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A STUDY OF THE SEPARATION OF A TRACE
OF SILVER FROM A MACRO AMOUNT
OF PALLADIUM BY ELECTROLYSIS.

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Chemistry Division

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A Study of the Separation of a Trace of Silver from a Macro Amount
of Palladium by Electrolysis.

J. C. Griess, Jr. and L. B. Rogers

* * * * *

June 21, 1948

Date Received: 7/20/48

AUG 10 1948
Date Issued: ~~AUG 01 1948~~



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Abstract

A study was made of the electroseparation of silver and palladium using several complexing agents. Cyanide was found to produce the most favorable separation while, at the same time, allowing a nearly complete recovery of silver. It has been shown that repeated electrolyses are feasible, and that one can thereby separate silver, produced by neutron bombardment of palladium, which has a high specific activity and which is chemically and radiochemically free from palladium.

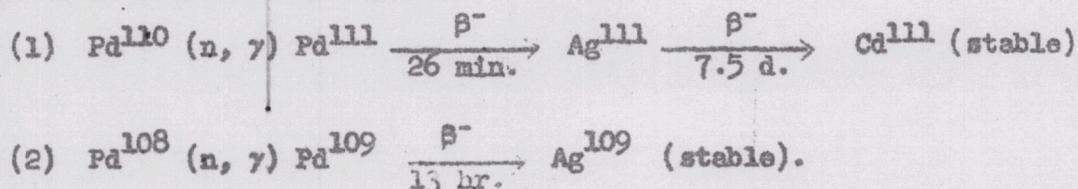
Introduction

When two or more elements can be electrodeposited from a given solution, it is sometimes possible to separate one element from the others by electrolysis with a carefully selected and well regulated potential. The selection of a suitable potential can be made on the basis of electrolytic information obtained polarographically (12). Regulation of the potential has been carried out manually and, in a technique popularized by Sand (18) and called "internal electrolysis" by chemical dissolution of the anode. In recent years, instruments have been designed for regulating electrode potentials automatically (3, 4, 6, 7, 11, 13, 16).

Studies involving the electroseparation of a trace usually require special consideration in order to minimize losses from adsorption and co-precipitation during a separation and from dissolution of the deposit during the washing process. The separation discussed below was favorable in that a trace element, silver was deposited and a macro constituent, palladium, left behind in solution. Furthermore, the separation concerned the deposition of silver, a process about which much information was available.

Suitable silver and palladium traces were prepared simultaneously by bombarding a sample of natural palladium with neutrons. By exercising care in the selection of the age of the bombarded sample, it was possible to work with

a mixture of a pure silver activity and a pure palladium activity. The chains of primary interest were:



The first chain was important because it was the source of the silver tracer; the second, because it was the source of the useful palladium tracer and, at the same time, more than 95% of the silver produced in the sample. The production of such a large amount of stable silver compared to radioactive silver was unimportant only because the total amount of silver produced was apparently negligible (less than 1%) compared to the amount of silver introduced as an impurity in the various reagents.

The fact that both Ag^{111} and Pd^{109} emit only β particles of nearly the same energy was a serious disadvantage. In order to analyze a mixture of these activities, it was necessary to prepare a decay curve or to make a radiochemical separation. The former was used in the present study.

Experimental Details

Apparatus

Polarograms of reactions at a stationary platinum electrode were recorded automatically by a modified (20) Sargent Model XX Polarograph. The modifications were similar to those later incorporated in the Model XXI. A potentiometer was used to check the initial and final voltages of each polarogram. The solutions were maintained at $25.0 \pm 0.1^\circ \text{C}$. by means of a thermostated bath.

All pH measurements were made with a Beckman Model G Meter equipped with a glass electrode having a small correction for sodium ion. The electrode was calibrated before each use with a standard buffer solution.

The electrolytic cells were of the type shown in Figure 1. The design was essentially that used by other workers (1, 2, 14) with the following

modifications introduced by Ehrlinger (5): (1) A "scotch tape" gasket between the glass cylinder and the platinum electrode, (2) Agar salt bridges to allow the anode and the reference electrode to be placed outside the solution. The use of a fresh set of salt bridges for each determination was facilitated by making each bridge in two sections which were connected by ball and socket joints (not shown in Figure 1).

The potential on the cathode was controlled within ± 3 mv. (often within less than ± 1 mv. during a fifteen hour period) by using a regulator designed at our laboratory (11, 16). The current that passed through the reference electrode, a saturated calomel electrode of about 50 cm² area, was 2×10^{-8} amp. per mv. unbalance. The capacity of the anode-cathode circuit was 1.0 amp.

All radioactive samples were counted by means of a thin mica end-window Geiger-Mueller counter tube contained in a standard aluminum-lined lead housing. The samples were maintained at a predetermined distance from the window by an aluminum support.

Preparation of Solutions

All chemicals used in this study were reagent grade, and all solutions were prepared with distilled water.

The radiation characteristics of Pd¹⁰⁹ and Ag¹¹¹ tracers checked those reported in the literature (15). The yield of Pd¹⁰⁹ was checked by adding a small amount of natural silver (as nitrate) to an aliquot of a solution of bombarded palladium, precipitating silver chloride, and counting the palladium remaining in solution. The yield of Ag¹¹¹ was determined in another aliquot by allowing the palladium activity to decay to a negligible value and then counting the silver.

Polarographic solutions contained 1.00×10^{-3} M. reducible ion and 0.1 M or more complexing agents as background electrolyte. The silver solutions

were prepared from weighed amounts of silver nitrate. Palladium solutions were prepared by dissolving a known amount of the metal in a mixture of hot sulfuric and nitric acids. After the bulk of the nitrate ion had been removed by fuming, the excess acid was neutralized by adding a solution of sodium hydroxide until a permanent precipitate appeared. Sufficient background electrolyte was then added so that, after dilution in a volumetric flask, the solution contained a known concentration of complexing agent plus an indefinite amount of sodium sulfate. Two exceptions were: (1) the thiocyanate solution where it was necessary to have a 0.3 M. background to prevent the slow precipitation of silver, and (2) certain cyanide solutions where the hydrogen wave, which followed the silver wave very closely, was shifted to more negative potentials by adding sodium hydroxide.

All solutions for electrolytic studies were prepared in exactly the same way as those just described for the polarography of palladium except that neutron-bombarded palladium was employed. The concentration of the background electrolyte and the palladium were the same as before but the solutions contained, in addition, about 10^{-9} M. silver exclusive of the amount introduced as an impurity. Table I shows the concentration relationships that were measured for the bombardment conditions employed in this investigation.

General Procedures

(a) Polarography - Reduction waves were obtained for 30 ml. portions of solutions in the usual way using dropping mercury and stationary platinum (17, 19) electrodes. All solutions were deaerated by bubbling oxygen-free nitrogen through the solution before a polarogram was begun. During the course of the polarization an atmosphere of nitrogen was maintained above the solution.

The polarograph was also employed to test the reversibility of reactions by changing the direction of polarization i.e., proceeding from negative to positive potentials. Whenever a regular polarographic solution was examined in this way, a reversible reaction produced a dissolution wave which was an extension of the

reduction wave. If a reaction were irreversible, the dissolution wave was displaced to a more positive potential so that it was no longer an extension of the reduction wave. Dissolution behavior of deposits was also studied by employing an electrode recently plated with silver or palladium and a solution containing only a background electrolyte. As shown in Figures 3 and 4, this empirical procedure produced results from which one could estimate the ready reversibility or irreversibility of a reaction. The method was used to study reactions in palladium solutions where irreversible reduction waves did not precede hydrogen discharge.

