increased radial non-uniformity of the deposition of the uranium. The method of stirring leaves an area in the center of the film which has less uranium deposited than the remainder of the disk. This light center becomes large at speeds of stirring of 800 r.p.m. and is practically non-existent at speeds of 200 r.p.m. and less.

In order to determine the effect of the speed of stirring on the specific alpha- and fission-activity, a series of films was plated at 300 and 800 r.p.m. The data are summarized in the table below:

	No. of 5 mg films	Mean alpha counts	± Per cent std. dev. of mean	No. of 5 mg films	Mean fission counts	± Per cent std. dev. of mean
300 r.p.m.	7	11527	0.11 (0.06)[a]	10	7361	0.11 (0.08)
800 r.p.m.	9	11549	0.10 (0.05)	12	7357	0.11 (0.07)

[a] The value in parenthesis was the theoretical std. dev. of the count.

Table 11. The Effect of Speed of Stirring on the Quality of the Electrodeposit using 2.0 millimoles of Ammonium Oxalate, 30 ml Plating Solution, with Monel as Base Metal.

Speed of anode rotation r.p.m.	No. of 10 mg films	Residue %	Mean A-value	± Per cent std. dev. of mean	Appearance of film
100	1	3.8	------	----	black, amorphous, non-adherent
200	1	4.7	------	----	
300	1	2.4	------	----	streaked with black
400	2	0.5	------	----	streaked with black
500	2	00.03	1.0017	0.10	good
600	2	0.01	1.0002	0.00	
700	2	0.03	1.0000	0.13	

Table 12. The Effect of Speed of Stirring on the Quality of the Electrodeposit using 4.0 millimoles of Ammonium Oxalate, 40 ml Plating Solution, with Monel as Base Metal.

Speed of anode rotation r.p.m.	No. of 10 mg films	Residue %	Mean A-value	± Per cent std. dev. of mean	Appearance of film
200	1	1.4	------	----	black, amorphous non-adherent
300	1	0.4	------	----	
400	2	0.2	------	----	
500	2	0.05	1.0015	0.14	excellent
600	2	0.04	1.0024	0.18	
700	2	0.03	1.0022	0.16	

Table 13. The Effect of Speed of Stirring on the Quality of the Electrodeposit using Standard Conditions with Nickel as Base Metal.

Speed of anode rotation r. p. m.	No. of 8 mg films	Mean A-value	± Per cent[a] std. dev. of mean	Appearance of film
100	2	0.986	2.30	black amorphous areas
200	2	0.987	1.00	black amorphous areas
300	2	1.002	0.30	brown spots
400	2	1.000	0.20	excellent
500	2	0.999	0.17	excellent
600	2	1.000	0.09	excellent
700	2	0.999	0.23	excellent

[a] Theoretical standard deviation of count for single film was 0.22%.

No significant difference was observed between the means of the films plated at 300 and at 800 r.p.m. It should be realized, however, that the radial non-uniformity produced by higher speeds of stirring does have an effect on the specific activity, but it is so small that it was not shown by the precision of these measurements. Because of the limitations below 300 r.p.m. and above 800 r.p.m., an anode rotation of 500 r.p.m. is considered satisfactory.

An exploring disk (c.f. page 15) was placed over 4 of the films made at 300 and 800 r.p.m. These data show, in Table 14, that the light center spot does have considerably less uranium deposited than the remainder of the film. This confirms the estimates of the thickness of the center spot made by observation of the interference colors.

A recent preliminary investigation has shown that excellent films can be made by stirring the plating solution with an up and down movement of the present platinum anode. Films weighing 1, 3, 10 and 18 mg were plated using standard conditions with the exception that the solution was stirred by moving the anode up and down a short distance by hand. The rate was roughly 1 cycle per second, care being taken not to lift the anode from the plating solution or allow the anode to come in contact with the cathode.

The film thickness was uniform over the entire area of the electrodeposit as evidenced by the interference colors. This uniformity was confirmed by use of the exploring disk and the data is shown in the last two lines of Table 14. Since the number of counts obtained from these films of normal uranium was small, the differences between the center and edge of the deposit should not be considered significant. The vertical

Table 14. Radial Distribution of Uranium at Two Stirring Speeds as Determined by Exploring Disks.

Film number	Size of hole in exploring disk (inches)	Speed of anode rotation (r. p. m.)	Film weight (mg)	Number of alpha counts per minute[a] from uncovered hole — Position[b] 1	2	3	4	Ratio of position 1 / position 3
69	3/8	300	4.0	1290 ± 6	1552 ± 1	1596 ± 6	1593 ± 0	0.81
80	3/8	800	4.0	596 3	1633 3	1635 5	1598 0	0.36
68	1/2	300	4.0	2252 16	2658 11	2918 24	2736 4	0.77
81	1/2	800	4.0	1168 9	2637 20	3015 20	2875 11	0.39
	3/8	1 cycle/sec.[c]	10.0	106		100		1.06
	1/2	1 cycle/sec.	18.0	326		320		1.02

[a] Each count is the mean of two 30 minute counts.
[b] Position 1--center of electrodeposit.
2--nearly tangent to center hole (position 1).
3--between position 2 and 4.
4--nearly tangent to the edge of the electrodeposit.
[c] Vertical movement of anode.

stirring shows promise for making uniform films, but does not warrant changing present apparatus.

Time of Plating.

The percentage uranium deposited as a function of time is shown in Table 10 and Figure 3. From these data it is apparent that essentially all of the uranium has been deposited well before the end of the 50 minute plating period. Even when the total volume of the plating solution was increased to 40 ml and 6.0 millimoles of Ammonium oxalate was used, 99.9% of the uranyl nitrate was plated in roughly 35 minutes as shown in Figure 5. This gave the slowest rate of plating of the conditions investigated and plotted in Figures 4 and 5. The additional plating time is used to insure the removal of the last traces of uranium from solution, and as a safety factor in case the temperature should be low or for some other reason the rate of plating should be slowed.

In order to obtain a quantitative deposit at the end of say 20 min., it is necessary to alter the plating variables in the direction of increasing the rate of plating. This results in less precision and decreased quality of the electroplated film. However rapid analysis with less precision can be made. While a short plating period would speed the analysis, precision must be sacrificed in an electrolysis of much less than 50 minutes.

ELECTROPLATING SOLUTION VARIABLES

Quantity of Electrolyte.

