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Electrodeposition Behavior of Traces of Silver

L. B. Rogers, D. P. Krause, J. C. Griess, Jr., and D. B. Ehrlinger

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Abstract

By means of radioactivity, the extent of silver deposition on platinum cathodes was determined at various potentials under conditions closely approaching equilibrium. For any specific solution having a concentration of silver of 10^{-5} M or greater, the resulting curve agreed well with the polarographic curve. For concentrations equal to or smaller than 10^{-7} M, the amount of silver was insufficient to cover the electrode and the resulting deposition curves often shifted to a potential several tenths of a volt more "noble" than that predicted by the Nernst equation. The shift which may be the result of alloy formation, was influenced greatly by the "inert" electrode material.

Changes in the electrode area and in the volume of solution were found to shift the position of the deposition curve in accordance with predictions based upon the Nernst equation. Complexing agents decreased and sometimes eliminated the shift toward noble behavior whereas, in one case, a higher concentration of acid produced a larger shift toward "nobility".

Introduction

The question of whether or not the electrodeposition behavior of traces can be predicted by the Nernst equation is a classical one. Haissinsky (1), in reviewing the subject, pointed out that there are many contradictory conclusions in the literature, some of which undoubtedly stem from the fact that some investigators have tested an abridged equation rather than the complete Nernst expression. It appears that the complete Nernst expression plus an additional term to account for differences in free energy arising at the deposit-electrode interface from the use of

different "inert" electrode materials may be correct (2). It was suggested that the deposition behavior of traces should be affected by changes in area of the electrode and volume of the solution but not by changes only in the total amount of trace element undergoing reaction. The experiments described in the present paper were designed to test these predictions and to provide information concerning the types and the magnitudes of errors encountered in the various procedures.

Silver was selected for this study because of its favorable chemical and radiochemical properties. The electrode reactions of silver are one-electron transfers which are readily reversible. The relatively "noble" potentials at which many of the reactions take place help to minimize dissolution losses in handling the electrodeposits. Furthermore, although silver is an uncommon impurity in reagents, it can if present, be reduced to a very low concentration by electrolysis. Finally, silver has a radioactive isotope (Ag^{111}), having a 7.5 day half-life and a 1.0 Mev. β^- particle, which can be produced with an adequately high specific activity to allow accurate measurement of the relative amount of silver in a very dilute solution.

All of the data were calculated on the basis of formal potentials (3) which were first obtained polarographically and then checked by electrodeposition using 10^{-5} M solutions. Factors such as activity coefficients, junction potentials, and concentration of the complexing agent were held constant throughout the series of experiments involving a particular background solution.

Experimental Detail

Apparatus

All of the equipment employed in this study was the same as that reported previously (4): A modified Sargent Model XX polarograph, a constant-

voltage regulator capable of control to ± 3 mv., a Beckman pH meter fitted with a special electrode having a small correction for sodium ion, special electrolytic cells enabling the deposition to be confined to a fixed area on one side of a platinum foil, and standard equipment for β^- particle counting consisting of a thin mica end-window Geiger-Muller tube, an aluminum-lined lead shield, and a scaling circuit.

Reagents and Solutions

Reagent grade chemicals were used throughout this investigation. Distilled water was used in most of the experiments except those involving traces of silver where triply-distilled water was employed. The triply-distilled water was prepared from the laboratory supply of distilled water by distillation in an all-glass apparatus, first from alkaline permanganate and then from phosphoric acid. Starting in each case with two liters of water, the fraction between 25% and 75% was collected. The final distillate did not give a positive test for silver when examined with a procedure sensitive to 0.05 ug/ml. (5).

Whenever possible, a solution of each reagent was freed from natural silver by electrolysis before the tracer was added. Such a procedure was deemed advisable even for the palladium (Baker and Co.) which sometimes contained spectrographically-detectable amounts of silver of the order of 50 ppm. (6). The procedure for the removal of silver impurity was the same as that used to recover the silver tracer following the neutron-bombardment of palladium. In addition, two steps were necessary in order to recover the purified palladium metal prior to activation. The entire procedure is outlined below.