(b) Electrolysis - A 20 ml. portion of solution was electrolyzed with stirring for a fixed length of time. Then, without breaking the electrical contact, a large part of the solution was removed by suction and the remainder displaced by flushing the cell with about 200 ml. of a salt solution such as 0.1 M. sodium chloride, perchlorate, nitrate or sulfate. Finally, after washing the cell with 100 ml. of distilled water, electrical contact was broken and the cathode removed, dried under an infra red lamp and counted.

At the completion of a determination, the cathodes were cleaned by boiling them in concentrated nitric acid which removed the scotch tape as well as a large part of the active silver. In order to remove the remainder of the activity, it was necessary to allow the electrodes to stand in a concentrated solution of sodium cyanide. After removal from the cyanide, the electrodes were washed thoroughly with distilled water, dried under an infra red lamp, and checked with a counter. It was usually necessary to allow the electrodes to remain in the cyanide for an hour or more to reduce the activity on the electrode to "background" level.

(c) Counting - The procedure used in the radiochemical analyses was the same as that described by Hume, Ballou, and Glendenin (8). Liquid samples were analyzed by evaporating an aliquot of the sample, usually 0.100 ml., on a 1 in. watch glass. At the completion of the evaporation, the watch glass was covered

with thin cellophane (3 mg/cm^2) and mounted in the center of a $2 \frac{1}{2}'' \times 3 \frac{1}{2}''$ aluminum sheet having a hole in the center which was slightly larger than the watch glass. The electrodes were mounted in the same manner. All counts were corrected for decay, coincidence, size of aliquot and counter geometry. All samples that were counted on platinum were corrected for the difference in back-scattering between platinum and glass.

Results

Polarography

Information about the polarographic behavior of silver is rather limited. Because silver is more noble than mercury, solutions of silver react spontaneously with mercury producing waves of the type shown in Figure 2. Laitinen and Kolthoff (10) illustrated the general applicability of a solid polarographic electrode by using a solution of silver nitrate, but polarographic information about the complexes employed in the present investigation has not been reported. The curves shown in solid lines in Figure 3 are exact reproductions of silver waves obtained with a platinum electrode using automatic recording.

The polarographic behavior of palladium at a dropping mercury electrode has been reported by another investigator (22) so Figure 4 contains only the curves for reactions at a platinum electrode. Reduction waves were not found in cyanide and thiosulfate media where reduction of palladium was preceded by hydrogen evolution.

Deposition

(a) Studies of Rates - The difference between the half-wave potentials for two reactions in a given solution is a crude measure of the degree of success that one might expect in attempting to make a separation regardless of whether or not both reactions are reversible. If both reactions are reversible, an exact calculation of the separation at any potential should be possible. If one or both of the reactions are not reversible, the separation must be determined experimentally. As shown by the dotted lines in Figure 3, all of the silver reactions are reversible.

A similar study on palladium is recorded in Figure 4, and it shows that the dissolution wave is displaced at least +0.2 V. from the reduction wave in each case. For this reason it was not possible to make exact calculations for the separations on the basis of polarographic data; hence actual depositions were needed to determine the separability of the elements. Since both the percentage of the silver recovered and the degree of separation might change with the time of the electrolysis, rates of deposition were studied briefly.

The deposition rates for silver and palladium were determined under constant conditions of stirring, electrode size and shape, and volume of solution. A 20 ml. portion of an active solution, either silver or palladium, was electrolyzed in a cell of the type shown in Figure 1. At various intervals of time, a 0.100 ml. aliquot was pipetted from the cell, evaporated on a watch glass, and counted. As shown in Figure 5, the relative rate of deposition, at potentials more negative than the polarographic wave, was independent of the ion and its initial concentration. Palladium deviated noticeably toward the end of the electrolysis only because deposition was not complete under the conditions employed for the experiment.

A comparison of the half-wave potentials for silver and palladium in a given medium revealed that the reduction wave for silver always preceded that for palladium (See Table II). Since, in making a separation, one would work at potentials more positive than the palladium reduction wave (but more negative than the palladium dissolution wave), a knowledge of the rate of palladium deposition in this "irreversible" region was desirable.

Figure 6 shows the data for cyanide and thiocyanate solutions. The data for cyanide were reproducible and indicated that equilibrium was attained in three hours; the data for thiocyanate were too scattered to allow a reliable curve to be drawn, and they did not indicate that equilibrium was being approached. In both cases, the percentage of palladium deposited, though small, represented an amount which was very large when compared to the total amount of silver in the

original solution.

These experiments illustrate the usefulness of a polarograph in making rough estimates of the relative rates of deposition where an irreversible reaction is concerned. It is important to remember that changes in the concentration of either element will change the separation of the polarographic waves (and the deposition potentials) with a consequent change in the separability of the elements.

(b) Studies of Separations - It was necessary to determine the separability of silver and palladium by carrying out deposition experiments because of the irreversible behavior of palladium and because of the absence of polarographic reduction waves for palladium in two complexing agents. Furthermore, insufficient information was available to allow one to predict with certainty the deposition behavior of traces. For that reason, it was necessary to study the electrolysis of silver experimentally. Although the resulting data should only apply strictly to the specific concentrations that were studied, moderate changes in the silver concentration have been found not to affect the results noticeably.

Electrolyses were carried out on 20 ml. portions of millimolar palladium solution, the palladium having previously been irradiated in the pile. Potentials were selected which were at least 0.1 V. more positive than the palladium polarographic half-wave potentials and at the same time sufficiently negative to deposit some silver. In all of the studies, the initial concentrations of silver and of palladium, the rate of stirring and the time of electrolysis (30 min.) were held constant.

The degree of separation was calculated in terms of a separation factor which was arbitrarily defined as the fraction of the silver deposited divided by the fraction of the palladium deposited. The fractions of silver and palladium deposited were derived by determining the original activity of each element by methods already described and by determining the activities of each element in the

deposit from decay curves similar to those in Figure 7.

The separation factors and the supporting data for several solutions are collected in Table III. Most of these factors could be duplicated within 25%. One should observe that the separations obtained in a cyanide solution are favorable primarily because of the small amount of palladium deposited. The amount of palladium plated from solutions other than cyanide varied appreciably with a change of 0.4 V. in the applied potential whereas the amount plated from cyanide did not. At the same time, the amount of deposited silver also changed and, in the case of cyanide solutions, this change was particularly advantageous. Although it is not shown in Table III, the behavior and the results for cyanide solutions containing no sodium hydroxide were the same as for the solutions containing both hydroxide and cyanide.

(c) Application of Repeated Electrolyses - It is evident that selective dissolution of one element in a deposit or complete dissolution of a deposit in a fresh electrolyte followed by a second electrolysis should result in a corresponding increase in purity of the deposit. Three different approaches to this problem were examined: (1) selective dissolution of silver, (2) selective dissolution of palladium, and (3) complete dissolution of the deposit followed by another electrolysis.

The first procedure was expected to present the problem of apparent insolubility of the silver as a result of its being buried almost completely in the palladium which would be present in great excess. Actually, the difficulty turned out to be quite different in that most of the palladium stripped from the electrode along with the silver in a short period of time. This is shown by Figure 7 which contains decay curves of a thiocyanate electrolyte and of a deposit after about one hour of electrolysis at a potential of -0.075 V. vs. S.C.E. It was evident that dissolution of palladium was comparatively rapid even in the irreversible region of potential.