Table 15 shows the effect of varying the quantity of electrolyte on the quality of the electrodeposit using monel as the base metal. From these data it is apparent that the quantity of electrolyte from 2.0 to 6.0 millimoles has little effect on the specific activity when the plating is carried out for 50 minutes. The quantity of electrolyte does not seem to appreciably reduce the rate of deposition of uranium, for the films are quantitative with as much as 6.0 millimoles. The next section on Volume of Plating Solution will give additional data. If slightly less than 2.0 millimoles is used, the quantity of electrolyte is insufficient to obtain an adherent deposit. These data definitely indicate that the quantity of 2.0 millimoles which was recommended for electroplating on platinum is on the extreme lower limit when monel is used.

The effect of varying the quantity of oxalate when nickel is used as the base metal is indicated in Table 16. In this case 2.8 millimoles of ammonium oxalate must be used before a satisfactory film is produced. Six millimoles gives excellent results. From these data, it would appear that from 3 to 6 millimoles gives good electroplated films and 4 to 5 millimoles is recommended. As more electrolyte is used, it should be realized that the rate of plating is decreased slightly, and the other conditions such as current density and particularly temperature must be maintained to insure quantitative plating.

Table 15. The Effect of the Quantity of Electrolyte on the Quality of the Electrodeposit using Monel as Base Metal.

Quantity of ammonium oxalate millimoles	No. of 9 mg films	Residue %	Mean[a] A-value	±Per cent std. dev. of mean	Appearance of film
0.4	1	----	------	----	black, amorphous non-adherent.
0.8	1	----	------	----	
1.2	1	----	------	----	
1.6	2	0.31	0.9950	0.16	poor adherence, black steaks.
2.0	2	0.02	1.0006	0.18	
2.4	2	0.07	0.9996	0.01	
2.8	2	0.01	0.9978	0.15	
3.2	2	0.05	0.9993	0.06	
3.6	2	0.02	0.9991	0.20	
4.0	2	0.04	1.0008	0.06	good
4.4	2	0.08	0.9996	0.06	
4.8	2	0.01	0.9996	0.03	
5.2	2	0.01	0.9998	0.02	
5.6	2	0.03	0.9998	0.16	
6.0	2	0.05	0.9990	0.05	

[a] The t-test indicated no significant difference between any two A-values obtained from 2.0 to 6.0 millimoles of ammonium oxalate.

Table 16. The Effect of the Quantity of Electrolyte on the Quality of the Electrodeposit using Nickel as Base Metal.

Millimoles ammonium oxalate	No. of 10 mg films	Mean[a] A-value	±Per cent[b] std. dev. of mean	Appearance of film
2.0	4	0.990	0.25	black, amorphous, residues high.
2.4	4	1.000	0.05	black, amorphous.
2.8	4	1.001	0.05	excellent, uniform, very adherent.
3.2	16	1.000	0.08	
4.0	4	0.998	0.05	
6.0	8	0.998	0.13	

[a] The t-test shows no significant difference between any of the values from 2.4 to 6.0 millimoles.

[b] Theoretical standard deviation of count for a single film was 0.18%.

Volume of Plating Solution.

The effect of varying the volume of plating solution as well as the quantity of ammonium oxalate appears in Table 17 where monel was the base metal. Increasing the total volume of the plating solution to 40 ml gave excellent, smooth, adherent films with quantities of 4.0 to 10.0 millimoles of ammonium oxalate. When the total solution volume was increased to 50 ml using from 4.0 to 10.0 millimoles of electrolyte, the resulting films for the most part were not quantitative This was particularly true with the larger oxalate concentrations.

Effects with nickel very similar to those with monel were obtained by varying the total volume of the solution and the quantity of ammonium oxalate. Films made with a 50 ml plating solution were of better quality than those on monel. These data are summarized in Table 18. In order to determine if any significant difference existed in the specific activity of films plated with 30 ml total solution and 2.0 millimoles of oxalate compared with 40 ml total volume and 4.0 millimoles of ammonium oxalate, two series of films were plated. Eight films under the first conditions gave a mean A-value of 0.9996 $\pm$ 0.0026, while the second conditions gave a mean A-value of 0.9993 $\pm$ 0.0028. Obviously, no significant difference can be shown between these means.

In Figure 5 is plotted the logarithm of the quantity of uranium in solution vs. time of plating for a total cell volume of 40 ml and 6.0 millimoles of ammonium oxalate compared with 30 ml total volume and 4.0 millimoles of electrolyte using nickel as the base metal. This graph indicates that the rate of plating is not appreciably reduced by the larger volume and increased electrolyte concentration.

Table 17. The Effect of Volume of Plating Solution and Quantity of Electrolyte on the Quality of the Electrodeposit using Monel as Base Metal.

Total volume of plating solution	Film weight	Millimoles ammonium oxalate	Residue	Mean A-value	Appearance of film
ml	mg		%		
40	9	4.0	----	0.9981)	good
40	9	4.0	----	0.9988)	
40	9	6.0	----	0.9952)	
40	9	6.0	0.10	0.9989)	
40	9	8.0	0.10	0.9998)	
40	9	8.0	0.20	0.9994)	excellent[a]
40	9	10.0	0.09	0.9979)	
40	16	8.0	0.04	1.0006)	
40	11	10.0	0.05	0.9957)	
50	9	4.0	0.01	0.9982)	
50	9	4.0	0.01	0.9982)	fair adherence
50	9	6.0	0.7	0.9961)	
50	9	6.0	1.6	------)	non-adherence
50	9	8.0	1.6	0.9789)	
50	9	10.0	3.5	0.9460)	
50	16	8.0	3.5	0.9760)	
50	16	10.0	8.5	0.9135)	fair adherence
50	13	8.0	3.2	0.9683)	
50	13	10.0	10.3	0.8736)	

[a]All of these films were of the highest quality. The adherence was so good that the deposit could not be scratched with the thumb-nail. Several films counted after this treatment indicated that none of the deposit had been removed. The light center spot was smaller and the overall uniformity of the film better than when 30 ml plating volume was used.

Table 18. The Effect of Volume of Plating Solution and Quantity of Electrolyte on the Quality of the Electrodeposit using Nickel as Base Metal.

Total volume of plating solution	Film weight	Millimoles ammonium oxalate	Mean[a] A-value	±Per cent std. dev. of mean	Appearance of film
40	7.8	4.0	1.000	0.16	
40	7.8	6.0	1.002	0.14	excellent
40	7.8	8.0	0.999	0.17	
40	19.8	6.0	1.002	0.10	
50	7.8	4.0	-----	----	non-adherent
50	7.8	6.0	1.000	0.13	
50	7.8	8.0	1.000	0.15	fair adherent
50	7.8	10.0	0.997	0.25	
30	3.9	4.0	1.001	0.16	
35	3.9	6.0	0.998	0.21	excellent
40	3.9	6.0	0.999	0.19	
45	3.9	8.0	1.000	0.05	
50	3.9	8.0	0.999	0.12	

[a]Each value represents the mean of four films.