A 50 mg. portion of palladium metal was dissolved in a mixture of nitric and sulfuric acids. After cooling, the solution was diluted to about

100 ml., neutralized by adding pellets of sodium hydroxide slowly, and then made 1.0 M in sodium hydroxide and 0.10 M in sodium cyanide. This solution was electrolyzed for three hours using a platinum gauze electrode maintained at -1.2 V. vs. the saturated calomel electrode (S.C.E.). After removing the electrode, the electrolysis was repeated using a second clean electrode. Then, palladium cyanide was precipitated by adding sulfuric acid, and washed with triply-distilled water. The final step of the purification consisted of dissolving the palladium cyanide in sulfuric acid followed by the precipitation of palladium metal by formaldehyde. The product was always spectrographically-free from silver, i.e. less than about 10 ppm. (6).

Ag^{111} tracer having a high specific activity was prepared by bombarding natural palladium with neutrons,

$$Pd^{110}\ (n,\gamma)\ Pd^{111} \xrightarrow[26\ m.]{\beta^-} Ag^{111} \xrightarrow[7.5\ d.]{\beta^-} Cd^{111}\ (\text{stable}),$$

dissolution of the palladium, and recovery of the silver by electrolysis with a platinum electrode (4). By carrying out three electrolyses in series, the amount of palladium accompanying the silver was reduced to a very small value (calculated to be less than 1% of the amount of silver). However, small amounts of platinum undoubtedly dissolved from the cathode along with the silver when the latter was stripped from the electrode into the desired background solution. Calculations indicated that if one could neglect the amount of silver introduced as an impurity, the resulting tracer solutions were about 1×10^{-9} M in silver.

Procedures

Polarograms for silver in various background electrolytes were recorded automatically using a solid electrode, usually platinum and an outside saturated calomel electrode (7, 8).

Electrolyses were carried out in essentially the same way that has

been described previously (4). A glass tube having both ends open, was clamped onto a platinum foil to define a circle having a plane area of about 5 cm^2. The capacity of a cell was about 35 ml. but 25.0 ml. was used for most of the experimental work. The solution was stirred at 300 rpm using a glass rod having a single small paddle. All glass surfaces, including those of the stirrer and the agar bridges, were given a fresh coat of ceresine wax before each experiment in order to minimize losses from sorption. Platinum electrodes were usually sufficiently free from silver (and radioactivity) to be used again after a preliminary cleaning in boiling nitric acid followed by immersion in a solution of sodium cyanide for several hours.

In the interest of minimizing losses of deposited silver while the electrode was being washed, the following variation was introduced: After the stirring had been stopped and most of the active solution removed by suction, the potential of the cathode was made about 0.5 V. more negative. The amount of material plated from an unstirred solution was negligible but the additional voltage appeared to help in holding the deposit while it was being washed with the recommended (4) nitrate or perchlorate solution. The activity on the cathode was then dissolved in a solution of cyanide by electrolysis for a few minutes at a positive potential to strip the radiosilver from the electrode. The activity in a sample of the "strip" solution was then determined.

Some studies were made by depositing the trace completely and then adjusting the potential to the desired value. This proved to be a useful method for finding the approximate (sometimes exact) location of a deposition curve because a number of potentials could be examined consecutively in a short time. In general, a stripping procedure allowed one to approach more closely to an equilibrium value in a short interval of time than a deposition

procedure did. Sampling (50 or 100 µl.) of the supernatant between each setting of potential resulted in negligible losses of solution.

Standard radiochemical techniques were used for the estimation of activity. All counts were made under conditions such that back-scattering, self-scattering, and geometry were held constant. Coincidence corrections were made when necessary. All measurements were relative rather than absolute.

Results

Change in $E_{50\%}$ with Concentration of Silver

The change in $E_{50\%}$, the potential at which half of the silver is precipitated on a silver electrode can be predicted from the equation

$$E = E^{o}_{f} + \frac{RT}{nF} \ln C \qquad (1)$$

where E^{o}_{f} is the formal potential for the reaction in question, C is the molar concentration of the reducible ion, and the polarographic convention is used for signs. Providing overvoltage from factors other than concentration polarization can be neglected, $E_{50\%}$ for an electrodeposition should agree with the polarographic halfwave potential ($E_{1/2}$).