The second experiment in selective solution involved the use of cyanide to dissolve palladium from an electrode which was maintained a potential sufficiently negative to deposit silver completely and hence, presumably, to retain it. Probably because the palladium was present in great excess, and thereby was able to "carry" silver (or disengage it) from the electrode, the cyanide removed the bulk of the activity from the electrode almost immediately. As a result, no enrichment of the deposit could be measured.

Because the above experiments on selective solution indicated that the deposit was removed almost completely in a very short time upon being exposed to a fresh solution of complex-forming electrolyte, it appeared that one would always be faced with the necessity of making a second complete electrolysis in order to effect an appreciable increase in the purity of the silver as well as to effect a better (preferably complete) recovery of the silver. Experiments using cyanide to strip the activity completely off the cathode followed by a period of electrolysis sufficiently long to recover most of the silver are shown in Figure 8. Palladium activity could not be detected in the deposit recovered from the second electrolysis whereas the activity remaining in the solution after the second electrolysis was primarily palladium. From the decay curves it was possible to calculate that the separation factor for each electrolysis was approximately the same, i.e. about 10^3 . Assuming that the solution was initially 10^{-7} M. silver and 10^{-3} M. palladium, the second deposit contained about 1% palladium. A third electrolysis should produce a correspondingly purer deposit of silver.

Some values for the overall recovery of silver from double electrolyses were 79%, 78% and 76% which in turn represented 85%, 86% and 85% respectively of the recoveries permitted by the lengths of time employed for the electrolyses. It is not unlikely that these recoveries could be improved by modifying the procedure since the emphasis of these studies was placed on examining the purity of the deposit rather than on obtaining complete recovery of the silver.

Discussion

Electrolytic Procedure

Whenever a complex-forming electrolyte was displaced from the cell by distilled water at the conclusion of an electrolysis, serious loss of activity from the deposit always resulted even though care was taken to make certain that electrical contact was not broken. For example, after one experiment in which pure silver activity was deposited from cyanide solution, 0.2% of the original activity remained in the solution at the completion of electrolysis, but, after washing the cell with water, the wash liquid contained 17% of the activity and only 81% was later found on the cathode. Repetition of this experiment always gave similar results. Part of the difficulty appeared to be that the regulator could not maintain the proper potential on the electrode when the resistance of the solution changed rapidly. For that reason, solutions of electrolytes were substituted for the distilled water.

Attempts to flush cyanide solution from a cell by using a fresh portion of cyanide solution also resulted in a serious loss of silver activity from a deposit containing substantial amounts of palladium. On the other hand, the use of an electrolyte such as sodium nitrate or sodium perchlorate, with which neither silver nor palladium formed stable complexes and hence toward which both elements were electrochemically more "noble", gave satisfactory results. One representative set of values for silver activity was: solution after electrolysis, < 0.1%; solution after washing cell, 0.4%; activity found on cathode, 97%.

During the course of this study several observations have been made concerning losses from sorption which may be helpful in devising procedures for other elements. For example, little difficulty was experienced with sorption on glass or agar surfaces when dealing with the very stable cyanide complex. Interference became noticeable but not important for solutions containing the ammonia complex of silver. On the other hand, serious losses from sorption, which

took place primarily on the glass surfaces, always occurred when working with solutions of nitrate and perchlorate. The rate of loss due to this factor was reproducible. Figure 9 indicates that an appreciable amount (about 15%) was very rapidly sorbed. By coating all of the glass surfaces with ceresine wax, the sorption losses for a five hour electrolysis of a nitrate solution were usually decreased to less than 5% (9) (21). According to Krause (9), some activity is sorbed on the scotch tape gasket from solutions of weak complexes, and the use of writing paper coated with ceresine wax will reduce this source of loss to a negligible figure.

Radiochemical Considerations

It is readily apparent from the experiments described in the present paper, that the authors were concerned only with relative measurements. No attempt was made to determine the absolute number of counts or disintegrations in a sample except in making the rough checks of the yields of Pd¹⁰⁹ and Ag¹¹¹. The need for absolute values of self-scattering and back-scattering were eliminated by reducing all measurements to a single set of conditions.

It was necessary to determine the relative amounts of back-scattering on platinum and on glass because most radiochemical analyses of solutions were made by evaporating an aliquot on a watch glass whereas most of the electrolytic deposits were counted on the platinum cathode. A glass-to-platinum ratio of 0.74 was found to be very reproducible (5).

There appeared to be a need for considering self-scattering because the activity of a solution before an electrolysis was determined by evaporating and counting a portion containing several milligrams of solid material whereas the activity on a cathode was usually measured with less than 0.1 mg. of solid present. Experiments showed that a maximum error of about 5% might be introduced from this source so this factor was ignored.

During the course of experiments not reported in the present study, it was noted that the material balance for a particular electrolysis was often

better than 95%, but many times it fell between 90 and 95%, and sometimes as low as 85%. In no case was a significant amount of activity found in the wash solution, the agar bridges, or on the glass surfaces. The low recoveries appeared, therefore, to be the result of an unequal distribution of activity on the electrode, and radioautographs proved this to be the case. The data in Table IV illustrates the extent to which the errors arising from the geometry of the deposit (as well as errors arising from differences in self-scattering) were decreased by dissolving the deposit in a solution containing approximately the same weight-percentage of solid (and often the same salts) as the original solution. After introducing this additional step, the material balances were almost always better than 96%, and they often fell above 98%. The latter figure was considered to be within the experimental limit of error of complete recovery for counting procedures of this type.

Errors arising from variations in the geometry of the deposit probably could have been avoided by using a different type counter and/or a smaller cathode. However, the counter employed for this study had the advantage of being a widely used design. The alternative of using a smaller cathode was avoided because it would have necessitated longer periods of electrolysis as a result of the slower rate of plating. Such a change would have been unfavorable in working with the relatively short half-life of Pd^{109} .

Conclusions

It has been shown that polarograms obtained with a solid electrode provide a practical basis for judging the feasibility of a separation whether or not the reaction is thermodynamically reversible. After a deposition had been completed, a satisfactory recovery was made by the use of a wash liquid containing an electrolyte toward which the deposit was relatively "noble". The precision and the accuracy of the results was improved by dissolution of the deposit and estimation of the activity in the resulting solution.

Of the solutions tested, cyanide produced the best separation. By

repeating the electrolysis, correspondingly purer silver was produced. Although the experimental data can only be applied strictly to solutions having the same concentration of silver, the information is sufficiently general to be useful for a comparatively wide range of trace concentrations.

Acknowledgements

The authors wish to thank D. B. Ehrlinger for checking the radiation characteristics of Pd¹⁰⁹ and Ag¹¹¹ and for determining the back-scattering ratio of glass to platinum. The authors also wish to thank D. P. Krause for his scorpion studies and Cyrus Feldman for his spectrographic analyses of palladium.

This work was performed under Atomic Energy Commission contracts No. W-35-058 eng. 71 with Monsanto Chemical Company and No. W-7405 eng. 26 with the Carbide and Carbon Chemical Corporation.

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Table I

Relative Amounts of Certain Silver and Palladium Isotopes Following a Neutron
Bombardment of Natural Palladium.