With the more uniform and more adherent nature of the electrodeposit obtained when using a total cell volume of 40 ml. and 6.0 millimols of ammonium oxalate, it seems advisable to recommend these conditions.

pH of Plating Solution

To determine if the pH of the plating solution had an effect on the quality of the films, solutions were adjusted to different pH values. Sufficient nitric acid or ammonium hydroxide was added to give the plating solutions initial pH values of 1.0, 2.0, 3.6, 5.0, 6.3, 7.0, and 9.0. The uranyl nitrate solution alone had a pH of 3.6, and after addition of the electrolyte it was 6.3. Four films from each of these solutions of different pH values were plated. After the electrolysis, the pH of one plating cell was determined from each set of four.

From the data in Table 19, it is apparent that the pH of the plating bath before electrolysis can be varied widely without affecting the specific activity. No significant difference can be determined between any two pH values from 2.0 to 9.0. Only when the initial pH was 1.0 did the count change appreciably. In this case, it should be noted that the pH of the plating bath after the 50-minute electrolysis was only 1.2. In all other cases, regardless of the initial pH, the final values were in the range 8.5 to 8.9 with no apparent correlation between initial and final pH values. The physical appearance of the plated films was essentially the same although there was a tendency for films plated at a low pH to have a darker color than those plated at a high pH.

From the above data, it would appear that the rate of plating in an acid solution is slow. This was substantiated by determining the quantity

Table 19. The Effect of the Initial pH of Plating Solution on the Quality of the Electrodeposit.[a]

Initial pH[b] of plating solution	pH solution at end of electrolysis	pH of nitrate[c] solution before addition of ammonium oxalate	No. of 10 mg. films	Mean No. alpha counts/ minute	±Percent std. dev. of mean
1.0	1.2	-	4	1076	15.4
2.0	8.9	-	4	6444	0.17
3.6	8.6	1.0	4	6456	0.12
5.0	8.5	2.0	4	6474	0.08
6.3	8.7	3.6	4	6459	0.18
7.0	8.7	-	4	6472	0.09
9.0	8.7	-	4	6462	0.05

[a] The films plated at pH of 1.0 had a tendency to be non-adherent. The remainder of the films were all of good quality, although there was a tendency for films plated at the lower pH values to be somewhat darker in color.

[b] pH values 5.0 to 6.3 represents the initial pH of plating solutions using standard procedure.

[c] The nitric acid or ammonium hydroxide was added to the uranyl nitrate solution before the ammonium oxalate.

of uranium plated at the end of different intervals of time employing plating solutions having different initial pH values. The data is shown in Table 20 and Figure 6. The slow rate of plating in acid solution is probably caused by the high mobility of the hydrogen ion or re-solution of the deposit. This results in a smaller fraction of the current being carried by the uranyl ion present. The gradual transformation of the electrolyte from ammonium oxalate to ammonium carbonate, and the subsequent loss of carbon dioxide during electrolysis results in the neutralization of the nitric acid present and an increase in the pH value.

The curves in Figure 6 clearly show that the rate of plating is slowed considerably at an initial pH of 2.0 or less. At a pH of 1.0, the rate of plating is extremely slow. It is realized that the curves drawn representing pH values of 1.0, 1.5, and 2.0 are not precisely fixed by sufficient points or by the accuracy of each point. However, the object of this experiment was to show the delay in plating caused by a low initial pH, and that point is clearly demonstrated. In the case of an initial pH of 1.0, the results were very erratic. Apparently this is a critical range, and small changes in temperature and other plating variables caused the pH to change at different rates and produced large effects on the rate of plating. In order to obtain precise curves of low initial pH vs. time of plating, the variables must be closely controlled, and that is not possible with the present apparatus. The four values obtained at the end of 50 minutes (dotted line, Figure 6) were plated on a separate day from the other solutions of pH 1.0.

This investigation has shown that an initial pH of the plating solution from 2.0 to 9.0 gives satisfactory electrodeposits. The present

Table 20. The Effect of the Initial pH of Plating Solution on the Rate of Plating.

Initial pH of plating solution	pH of solution at end of electrolysis	Time of electrolysis minutes	No. of 10 mg films	Percent plated
1.0[a]	-	10	1	0.15
1.0	-	20	1	0.15
1.0	-	30	1	7.5
1.0	-	32	1	31.8
1.0	-	40	1	97.3
1.0	-	40	1	48.0
1.0	8.5	50	1	96.9
1.0	1.2	50	1	16.6
1.0	1.3	50	1	19.6
1.0	1.2	50	1	9.5
1.0	1.3	50	1	21.3
1.5	-	5	1	1.57
1.5	-	10	1	17.0
1.5	-	20	1	98.3
1.5	-	30	1	100.0
1.5	-	50	1	100.0
2.0	3.4	6	1	5.9
2.0	4.9	10	1	21.0
2.0	3.6	11	1	26.4
2.0	7.1	13	1	42.8
2.0	8.6	20	1	98.8
2.0	8.9	50	4	100.0
6.3	-	3	4	14.1
6.3	-	5	4	46.8
6.3	-	8	4	71.6
6.3	-	10	4	81.7
6.3	-	15	4	95.8
6.3	-	20	4	98.6
6.3	-	25	4	99.6
6.3	-	30	4	99.9
6.3	-	35	4	100.1
6.3	-	40	4	99.8
6.3	-	45	4	100.2
6.3	8.7	50	4	99.9

[a] Since the films plated from a solution with an initial pH of 1.0 were so erratic, the individual values have been given for each film instead of a mean.

Figure 6. Effect of Initial pH of Electroplating Solution on Rate of Plating.