Typical evidence of such agreement for solutions having initial concentrations of silver equal to or greater than 10^{-5} M. is shown in Table I. It was generally possible to reproduce the values for $E_{1/2}$ or $E_{50\%}$ within ±0.01 V. Deposition results for a solution of 0.1 M sodium perchlorate at pH 4 are not shown because they agreed with those for nitrate. It was found that the disagreement between $E_{50\%}$ and $E_{1/2}$ for a solution containing 0.1 M cyanide and 1.0 M hydroxide could be eliminated by changing manually the potential on the polarographic slidewire and waiting 15 minutes or more at each potential before reading the current. The disagreement, therefore, was attributed to overvoltage in the automatically recorded polarographic curve.

Calculations showed that 25 ml. of a 5×10^{-7} M solution of silver

would be sufficient to form a monolayer on a 5 cm^2 area. It was not surprising, therefore, that 10^{-7} M and more dilute solutions deviated from values calculated from equation 1.

However, this behavior is in accordance with the predictions of an equation based upon an early suggestion of Herzfeld (9) that the activity of the deposit might vary with the fraction of the surface covered with deposit. This can be stated as (2):

$$E = E_f^{\circ} + E_a + \frac{RT}{nF} \ln \frac{A_e f_1}{V N_a A_a f_3} + \frac{RT}{nF} \ln \frac{1-x}{x} \qquad (2)$$

where E°_f = formal potential for a covered electrode

E_a = Potential associated with free energy of alloy formation (at the deposit-electrode interface)

x = Fraction of the initial amount of element deposited at potential E.

V = The volume of solution.

A_e = The electrode area.

A_a = The area of a deposited atom.

N_a = Avogadro's number.

f_1 and f_3 = Activity coefficients of the ion and deposited atom respectively.

By combining the first three terms one obtains $E_{50\%}$ for a particular set of experimental conditions:

$$E_{50\%} = E_f^{\circ} + E_a + \frac{RT}{nF} \ln \frac{A_e f_1}{V N_a A_a f_3} \qquad (3)$$

It is apparent from equation 2 that one would expect the position of the deposition curves for trace amounts to be independent of initial concentration when the electrode area and volume of solution are held constant.

The examples shown in Figure 1 illustrate the types of curves that were found. One very important aspect of a curve for trace amounts is its comparatively poor reproducibility which usually corresponded to nearly

$\pm$ 30 mv. despite the fact that the regulators controlled the potential to $\pm$ 3 mv. or better. Other factors, particularly differences in areas of the electrodes, contributed errors which will be discussed later.

As one might have expected, 10^{-6} M solutions gave a curve having certain characteristics of both "macro" and trace curves. The results in Figure 2 indicate that, except for one curve, the $E_{50\%}$ value fell close to $\pm$ 0.14 V., the value predicted from equation 1. However, in common with curves for trace amounts, there was appreciable plating at potentials several tenths of a volt more positive than the $E_{50\%}$. Furthermore, the amount of scatter in the values for percentage of silver deposited at any specific potential more positive than $E_{50\%}$ was characteristic of that found in experiments with trace amounts.

Two important conclusions can be drawn from the results that have been presented. The first is that the behavior of an ion in contact with an incompletely covered electrode may be quite different from its "macro" behavior. Instead of changing with the initial concentration of solution in accordance with equation 1, the $E_{50\%}$ for traces was constant within the rather wide limits of error. This was demonstrated by agreement between curves for 10^{-7} M and "trace" solutions. It is true that one can argue that the amount of impurity remaining in reagents was the limiting factor which remained constant but it appears highly probable that such was not the case in view of extraordinary precautions which were taken to reduce the silver content of all reagents.

The second conclusion one can draw from the deposition curves for traces is that E_a can cause a sizable shift in the deposition curve. If E_a were zero the curve for trace amounts would be displaced from E^o_f by an amount $+ \frac{RT}{nF} \ln \frac{A_e f_1}{V N_a A_a f_3}$. Table I shows that such a displacement was

found for cyanide solution. On the other hand, substantial shifts of the deposition curve to positive potentials were found in ammonia, nitrate and perchlorate solutions.