Ratio	End of Bombardment	4 Hours After Bombardment	8 Hours After Bombardment
$\frac{\text{Total Pd}}{\text{Pd}^{109}}$	7.0×10^6	8.6×10^6	1.1×10^7
$\frac{\text{Ag}^{109} \text{ (stable)}}{\text{Ag}^{111}}$	56	61	65
$\frac{\text{Pd}^{109}}{\text{Ag}^{111}}$	22	18	15
$\frac{\text{Total Pd}}{\text{Ag}^{111}}$	1.5×10^8	1.6×10^8	1.6×10^8

Table II

Half-Wave Potentials of Millimolar Palladium and Silver Solutions Obtained With Stationary Electrodes Using Automatic Recording.

Background Solution	$E_{1/2}$ vs. S.C.E. in Volts	
	Silver	Palladium
0.1 M NH_4OH	-0.02	-0.50
0.3 M KCN	-0.22	-0.43
0.1 M $\text{Na}_2\text{S}_2\text{O}_3$	-0.41	---*
0.1 M NaCN	-0.84 ^{**}	---*
0.1 M NaOH and 1.0 M NaOH	-0.79 ^{**}	---*

*Hydrogen evolution preceded the palladium reduction wave.

**Exact value depends on rate of polarization.

Table III

Separation of "Carrier-Free" Silver from 10^{-3} M Palladium Using Various
Complexing Agents.

Supporting Electrolyte	Cathode Potential vs. S.C.E.	% Palladium Plated	% Silver Plated	Separation Factor $\times 10^{-2}$
0.1 M $\text{Na}_2\text{S}_2\text{O}_3$	-0.250	0.016	4.3	2.7
	-0.410	0.018	12	6.7
	-0.500	0.086	22	2.6
0.1 M NH_4OH	+0.150	0.008	8.4	10
	-0.015	0.017	21	12
	-0.350	0.14	47	3.4
0.3 M KCNS	-0.100	0.069	16	2.3
	-0.220	0.15	27	1.8
	-0.350	0.80	44	0.55
0.1 M NaCN 1.0 M NaOH	-0.805	0.008	0.35	0.4
	-0.860	0.004	0.33	0.8
	-0.950	0.008	0.40	0.5
	-1.025	0.005	1.7	3.4
	-1.210	0.006	25	42

Table IV

Percent Silver on Cathode Determined by Two Different Methods.

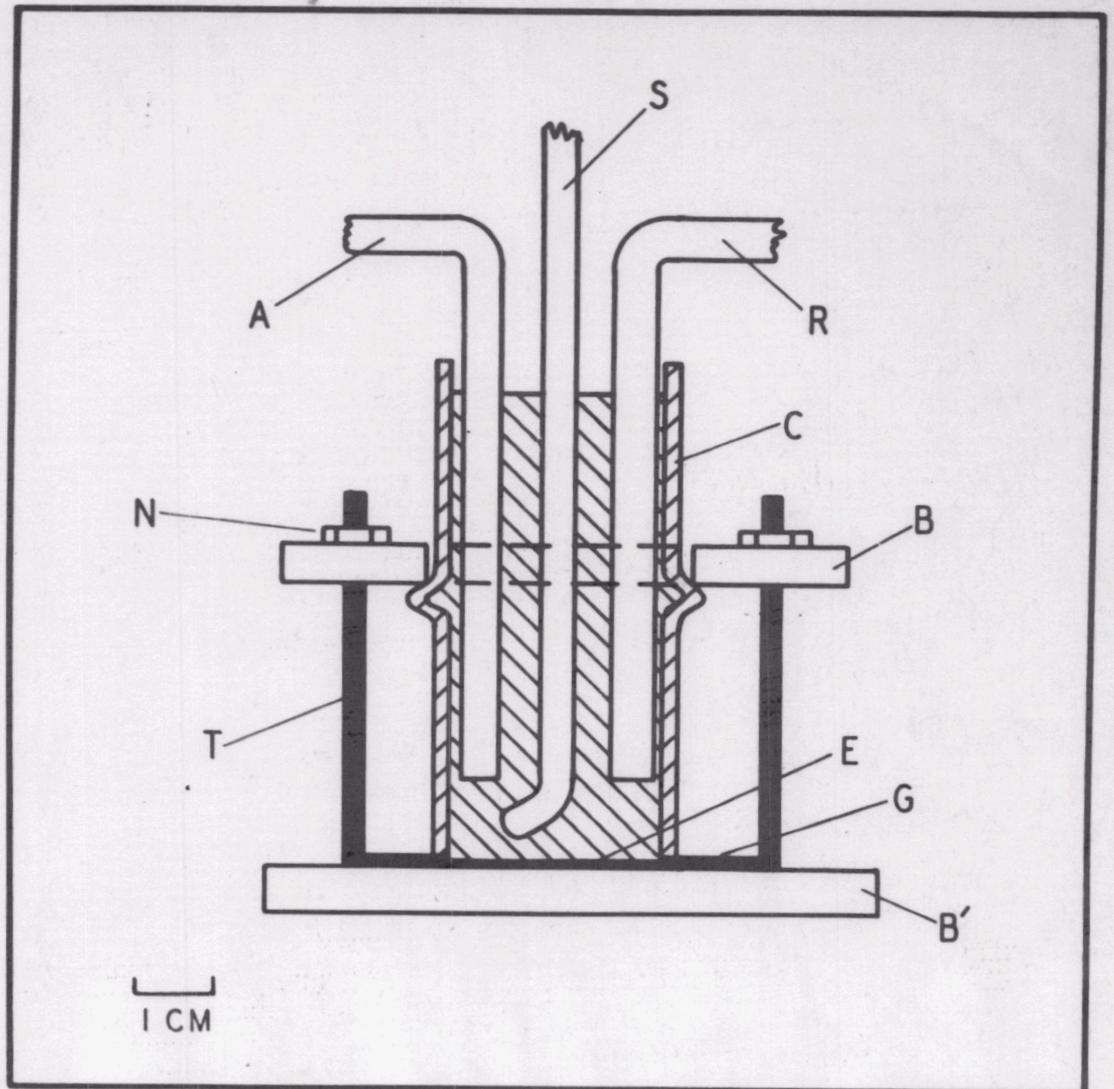
Percent Silver on Cathode

By Count of Cathode	By Count of Strip Solution
96	98
86	89
86	95
75	80
66	74
32	37



Figure 1. Electrolysis Cell.

FIG. 1



- A ANODE BRIDGE
- B BRASS COLLAR
- B BRASS BASE
- C GLASS CYLINDER
- E ELECTRODE
- G GASKET
- N BRASS NUT
- R BRIDGE TO REFERENCE ELECTRODE
- S STIRRER
- T THREADED BRASS BOLT

Figure 2. Polarograms of Millimolar Silver Complexes Obtained with a Dropping Mercury Electrode Using Automatic Recording.