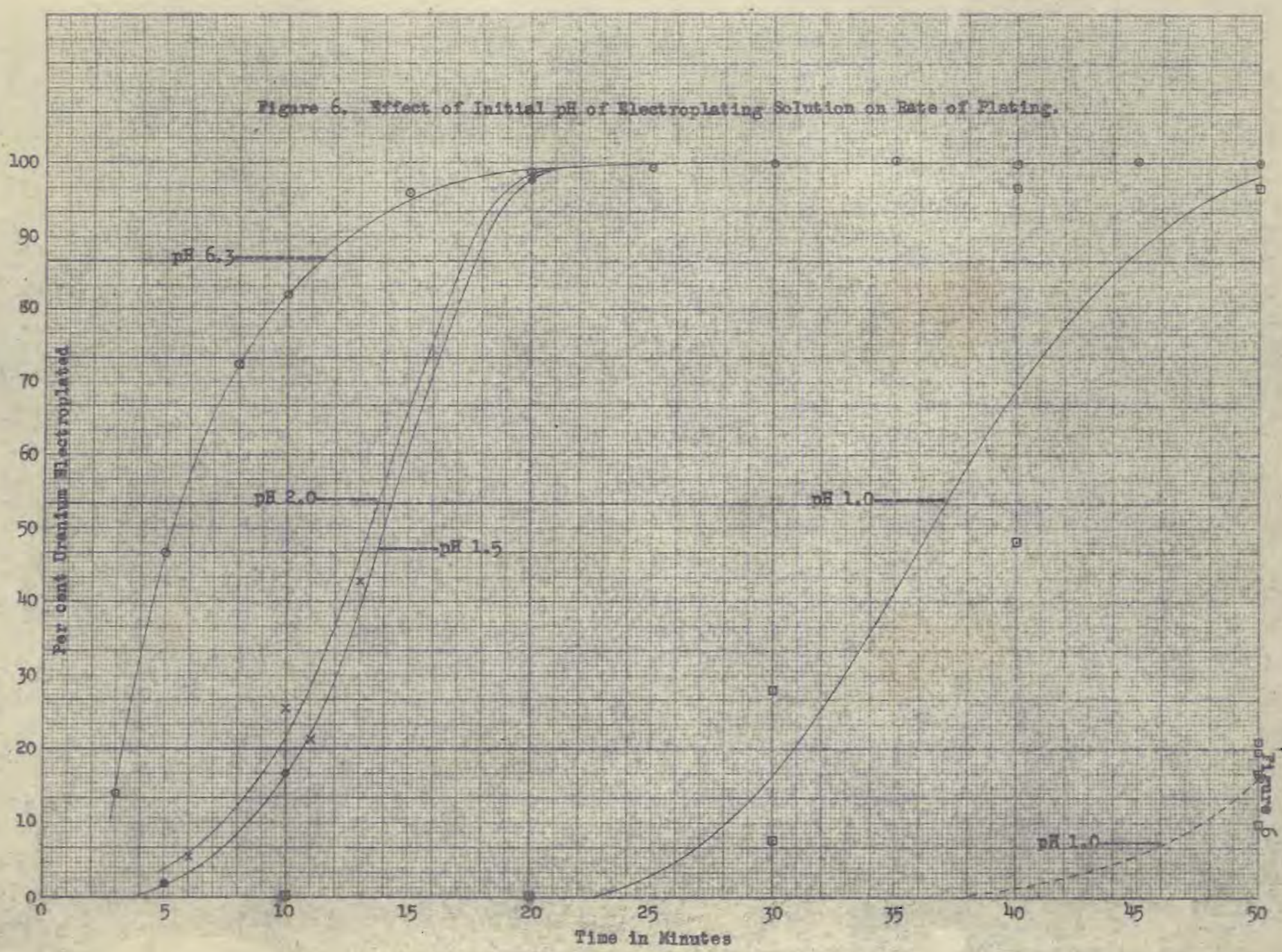

Figure 6

nitrate solutions when prepared for electroplating have a pH of 5.0 to 6.6, well within the limits as stated above.

Rate of Re-solution of Electrodeposit

It was desirable to determine the rate of re-solution of the electrodeposit in order to know how rapidly the plating solution must be removed and the film dried after interruption of the current at the end of the electrolysis. It would also indicate the need of adding an inert liquid such as methanol.

A series of 5 mg. films were plated under standard conditions with the exception that methanol was not added to the cell at the end of the electrolysis. The hot residual plating solution was allowed to stand in contact with the film for various lengths of time, Table 21. These data indicate that there was no significant re-solution of the electrodeposit even at the end of one hour. A second series of 5 mg. films plated under standard conditions including the addition of methanol gave similar results after standing in contact with the film, Table 21. These results were unexpected and in marked contrast to the results obtained on platinum reported by Cohen and Hull*, where at the end of one hour 383 micrograms of U_3O_8 had dissolved from a film plated for 50 minutes.

Because of this apparent difference, additional work was undertaken using various conditions and the results are summarized in Table 22. It is seen that when the hot plating solution is allowed to remain in contact with the completed film, there is no noticeable re-solution of the electrodeposit, condition 1.

*See footnote page 4

Table 21. Rate of Re-solution of Electrodeposit.

Time in contact with hot plating solution, 80°C.	A-value[a]	U_3O_8 dissolved	Time in contact with plating solution plus methanol	A-Value[a]	U_3O_8 dissolved
minutes		micrograms	minutes		micrograms
0	1.759[b]	1.0	0	1.877[c]	-
1/2	1.765	1.0	2	1.881	0.0
1	1.759	2.5	2	1.880	0.5
1	1.756	2.0	2	1.870	1.3
2	1.756	2.2	2	1.877	0.0
5	1.756	1.8	5	1.872	0.0
60	1.763	1.8	5	1.883	0.7
60	1.767	8.7[d]	15	1.880	1.5
60	1.763	0.0[d]	15	1.881	1.5
60	1.768	1.8[d]	15	1.875	4.5
60	1.762	1.5[d]			

[a] Each value represents one 5 mg. film.

[b] Mean of 8 films using standard conditions.

[c] Mean of 20 films using standard conditions.

[d] The residual uranium was determined by plating the solution for 50 minutes using 4.0 millimols additional ammonium oxalate.

Table 22. Re-Solution of Electrodeposit in Residual Plating Solution and in Distilled Water.

	Condition[a] 1		2		3		4		5	
	Film weight mg.	U_3O_8 dissolved micrograms	Film weight mg.	U_3O_8 dissolved micrograms	Film weight mg.	U_3O_8 dissolved micrograms	Film weight mg.	U_3O_8 dissolved micrograms	Film weight mg.	U_3O_8 dissolved micrograms
	9.7	5.5	9.7	59	7.4	1.9	7.3	175	9.7	6.5
	9.7	6.5	9.7	27	7.4	1.6	7.3	74	9.7	7.8
	9.7	7.3	9.7	35	7.4	3.7	7.3	51	9.7	6.4
	9.7	5.3	9.7	49	7.4	1.6	7.3	91	9.7	5.0
	7.3	3.6	9.7	129	7.4	7.3				
	7.3	0.0	9.7	77	7.4	7.9				
	7.3	2.2	9.7	38	7.4	4.8				
	7.3	1.0	9.7	62	7.4	5.7				
	9.7	7.1[b]	7.3	82						
	9.7	8.1[b]	7.3	60						
	9.7	3.2[b]	7.3	77						
			7.3	44						
Mean		4.5		62		4.3		98		6.4

[a] Condition 1 - Standard procedure, methanol not added, hot residual plating solution allowed to stand in contact with film for one hour. Solution replated using 4.0 millimols additional ammonium oxalate.