The fact that E_a is not independent of the medium can be explained if one assumes that the anion substantially affects the rate of dissolution of the "inert" electrode. Qualitatively, there are many pieces of evidence to support this assumption: (1) At comparable potentials, the silver can be removed from an electrode much faster with a cyanide solution than with a nitrate solution. Complete removal of activity is also easier to effect. (2) In working with trace amounts, stripping curves agree very well with deposition curves for cyanide solution whereas for nitrate, perchlorate and ammonia solutions the stripping curves are displaced about +0.2 V. from the respective deposition curves.

Since the value for E_a should be the same for each solution only if the rate of dissolution of the "inert" electrode is the same, the maximum value for E_a should be found for the solution for which the rate of dissolution of the "inert" electrode is slowest. One would expect to find the maximum value for E_a in nitrate or perchlorate medium since these anions would form the least stable complexes (if any) with the platinum. It is conceivable that the rate of dissolution of an inert electrode in certain solutions might be so fast that the deposition curve for a trace would be displaced to a value more negative than that calculated from equation 2 on the assumption that E_a were zero.

The observed effect of perchloric acid in increasing the nobility of silver on platinum can be interpreted on the forgoing basis. However, it is also possible that a mechanism involving changes in the amount of platinum oxide (or hydrogen) on the surface of the electrode might be involved. More evidence is needed before a definite statement can be made.

Change in $E_{50\%}$ with Volume of Solution

Equation 3 predicts that if two solutions initially contain the same total number of reducible ions and are electrolyzed under otherwise identical conditions, the solution having the smaller volume will have the larger number of ions removed by deposition. The procedure which follows was designed to test that prediction.

A 5.00 ml portion of 0.1 M potassium nitrate solution at pH 4.0 to which silver tracer had been added was electrolyzed at a potential sufficient to precipitate most, if not all, of the silver. The activity of the solution was determined both before and after electrolysis by counting an aliquot of the supernatant. After the potential had been changed to strip the activity from the electrode the supernatant was sampled again. The analysis of the first supernatant together with the difference between the two was assumed to represent the percentages actually involved in the deposition equilibrium. The difference in activity between the second sample of the supernatant and the amount initially present before electrolysis represented the loss due to sorption and to diffusion into the salt bridges.

The volume of the solution was then increased to 25 ml by the addition of 20 ml of 0.1 M KNO_3 (pH 4.0) and the silver redeposited. Again the activity of the supernatant was determined before and after stripping the deposit from the electrode. The position of the $E_{50\%}$ for the silver in each volume was calculated by substituting the equilibrium values into equation 2 to determine $E_{50\%}$. The deposition curves were assumed to be symmetrical in making the calculation.

The data shown in Table II substantiate very satisfactorily the prediction of equation 3. The fact that the data were so good is probably the result of having only one electrode of fairly constant area involved in each comparison. The agreement obtained in these experiments (plus the

fact that all of the changes were somewhat greater than predicted) is evidence that the wide limits of error found in the deposition curves where several electrodes were involved was largely the result of differences in the electrode area.

Change in $E_{50\%}$ with A_e

Indirect evidence has already been presented to support the idea that the electrode area is an important factor affecting the extent of deposition of a trace. It was evident that any attempt to evaluate this factor quantitatively would be limited by the reproducibility of the curves. This reproducibility was first determined by calculating the $E_{50\%}$ value for several points on a curve using the equation

$$E = E_{50\%} + \frac{RT}{nF} \ln \frac{(1 - x)}{x} . \qquad (4)$$

When this was done for a number of curves, the values were regularly found to spread over 50 - 60 mv. An independent check was then made by determining one experimental point 15 times using a different electrode each time. After being boiled in nitric acid for 30 minutes, electrodes 1 through 8 were allowed to stand in a warm solution of cyanide for an hour before being used whereas electrodes 9 through 15 were not removed from the cyanide for 64 hours. From the averages of the percentage plated on the two groups of cathodes, one can calculate that the average increase in area resulting from the prolonged treatment with cyanide was 2.7 fold. This change might have been somewhat greater if new platinum electrodes had been used for the first group of experiments instead of electrodes which had already been used many times. However, an overall average of the data in Table III represents the extremes encountered in the present study in selecting an electrode at random and cleaning. It is important to note that the maximum spread of 54 mv. confirms the other results.