- I. 0.1 M NH_4OH
- II. 0.3 M KCNS
- III. 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$
- IV. 0.1 M NaCN

FIG. 2

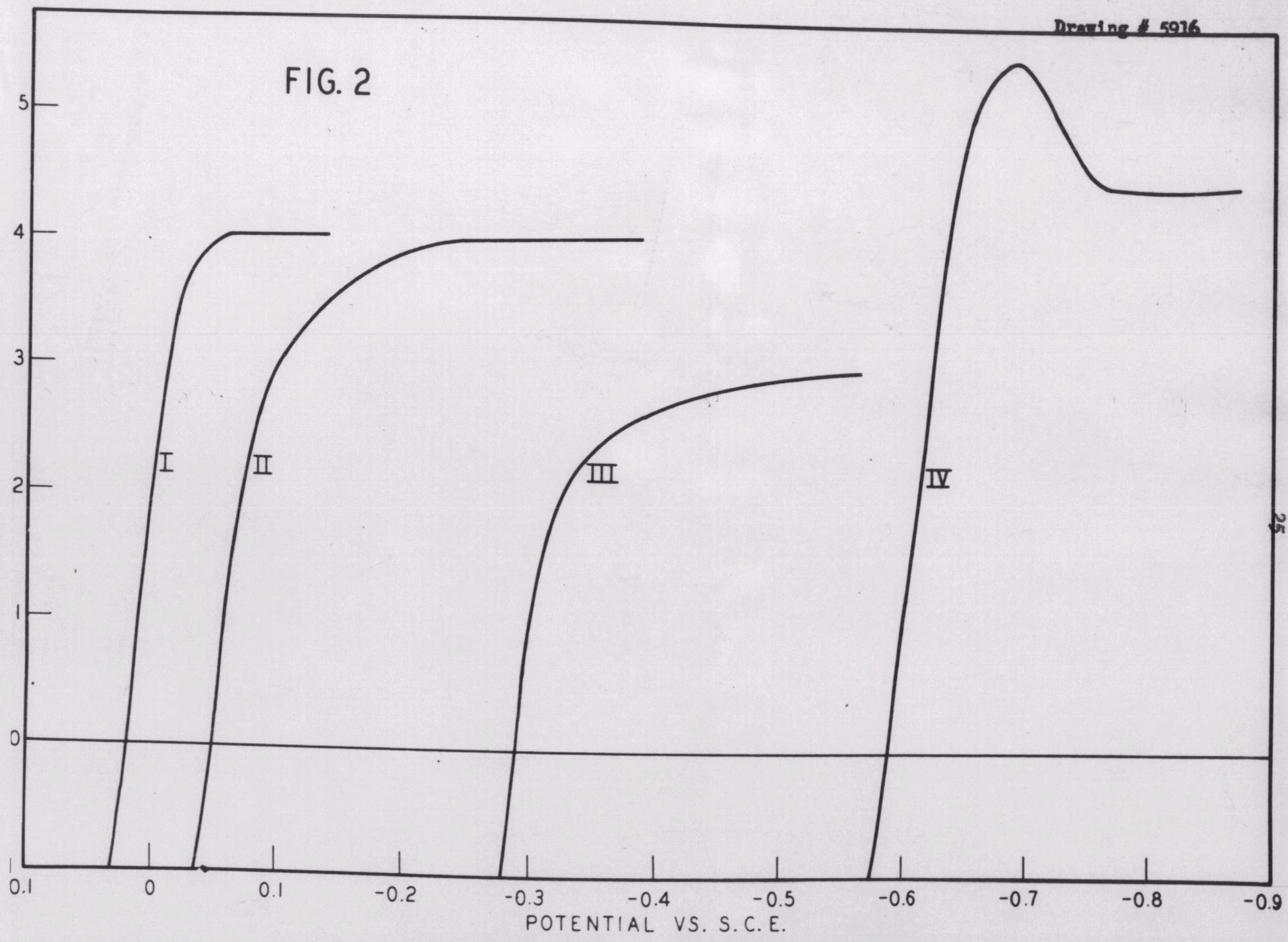
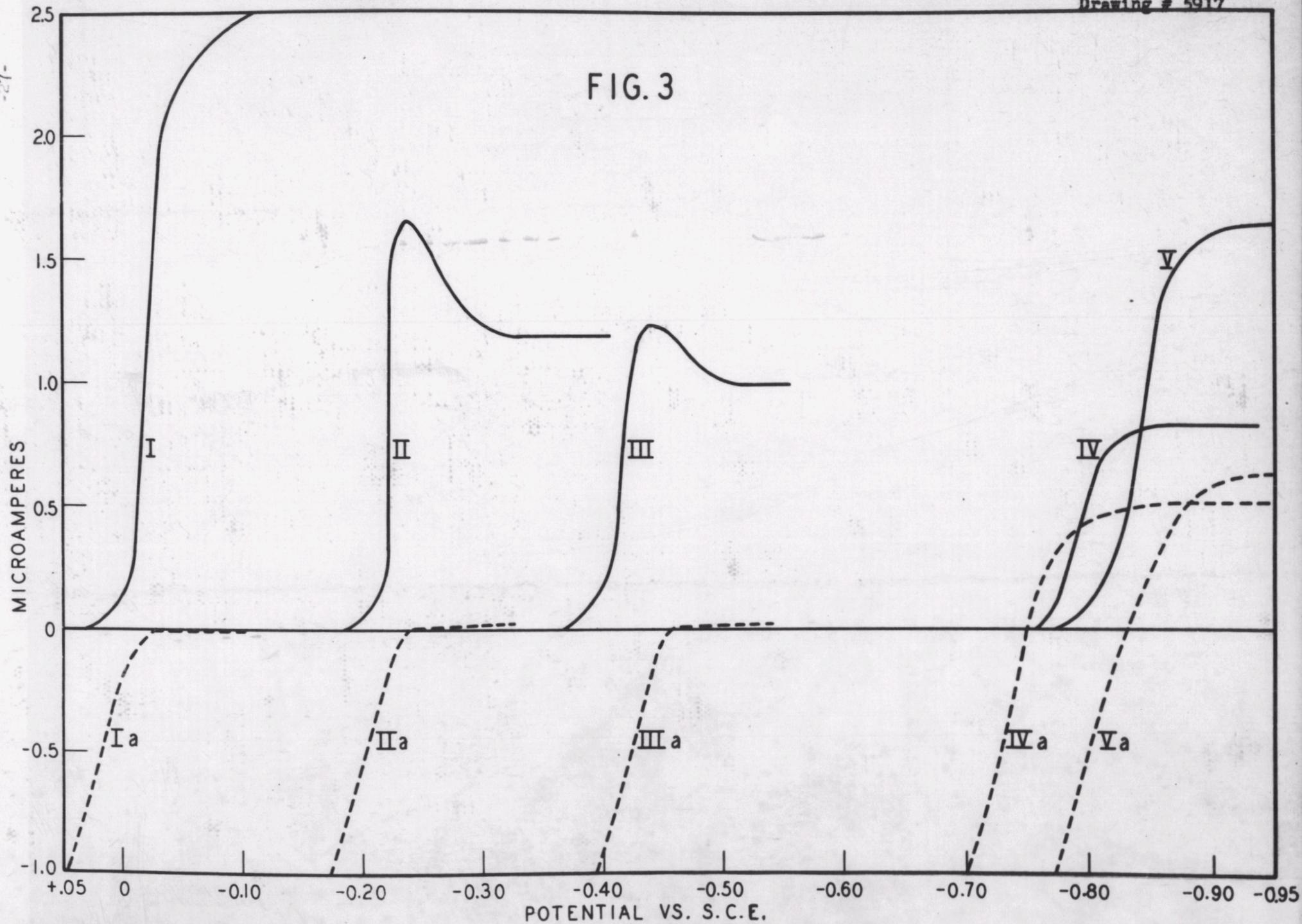


Figure 3. Polarograms of Millimolar Silver Complexes Obtained with a Stationary Platinum Electrode Using Automatic Recording.