Condition 2 - Standard procedure, hot residual plating solution discarded, cell washed thoroughly with distilled water, 30 ml. distilled water allowed to stand in contact with film for one hour. 30 ml. water plated using standard procedure.

Condition 3 - Standard procedure except plated for only seven minutes, 75% of uranium plated giving 7.4 mg. films, hot residual plating solution discarded, cell washed thoroughly with distilled water, 30 ml. distilled water allowed to stand in contact with film for one hour. Water replated.

Condition 4 - Standard procedure, methanol not added, hot plating solution discarded, cell rinsed with 80°C. distilled water. 30 ml. distilled water, 80°, allowed to remain in contact with film for one hour. The 30 ml. of water was plated.

Condition 5 - Standard procedure, methanol not added, hot plating solution discarded, cell rinsed with distilled water (pH 8-9), 25°. This water allowed to remain in contact with film for one hour.

However, if the residual plating solution is replaced with hot or cold distilled water a significant quantity of the electrodeposit is dissolved, conditions 2 and 4. This amount is only about one-fifth that reported by Cohen and Hull on platinum. There apparently is no difference in the rate of re-solution using cold, 25°, or hot, 80°, distilled water.

The pH of the distilled water used was roughly 6.3, while the residual plating solution had a pH value of approximately 8.5. To determine if pH was the reason for the observed difference between the distilled water and the plating solution, 10 mg films were plated using standard conditions, and then allowed to remain in contact with cold distilled water, pH 8 to 9, condition 5. The quantity of U_3O_8 dissolved from these four films was small and not significantly different from the amount dissolved by the residual plating solution. This clearly indicates that it is the slightly acidic nature of the distilled water that causes the resolution of the film.

Noting condition 3, Table 22, it will be seen that there was no re-solution of the electrodeposit when cold water was allowed to stand in contact with the film for 1 hour, the films having been plated only 7 minutes. These data should be compared with conditions 2 and 4 where cold and hot water both dissolved significant quantities of the electrodeposit of films plated for 50 minutes. This means that the electrodeposit obtained after only 7 minutes is more resistant to re-solution than films of comparable weight after 50 minute electrolysis. This is exactly opposite to results reported by Cohen and Hull where platinum was used as the base metal. At the moment no explanation is available other than that the electrodeposit undergoes some change in hydration or crystalline structure with prolonged heating and electrolysis.

Considering the extremely slow rate of re-solution of the electrodeposit in the hot residual plating solution, the addition of the 60 ml of methanol to the plating cell at the end of the electrolysis seems of no value. It is proposed that the hot plating solution be poured out, and the cell rinsed with a spray of methanol from a wash bottle to remove the liquid from the film prior to ignition.

MISCELLANEOUS VARIABLES

Ignition of Film.

Ignition of the electroplated film with the subsequent increase in specific activity indicates that during the electrolysis varied amounts of impurities are deposited in addition to the uranium. These impurities probably are oxygen and carbon. The loss or partial loss of these impurities by ignition decreases the amount of alpha or fission particle absorption.

With platinum as base metal, the films were ignited at a temperature of 700° C. However, the oxidation of monel and nickel prohibited this high ignition temperature. In order to obtain a reproducible specific activity from electroplated films, a series was plated and then ignited at various temperatures and for different lengths of time. Monel, since it was used as a base metal before nickel was investigated first. The data are summarized in Tables 23 and 24. Igniting films for 10 minutes at different temperatures showed roughly a 0.7% increase in A-value from no ignition to 350° C. From 350° to 500°, a plateau region was found where no significant difference in the A-value was observed.

Table 23. The Effect of Ignition Temperature on the A-value using Monel as Base Metal.

Ignition temperature (10 minutes) °C	Number of 8 mg films	Mean[a] A-value	±Per cent std. dev. of mean
no ignition	2	1.0000	0.15
250	2	1.0035	0.13
300	2	1.0040	0.10
350	2	1.0071	0.01
400	2	1.0066	0.05
450	2	1.0075	0.10
500	2	1.0076	0.04

[a]A-value of unignited film arbitrarily adjusted to 1.0000

Table 24. The Effect of Time of Ignition on the A-value of 8 mg Films Heated at 425° C.

Time of Ignition minutes	Mean A-value of 5 films	±Per cent std. dev. of mean
0	1.0000	0.15
1	1.0035	0.05
5	1.0068	0.07
10	1.0074	0.11
30	1.0074	0.07
60	1.0070	0.05

[a]A-value of unignited film arbitrarily adjusted to 1.0000

Selecting the midpoint of this plateau region, 425°, a series of films was ignited for different periods of time. The A-value showed a 0.7% increase up to 10 minutes ignition, but from 10 to 60 minutes it was essentially constant.

Investigation of the effect of the temperature and time of ignition on the A-value of films plated on nickel is summarized in Table 25 and graphed in Figure 7. The results are very similar to those obtained using monel. As was expected, a rapid initial increase in A-value accompanies the increase in temperature. In the case of the 538° C ignition, a decrease in A-value was observed after 10 to 15 minutes, due to the oxidation of the nickel. This effect would probably be observed at 316° and 427° ignitions with prolonged heating. It is desirable to have the ignition time as short as possible, and the temperature in a region where variations in the electric furnace will not affect the specific activity. Considering the data on both nickel and monel, an ignition temperature from 425° to 525° C from 10 to 15 minutes showed no significant change in A-value. A time and temperature within these ranges are recommended.

Addition of Metallic Impurities.

As mentioned in a previous section, the films of inferior quality plated occasionally by routine production has been attributed to incomplete degreasing of the base metal. Before this fact was established, it was decided to investigate the effect of possible metallic impurities on the quality of the electrodeposit. While all such impurities which come in contact with the uranium hexafluoride are theoretically removed, some in small quantities may be

Table 25 The Effect of Temperature and Time of Ignition of the Electrodeposit on the A-value using Nickel as Base Metal.

Time of ignition minutes	Mean A-value ± per cent std. dev. of mean[a]				
	Temperature				
	93° C	204° C	316° C	427° C	538° C
0[b]	1.0000 ±0.12	1.0000 ±0.14	1.0000 ±0.19	1.0000 ±0.10	1.0000 ±0.16
1	0.9998 0.08	1.0010 0.03	1.0018 0.10	1.0046 0.02	1.0070 0.08
5	1.0008 0.08	1.0058 0.03	1.0045 0.13	1.0055 0.14	1.0078 0.12
10	1.0016 0.11	1.0033 0.12	1.0056 0.15	1.0077 0.18	1.0075 0.09
30	1.0040 0.04	1.0044 0.10	1.0085 0.09	1.0078 0.17	1.0075 0.18
60	1.0043 0.04	1.0058 0.15	1.0080 0.15	1.0071 0.18	1.0044 0.14

[a] At 93° and 204°, each mean represents 4 films. At the remaining temperatures, each mean represents 8 films. The theoretical standard deviation of the count was 0.22%.