To study the change of $E_{50\%}$ with area, convenience favored the choice of a smaller rather than a larger electrode for comparison with the standard 5.0 cm^2 electrode. It was found that a wire of about 0.14 cm^2 plane area would reach essentially an equilibrium value in 15 hours time when the volume of solution was 5.0 ml. A factor of 35 would barely produce a significant result, and even then only if a sufficiently large number of determinations were made to allow statistical reasoning to be used. Although the results presented in Table IV are too few to allow conclusions of quantitative nature to be made, they do indicate a trend in the proper direction, i.e., less plating on the smaller electrode.

The procedure was as follows: The amount plated onto a 5.0 cm^2 electrode was determined using the procedure described in the preceeding section. In getting data for the smaller electrode a sheet of waxed paper was substituted for the 5.0 cm^2 electrode in the regular cell. The micro electrode was prepared by sealing a platinum wire into a glass tube, immersing the wire and about three inches of glass tubing into melted max, and then scraping the wax from a measured portion of the wire with a razor blade. The exposed portion of wire was carefully cleaned in the usual way with nitric acid followed by cyanide. A study of the rate of plating from 5.0 ml showed that in 15 hours one reached greater than 97% of the equilibrium value, so a 15 hour electrolysis was made before determining the distribution of tracer.

Influence of the Electrode Material on $E_{50\%}$

All of the experiments that have been described above were carried out with platinum electrodes. There is much evidence in the literature (1, 10, 11, 12) that variations arising from differences in electrode materials are often very slight, but the results given below for tantalum, gold, rhodium,

palladium, and tungsten indicate such agreement may be exceptional.

The study consisted of three parts: (1) A polarographic study of the deposition of "macro" amounts of silver on the various elements, (2) A rapid non-equilibrium determination of a deposition curve for a trace of silver, and (3) A rapid non-equilibrium determination of the reversibility of the deposition. It was hoped that by running platinum along with the other metals, a rough control would be available by which to judge how far the last two types of curves for each element deviated from equilibrium values. Points were taken after 30 minutes at a particular potential.

The polarographic halfwave potentials for a millimolar solution of silver in 0.1 M perchlorate at pH 4.0 are listed in Table V. Although the values are rather close to one another, one should note that there is a spread of nearly 0.1 V. in the halfwave potential despite the fact that is is usually possible to duplicate halfwave potentials for a platinum electrode within $\pm$ 0.01 V. (7). It seems reasonable to conclude, therefore, that the differences in polarographic behavior are real.

It was interesting to find that the deposition curves for tracer silver followed essentially the same pattern as the polarographic curves (Figure 3). The $E_{50\%}$ for silver on gold was more noble while those for tungsten and tantalum were less noble than the value for platinum.

The respective stripping curves (Figure 4) produced very marked differences: (1) The wave for tungsten was poor and stripping was incomplete; (2) Tantalum, even at +2.6 V., had stripped only a few percent more than it had at + 1.2 V.; (3) While the platinum stripping wave shifted about +0.2 V. from the deposition wave, the dissolution wave for gold was shifted - 0.06 V.

Spectrographic analyses indicated that before any depositions had been made rhodium, tungsten, and tantalum were spectrographically free from silver while platinum, palladium and gold had trace amounts present. However, the observed differencesiin behavior cannot reasonably be attributed to

variations in the amount of silver in the materials.

Miscellaneous Studies

Before carrying out the experiments described up to this point, the relative importance of each experimental factor was evaluated as carefully as possible. For example, a determination of the time required for complete (98%) plating was carried out every time a change was made in electrode area, volume of solution or electrode material. Each rate-of-plating curve was established with five or more points.

Reproducibility tests were made for all plating and stripping curves. At the same time extensive studies of sorption losses were also made. Ceresine wax was found to be the most suitable substance for covering the glass surfaces. It was found, too, that in working with nitrate and perchlorate solutions the use of a waxed paper gasket was much better than one of scotch tape. The fact that absorption losses decreased with increasing stability of the silver complex suggests that better recoveries and improved analytical separations should result from the use of more stable complexing agents.