- I. 0.1 M NH_4OH
- II. 0.3 M KCNS
- III. 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$
- IV. 0.1 M NaCN + 1.0 M NaOH
- V. 0.1 M NaCN

The "A" curves are the corresponding dissolution waves.

FIG. 3



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Figure 4. Polarograms of Millimolar Palladium Complexes Obtained with a Stationary Platinum Electrode Using Automatic Recording.

- I. 0.3 M KCNS
- II. 0.1 M NH_4OH
- III. 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$
- IV. 0.1 M NaCN
- V. 0.1 M NaCN + 1.0 M NaOH

The "A" curves are the corresponding dissolution waves.

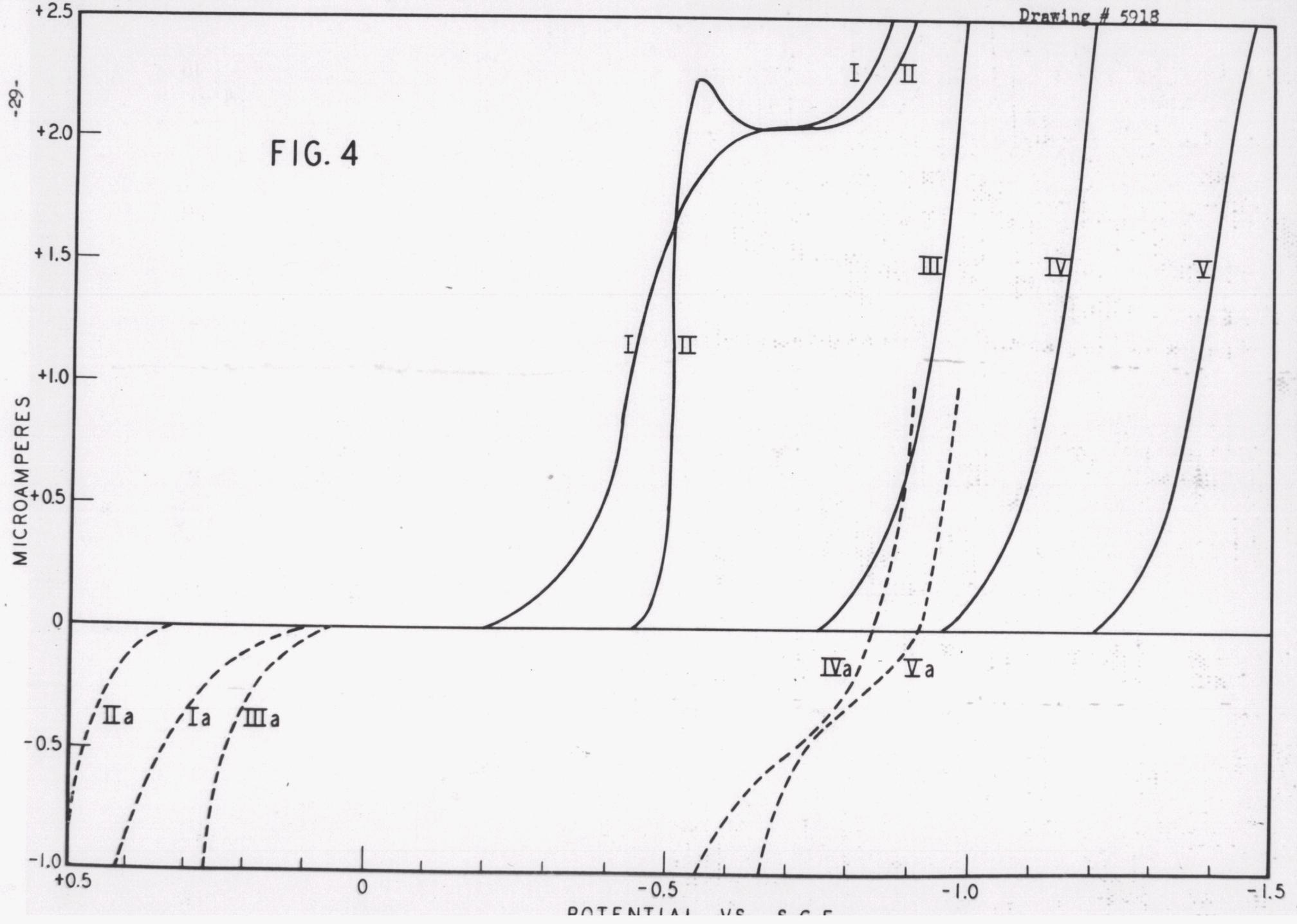


FIG. 4

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MICROAMPERES

POTENTIAL VS. S.C.F.

Figure 5. Rate of Deposition of Silver and Palladium at Potentials More Negative than the Polarographic Wave.

- - "carrier-free" silver in 0.1 M NaCN + 1.0 M NaOH electrolyzed at -1.200 V. vs. S.C.E.
- △ - 10^{-5} M silver in 0.1 M NaCN + 1.0 M NaOH electrolyzed at -1.100 V. vs. S.C.E.
- - 10^{-3} M palladium in 0.3 M KCNS electrolyzed at -0.900 V. vs. S.C.E.

FIG. 5

PERCENT REDUCIBLE ION IN SOLUTION.