[b] A-value of unignited films arbitrarily adjusted to 1.0000.

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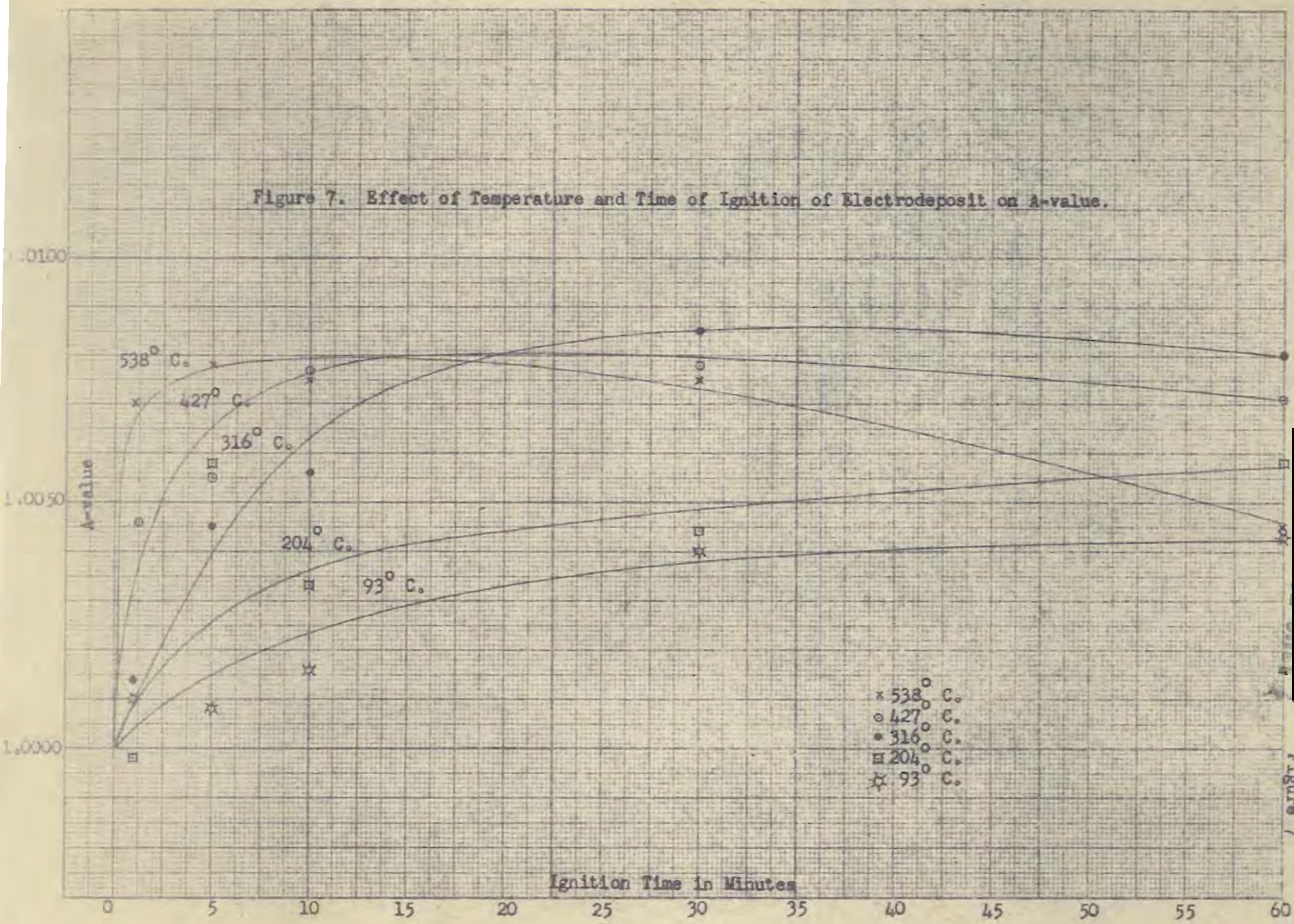

Figure 7. Effect of Temperature and Time of Ignition of Electrodeposit on A-value.

Figure 7

carried over in the distillation step by purely mechanical means. Hence a series of heavy metals were added to the plating solution. Much larger quantities were added than could possibly be present in order to magnify the results. The data are shown in Table 26, and summarized below:

1. Aluminum: The addition of 1.0 mg of aluminum as the nitrate does not lower the counting rate. The films are of good quality and appear normal in all respects.
2. Cadmium: This metal added as the nitrate caused the films to be dull in color and when 5.0 mgs of cadmium was added the films began to appear amorphous and non-adherent. The addition of cadmium did not lower the alpha activity. Strangely enough, considering the large cross-section of cadmium for slow neutrons, the addition of 5.0 mg of cadmium had no noticeable effect on the specific fission activity. It is entirely possible, however, that the cadmium was not plated with the uranium but remained in the plating solution. In any event, its presence in the plating solution has no apparent effect on the electrodeposit except to make the film less adherent to the base metal.
3. Chromium: This is the most probable of all contaminants since it could get into the solution after the purification steps. If any of the chromic acid used in cleaning the plating cell were not removed by the successive water rinses, chromium would remain and be introduced into the plating solution. When as little as four to five drops of this cleaning solution are added, the resulting film counts roughly 3% low. This addition does not cause the film to peel, but the interference colors are somewhat darker.

Table 26. The Effect of the Addition of Metallic Impurities to the Plating Solution on the Quality of the Electrodeposit.