The question of whether or not the curves represented equilibrium data is primarily a matter of definition. It was sometimes difficult to remove the activity entirely from an electrode, an experience that most investigators have encountered. Furthermore, in determining the rates of plating and stripping two very distinct rates were noted in each curve. For example, in plating silver from 25 ml of a solution onto a 5.0 cm^2 electrode, the rate of plating was rapid for the first five hours. During the following 24 hours, the activity in the supernatant dropped about 25%. An analogous study of stripping rates showed an abrupt change in rate between 15 and 30 minutes after electrolysis began, and, after 24 hours the activity of the supernatant had increased about 35%.

There is no doubt that silver diffused into platinum to form a solid

solution. A true equilibrium value would require a homogeneous solid solution to be in equilibrium with the aqueous solution and by using data obtained after 5 hours of plating, one is dealing with a constantly changing system. However, since the rate of diffusion in the solid is slow compared to the rate of plating, it should be possible to arrive at a first approximation to an equilibrium value by electrolyzing only until the rate of plating changed. The value thus obtained is in equilibrium only with respect to a thin layer of the "inert" electrode (13). Attainment of equilibrium with a homogeneous solid solution was impractical in these studies where it was desirable to use 4 mil. foil because of its sturdiness.

As yet, insufficient information is available to allow a reliable calculation of E_a to be made. It has been pointed out that factors other than E_a especially the rate of dissolution of the electrode, will influence the position of a deposition curve for a trace. It is apparent that before investigations can be undertaken to study changes in E_a (or f_3) with changes in the fraction of a surface covered by an "active" (in the thermodynamic sense) deposit, a more exact knowledge of electrode area and rates of dissolution is necessary.

It is also apparent that except for the solutions containing 1 M acid or base, the absence of a buffer resulted in appreciable changes in pH during an electrolysis. Changes as great as 4 or 5 units were quite common. For example, 0.1 M potassium nitrate at pH 4.0 was usually about pH 10.2 after a five hour electrolysis. Although such changes were undesirable, they were quite uniform at all potentials on a particular curve. For that reason the absence of a buffer was not felt to be serious, and its absence reduced the complexity of the solution.

Conclusions

Evidence has been presented to show that the volume of solution and

the electrode area affect the position of a deposition curve for a trace concentration of silver. The position of the curve is independent of the initial concentration of the trace. This behavior can be predicted from the Nernst equation providing one assumes that the thermodynamic activity of the deposit varies with the fraction of the "inert" electrode surface covered by the deposit. For that reason, the investigators who assumed that the activity of the deposit would always have a value of unity (1, 12, 14) were in error in concluding from their data that a Nernst-type expression did not describe the deposition behavior of traces. However, it does appear that the Nernst equation is inadequate for other reasons, namely, that the free energy of alloy formation and the rate of dissolution of the "inert" electrode must be considered.

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References

1. M. Haissinsky, J. chim. Phys., 43, 21 (1946).

2. L. B. Rogers and A. F. Stehney, ORNL-99, July, 1948.

3. E. H. Swift, "A System of Chemical Analysis", Prentice-Hall, Inc., New York, 1940, p. 50.

4. J. C. Griess and L. B. Rogers, ORNL-91, July, 1948.

5. I. M. Kolthoff and R. S. Livingston, Ind. Eng. Chem., Anal. Ed., 7, 209 (1935).

6. C. Feldman, Private communication.

7. L. B. Rogers, H. H. Miller, R. B. Goodrich and A. F. Stehney, MonC-236, November, 1947.

8. E. M. Skobets and S. A. Kacherova, Zavodskaya Lab., 13, 133 (1947).

9. K. Herzfeld, Phys. Zeit., 14, 29 (1913).

10. A. Coche, Compt. rend., 225, 936 (1947).

11. A. Coche and M. Haissinsky, Compt. rend., 222, 1284 (1946).

12. C. H. Haenny and P. Mivalez, Helv. chim Acta., 31, 633 (1948).

13. B. V. Rollins, J. Am. Chem. Soc., 62, 86 (1940). See also: G. V. Hevesy and M. Blitz, Z. physik. Chem., B, 3, 271 (1929); through reference #12.