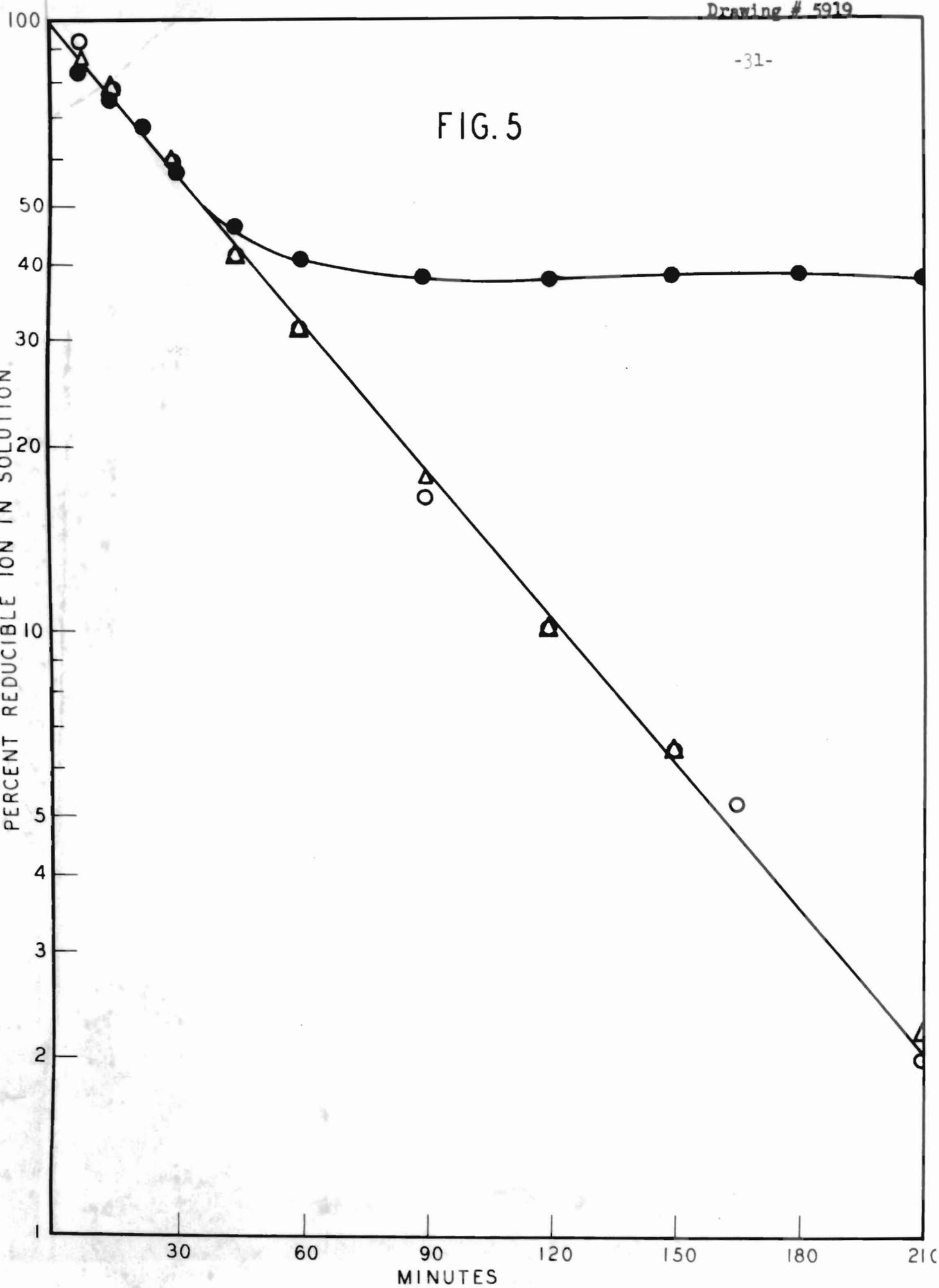


Figure 6. Rate of Deposition of Palladium at Potentials More Positive Than the Polarographic Wave.

- - 10^{-5} M palladium in 0.1 M NaCN + 1.0 M NaOH electrolyzed at -1.200 V. vs. S.C.E.
- - 10^{-3} M palladium in 0.1 M NaCN + 1.0 M NaOH electrolyzed at -1.200 V. vs. S.C.E.
- △ - 10^{-3} M palladium in 0.3 M KCNS electrolyzed at -0.100 V. vs. S.C.E.

FIG. 6

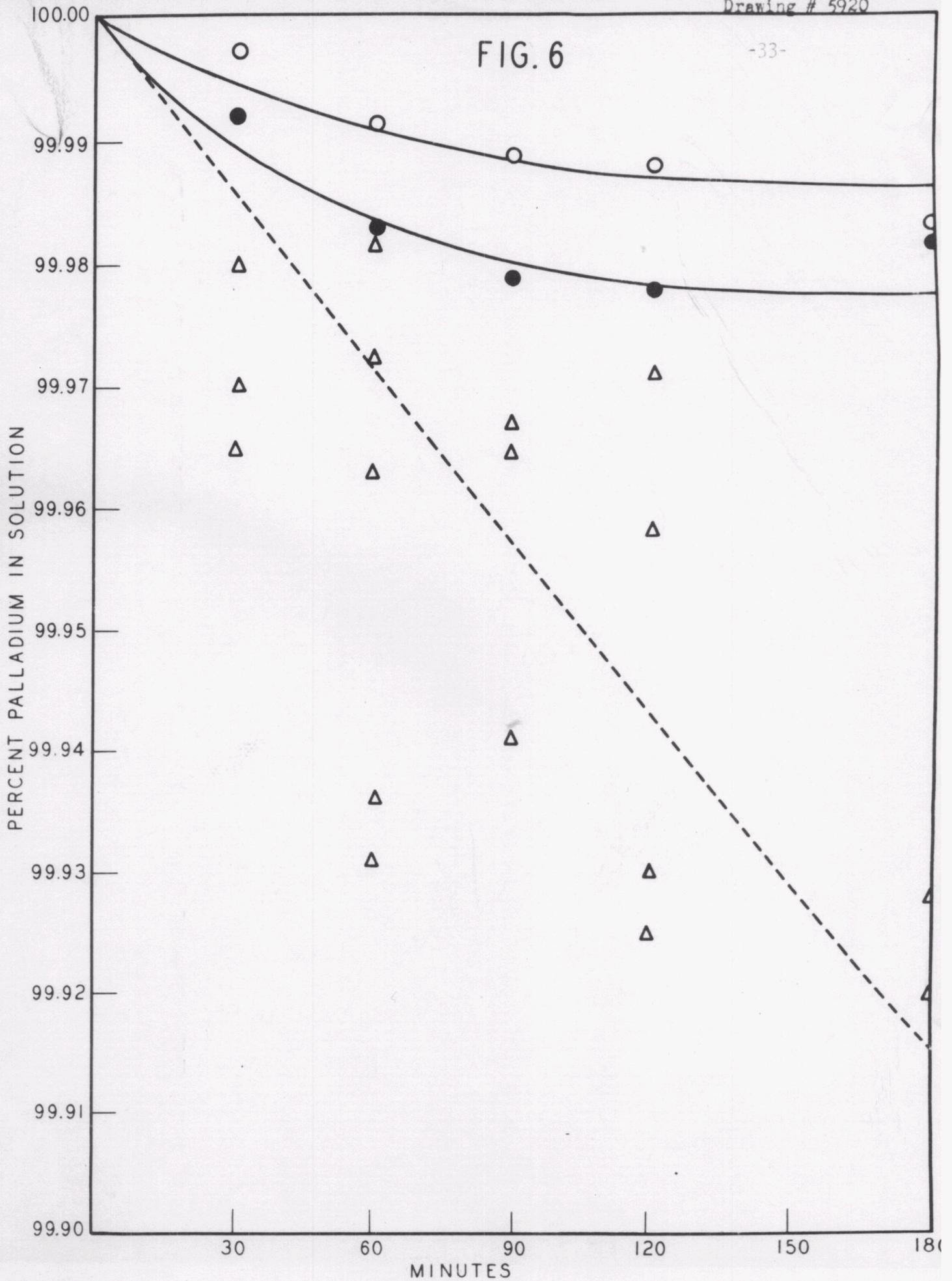


Figure 7. Decay Curves for Attempted Purification of Silver by Selective Dissolution of Silver in 0.3 M Potassium Thiocyanate.