Metal added	Quantity[a] added	Form	No. of 8 mg films	Mean A-value	± Per cent std. dev. of mean	Appearance of films
	mg					
Aluminum	1.0	Aluminum nitrate	4	0.999	0.23	good
Cadmium	2.5	Cadmium	4	0.998	0.18	dull color
	5.0	nitrate	4	0.996	0.10	dull color, slightly non-adherent.
Chromium	2 drops	Chromic acid	3	1.004	0.27	)
	4 drops	cleaning	3	0.977	1.05	) good
	5 drops	solution	3	0.968	1.03	)
Copper	2.5	Cupric nitrate	4	1.001	0.12	dull color
	20.0		4	0.850	2.15	black, amorphous, non-adherent.
Iron	2.5	Ferric	4	0.999	0.20	good
	5.0	sulfate	8	0.999	0.18	good
	20.0		4	0.935	1.31	dull, uneven
Manganese	1.0	Manganous sulfate	4	1.000	0.15	good
Nickel	2.5	Nickel	4	0.999	0.60	good
	5.0	chloride	8	0.996	0.32	slight brown streaks
	7.5		4	0.995	0.25	brown,
	20.0		4	0.954	2.83	black, amorphous, non-adherent
Tin	1.0	Stannous chloride	4	0.999	0.09	good

[a]Quantity calculated as the metal

[b]These films were also fission counted: 2.5 mg Cd--F-value of 0.997 ± 0.7
5.0 mg Cd--F-value of 1.004 ± 0.8

Chromic acid can cause the films to peel however. When the assembled cell is cleaned with chromic acid just prior to adding the various components of the plating solution, the nickel has a tendency to acquire dark brown-grey stains on its surface. When such a disk is used the resulting film very frequently peels over these stained areas. By omitting the cleaning solution and stains it puts on the disks, the plating procedure is improved and this added operation eliminated.

4. Copper: The addition of 2.5 mgs of copper as cupric nitrate caused the films to look dull, but had no apparent effect on the specific activity. With a large addition, 20 mgs, the films were black, amorphous and non-adherent.

5. Iron: This metal added in the amounts of 2.5 and 5.0 mgs had no noticeable effect on either the appearance of the film or the specific alpha activity. When 20 mgs was added, the films were uneven and dull in color. The A-value was lowered about 6.5%. It was interesting to note that after seven minutes electrolysis the plating solution became basic enough to precipitate the remainder of the 20 mgs of iron as ferric hydroxide.

6. Manganese: The presence of this metal had no apparent effect.

7. Nickel: The addition of nickel as the chloride in quantities comparable to the weight of U_3O_8 caused the films to be dull in appearance. The films plated with 20 mgs had black streaks and appeared partially amorphous and non-adherent. The specific alpha activity was lowered by 4.5%

8. Tin: Added as stannous chloride, tin had no apparent detrimental effects on the electrodeposit.

It can be seen from the amounts of heavy metal impurities which had to be added to obtain these effects that this source represents little or no danger to precise electroplating. When 20 mgs of metallic ion was added, the lowered A-value was due more to failure to plate properly than to absorption of alpha particles by the impurity. It is practically inconceivable that any metal, other than chromium, should pass the various purification steps in amounts comparable to the quantity of uranium in the sample, and it required such amounts to produce even these small effects.

The author desires to express his sincere appreciation to Dr. D. E. Hull and Dr. F. W. Hurd for their most able assistance and liberal direction of the work. Special acknowledgment is made to Mr. Warren Brehm, Mr. Joseph Fox and Mrs. Irene McAuliffe for their skillful performance of much of the experimental work. Without the above assistance, this investigation would not have been possible.

SUMMARY

A description of an efficient multiple plating unit is described including photographs and wiring diagram. A good electroplated film is described and methods of determining the quality is discussed.

In the counting methods of isotopic analysis, it is desirable to obtain with low concentrations of the 234 and 235 isotopes a smooth, adherent film as heavy as 16 mg per 24 cm^2. With platinum as the base metal, 4 mg appeared to be the upper limit plated consistently. Investigation of different metals, gold, silver, copper, aluminum, monel and nickel as possible substitutes for platinum, revealed that monel and nickel were superior, nickel being the better of the two. With the use of nickel, it is possible to plate 24 mg per 24 cm^2, although 16 to 18 mg is the upper limit for an excellent electrodeposit. Nickel or monel are used once and discarded, eliminating the counting of the disc for presence of residual uranium.

The surface roughness of the base metal has an effect on the specific activity of the plated uranium, but a cold rolled nickel or monel surface is reproducible and satisfactory. Investigation of methods of cleaning the nickel surface prior to electrolysis indicated a simple degreasing to be the best.

A comprehensive study of the quantitative electroplating method using nickel and monel as the base metal indicated the following conditions would give an excellent electrodeposit:

1. Ammonium oxalate selected from a series of ammonium salts.
2. Temperature of plating bath--$80^{\circ} \pm 5^{\circ}$ C.
3. Current density per 24 cm^2--3.0 amperes.
4. Speed of anode rotation--500 r.p.m.
5. Time of electrolysis--50 minutes.
6. Quantity of ammonium oxalate--6.0 millimoles.
7. Total volume of plating solution--40 ml.
8. Initial pH of plating solution--2.0 to 9.0
9. Temperature and time of ignition of electrodeposit--425° to 525° C for 10 to 15 minutes.

The rate of re-solution of the electrodeposit in the residual plating solution was negligible and the addition of small quantities of a number of metallic impurities to the plating solution has no significant effect on the quality of the electrodeposit with the exception of chromium and nickel. With careful technique, a standard deviation of 0.15% or less is the error of this electroplating method.

Using nickel or monel as a base metal, the quantitative electroplating method using the above mentioned conditions is capable of producing excellent electrodeposits of uranium for the alpha and fission counting methods of isotopic analysis.

[redacted]

A-3626 Supp. #1

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CLINTON ENGINEERING WORKS

CARBIDE AND CARBON CHEMICALS CORPORATION

Laboratory Division

Works Laboratory Department

QUANTITATIVE ELECTROPLATING OF URANIUM FOR ISOTOPIC ANALYSIS

Using

NICKEL AND MONEL AS BASE METALS

Supplement #1

J. A. Klacsmann

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[redacted]

Summary:

The following work supplements the report* by C. McAuliffe. The methods and apparatus used were identical. It was noted that difficulty existed in obtaining precise results when counting U_3O_8 films weighing less than 0.5 milligrams. To study this effect the experiments described in this paper were performed. These experiments indicate that for films weighing less than 0.6 mg. the precision of a given result is a function of the film weight.

Experimental:

Films weighing from 0.02 mg to 0.634 mg. were made using identical plating procedures. For each film weight investigated, 12 films were made from solutions obtained from the Counting Section. The following table correlates the film number, film weight, approx. F value of the uranyl nitrate solutions, and the amplifier on which each film was counted:

Film #	Film Wt.	Amplifier Used	Approx. F Val. of Sol.	Counting Sect. Sol. Number
RP 74 (1-12)	0.020	A	26	2365 A
RP 73 (25-36)	0.050	A	26	2365 A
RP 75 (1-12)	0.075	C	30	2364 B
RP 73 (13-24)	0.100	A	26	2365 A
RP 73 (37-48)	0.150	A	26	2365 A
RP 73 (1-12)	0.200	A	26	2365 A
RP 76 (1-12)	0.250	D	26	2365 A
RP 72 (25-36)	0.317	A	30	2364 B
RP 72 (13-24)	0.476	A	30	2364 B
RP 72 (1-12)	0.634	A	30	2364 B

The films in each series of films were plated in the conventional manner for 50 minutes and then heated for 10 minutes in the furnace at 800°F. After cooling, each of these films was counted for a total of

* Quantitative Electroplating of Uranium for Isotopic Analysis using Nickel and Monel as Base Metals. File # A3626.

Cont'd on Page 2

110,000 counts in order to attain a counting precision of 0.3% standard deviation for a single film.

Observations:

All films were firmly adherent to the nickel base plates. In general, those films, having a film weight of 0.200 milligrams, seemed to have more "pin wheeling" than films made of the other film weights. There seemed to be no evident relationship between the amount of "pin wheeling" on the films and the calculated standard deviation of a single determination.

Discussion of Results:

The results are tabulated in the following table 1 and are shown on a graph. A film thickness was calculated for each set of film weights using a density of 7.3 for U_3O_8 as a basis for the calculations.

A standard deviation of 0.33% for a single determination was obtained when a film weight of 0.634 mg. was used. No precision approaching this value (0.33% Std.Dev.) was obtained with films lighter than 0.634 mg. The best value, otherwise, obtained was a standard deviation of single determination of 1% for a film containing 0.476 mg. U_3O_8.

[redacted]

TABLE 1

Sample #	No.of Films	Film Wt.in Mg.	Number Counts (Mean)	Standard Deviation Single Det. Counts	%	Mean Counts	%	Limit of Error of Mean %
RP 72 (1-12)	12	0.634	12,426	41.5	0.33	12.0	0.10	0.22
RP 72 (13-24)	12	0.476	9,581	98.2	1.03	28.4	0.30	0.66
RP 72 (25-36)*	11	0.317	6,335	320	5.1	96.4	1.52	3.4
RP 76 (1-12)	12	0.250	4,111	589	14.3	170.2	4.1	9.0
RP 73 (1-12)	12	0.200	3,020	507	16.8	146.5	4.9	10.8
RP 73 (37-48)	12	0.150	2,440	250	10.3	72.3	3.0	6.6
RP 73 (13-24)*	11	0.100	1,540	180	11.7	54.2	3.5	7.8
RP 75 (1-12)	12	0.075	1,592	86.4	5.4	25.0	1.6	3.5
RP 73 (25-36)	12	0.050	844.6	49.3	5.8	14.2	1.7	3.7
RP 74 (1-12)	12	0.020	339.1	19.5	5.8	5.6	1.7	3.7

*RP 72-35
*RP 73-15 } films discarded due to operational errors.

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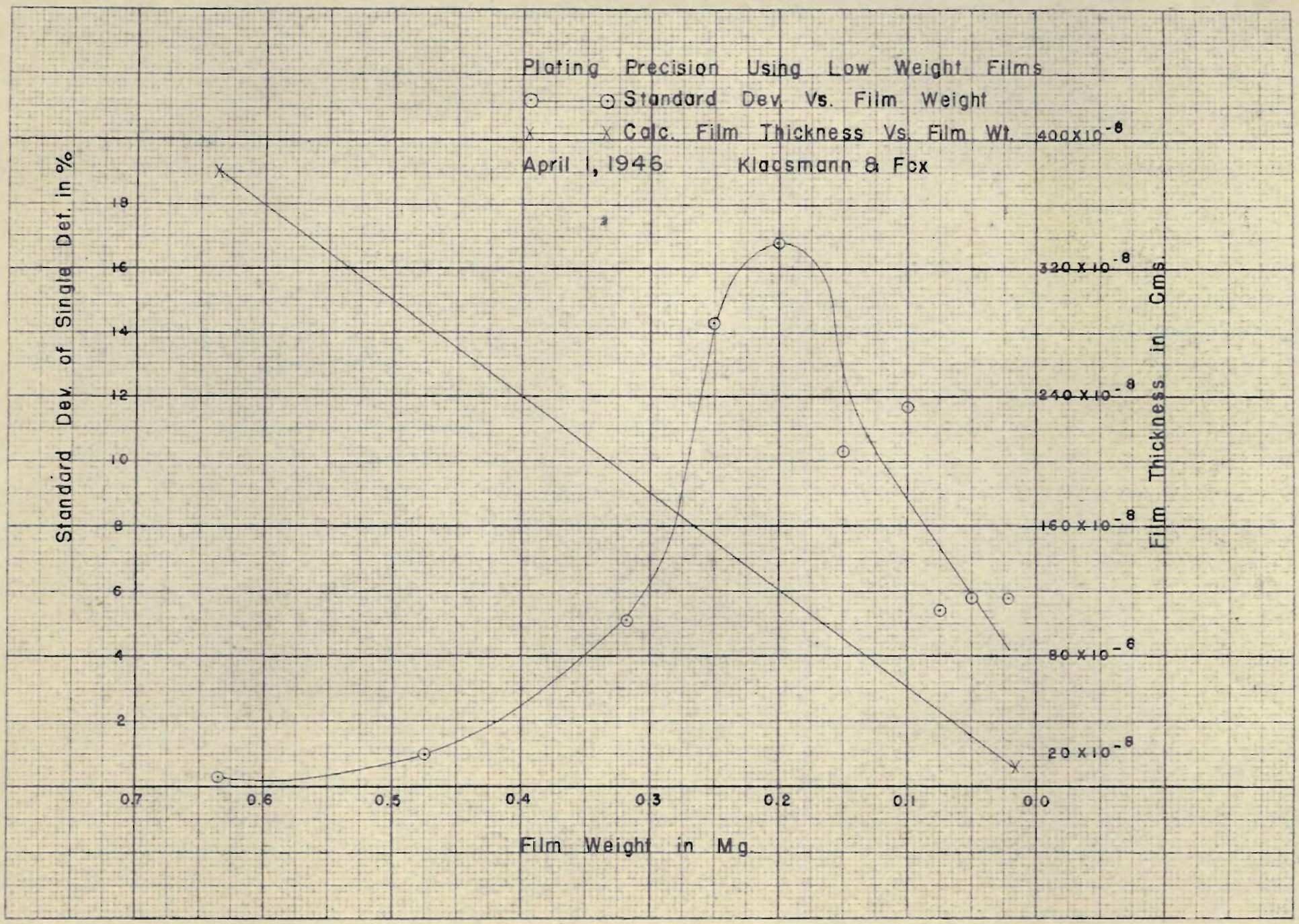

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