○ - electrolyte

● - cathode after electrolysis

FIG. 7

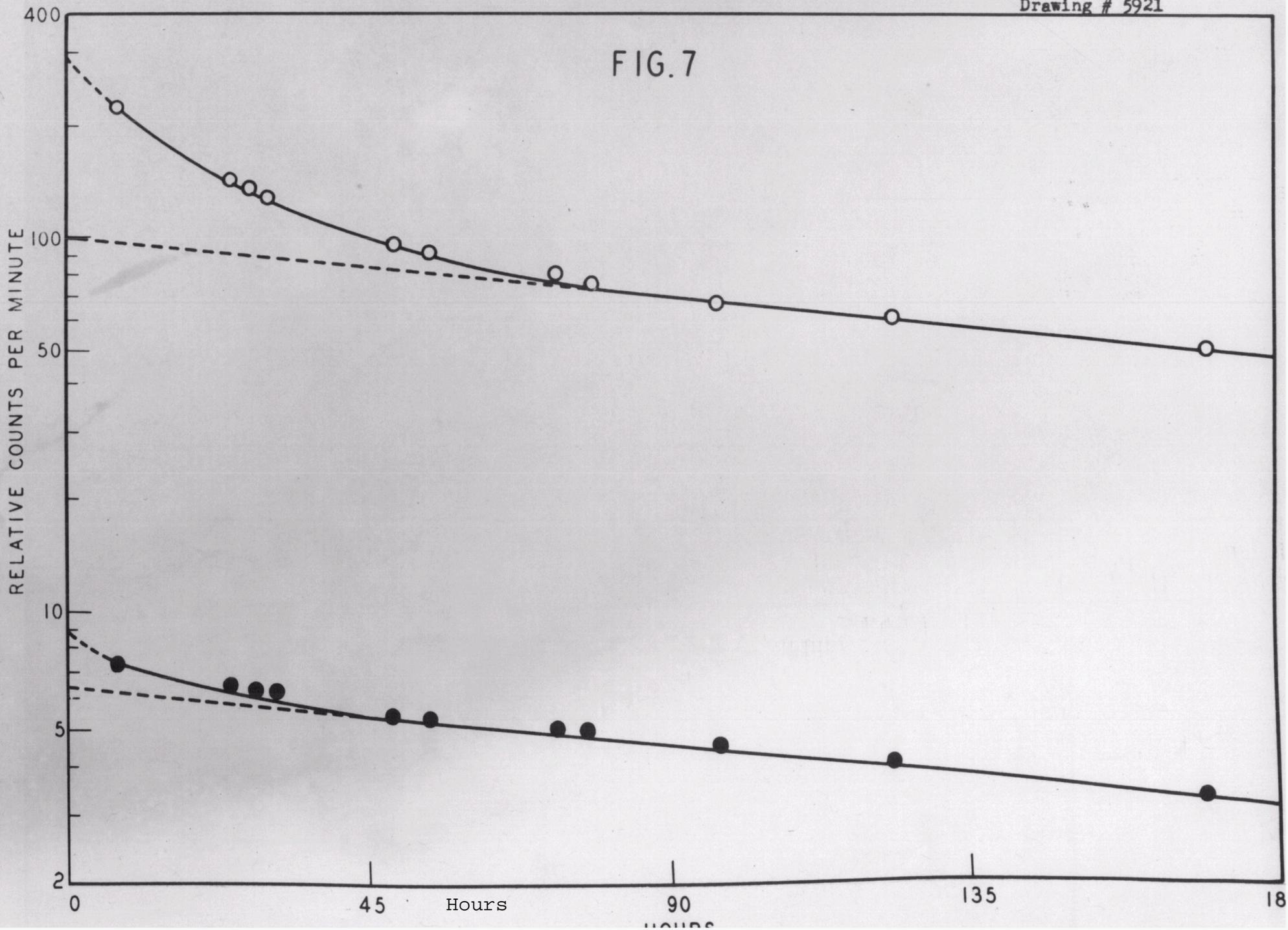


Figure 8. Decay Curves for two Successive Electrolyses in 0.1 M Sodium Cyanide plus 1.0 M Sodium Hydroxide.

- △ - deposit after first electrolysis
- - deposit after second electrolysis
- - electrolyte after second electrolysis

FIG. 8

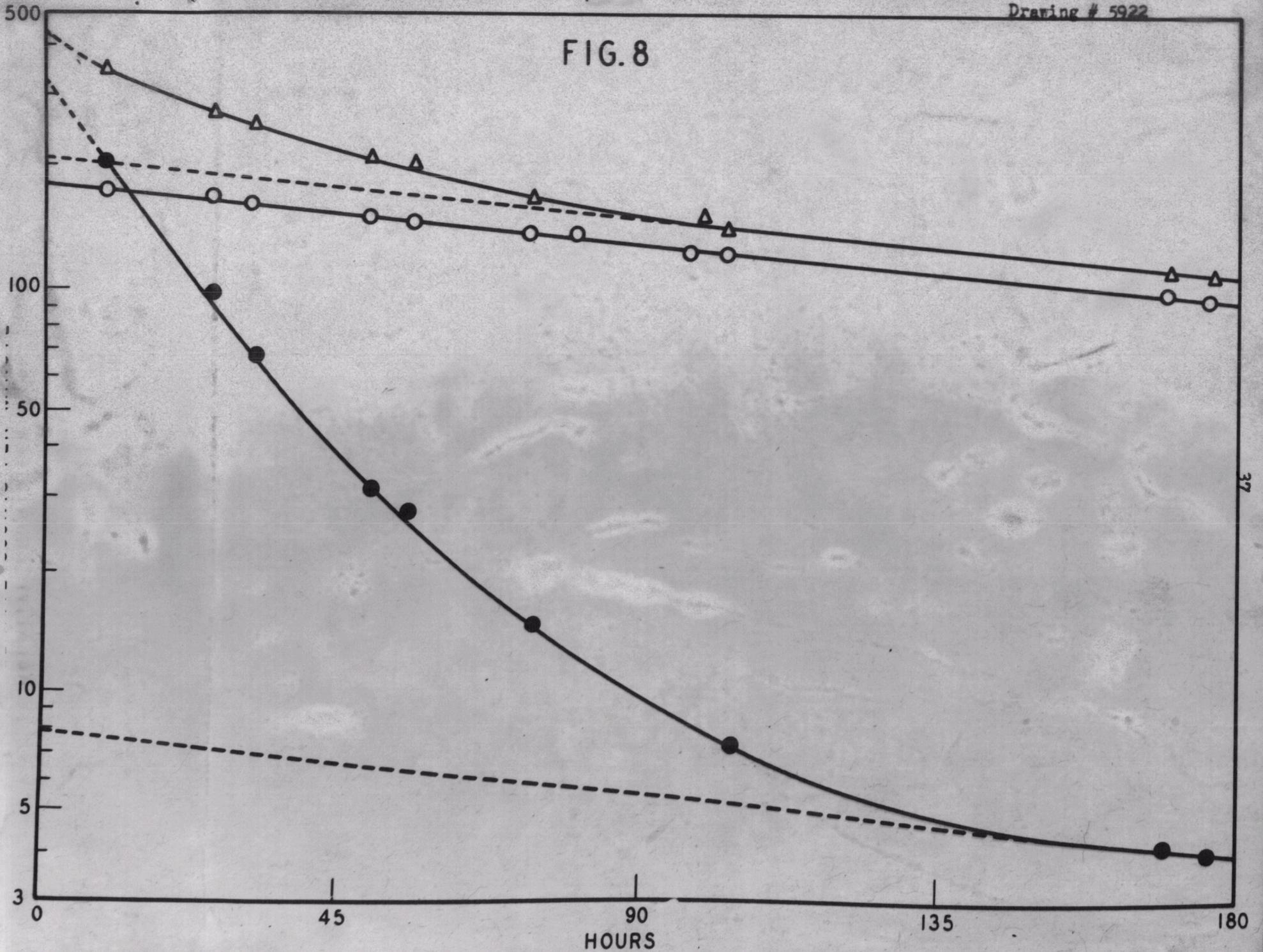


Figure 9. Rate of Sorption of "Carrier-free" Silver onto Glass from Nitrate and Perchlorate Solutions of pH 4.

- - "carrier-free" silver in 0.1 M NaClO_4
- - "carrier-free" silver in 0.1 M KNO_3

FIG. 9