14. H. G. Heal, Report MC-33 to National Research Council of Canada, December, 1943.

Table I

Comparison of Polarographic and Deposition Curves

Background Electrolyte	$E_{1/2}$ vs. S.C.E. 10^{-3} M.	$E_{50\%}$ for 10^{-5}M. vs. S.C.E.		$E_{50\%}$ for 10^{-7}M. vs. S.C.E.	
		Predicted From $E_{1/2}$	Experimental Value	Predicted From $E_{1/2}$	Experimental Value
0.1 M KNO_3 pH = 4.0	+0.32	+0.20	+0.21	+0.08	+0.48
0.1 M $NaClO_4$ 1.0 M $HClO_4$	+0.32	+0.20	--*	+0.08	+0.60
0.1 M NH_3	-0.02	-0.14	-0.10	-0.26	-0.05
0.1 M NaCN	-0.84	-0.96	-0.88	-1.08	-0.95
0.1 M NaCN 1.0 M NaOH	-0.79	-0.91	-0.89	-1.03	-0.99

*No experimental value obtained.

Table II

Effect of Volume on $E_{50\%}$ for a Trace of Silver

on 0.1 M KNO_3 at pH 4.0

Potential vs. S.C.E.	% Activity in Solution / % Activity on Cathode			Deviation from Calculated Value in mv.
	5 ml	25 ml	Calc. for 25 ml	
+0.470	3/97	31/69	13/87	29
+0.470	5/95	24/76	20/80	6
+0.500	20/80	54/46	53/47	1
+0.500	41/59	74/26	74/26	0
			Av.	9

Table III

Study of the Duplicability of the Percent Silver Deposited

From 5 ml. of 0.1 M KNO_3 (pH 4.0) on 5 cm^2 Platinum

at +0.500 V. vs. S.C.E.

Cathode No.	% Activity			% Material Balance
	Cathode	Supernatant	Bridges	
1	87	7	4	98
2	99	2	4	105
3	91	5	5	101
4	55	36	5	96
5	74	18	6	98
6	94	4	2	100
7	64	26	20*	110*
8	80	14	7	101
9	98	2	2	102
10	90	2	6	98
11	91	2	4	97
12	94	1	2	97
13	94	4	1	99
14	92	2	2	96
15	88	4	4	96
Ave.	86 ± 10	9	4	99

*Probably in error; omitted from average.

Ave. 1 - 8: 81 ± 12% = 23 mv. variation in $E_{50\%}$
Ave. 9 - 15: 94 ± 3% = 15 mv. variation in $E_{50\%}$
Ave. 1 - 15: 86 ± 10% = ± 27 mv. variation in $E_{50\%}$

Table IV

Effect of Electrode Area on $E_{50\%}$ for a Trace of Silver

on 5 ml. of 0.1 M KNO_3 at pH 4.0

Potential vs. S.C.E.	% Activity in Solution / % Activity on Cathode			Deviation from Calculated Value in mv.
	5.0 cm^2	0.14 cm^2	Calc. for 0.14 cm^2	
+0.470	$\frac{5}{95}$	$\frac{81}{19}$	$\frac{64}{36}$	23
+0.470	$\frac{5}{95}$	$\frac{66}{34}$	$\frac{64}{36}$	2
+0.500	$\frac{14}{86}$	$\frac{66}{34}$	$\frac{89}{11}$	38
+0.500	$\frac{14}{86}$	$\frac{92}{8}$	$\frac{85}{15}$	19
			Av.	20

Table V

Effect of Various Electrode Materials on the $E_{1/2}$ of a 10^{-3}M Silver Solution in 0.1 M $NaClO_4$ at pH 4.0

Electrode Material	$E_{1/2}$ vs. S.C.E.
Gold	+0.35 V.
Palladium	+0.32 V.
Platinum	+0.31 V.
Rhodium	+0.30 V.
Tantalum	+0.26 V.*
Tungsten	+0.28 V.

*Two smaller waves were found with halfwave potentials at +0.13 V. and -0.49 V.

Figure I

Typical Deposition and Stripping Curves

for Silver in Various Media

○ "Trace" silver in 0.1 KNO_3 pH 4.0

● 10^{-5}M silver in 0.1 M KNO_3 pH 4.0

△ "Trace" silver in 0.1 M NH_3

▲ 10^{-5}M silver in 0.1 M NH_3

□ "Trace" silver in 0.1 M NaCN + 1.0 M NaOH

■ 10^{-5}M silver in 0.1 NaCN + 1.0 M NaOH

The dotted lines indicate the corresponding stripping curves.

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FIG. 1

Drawing # 6052

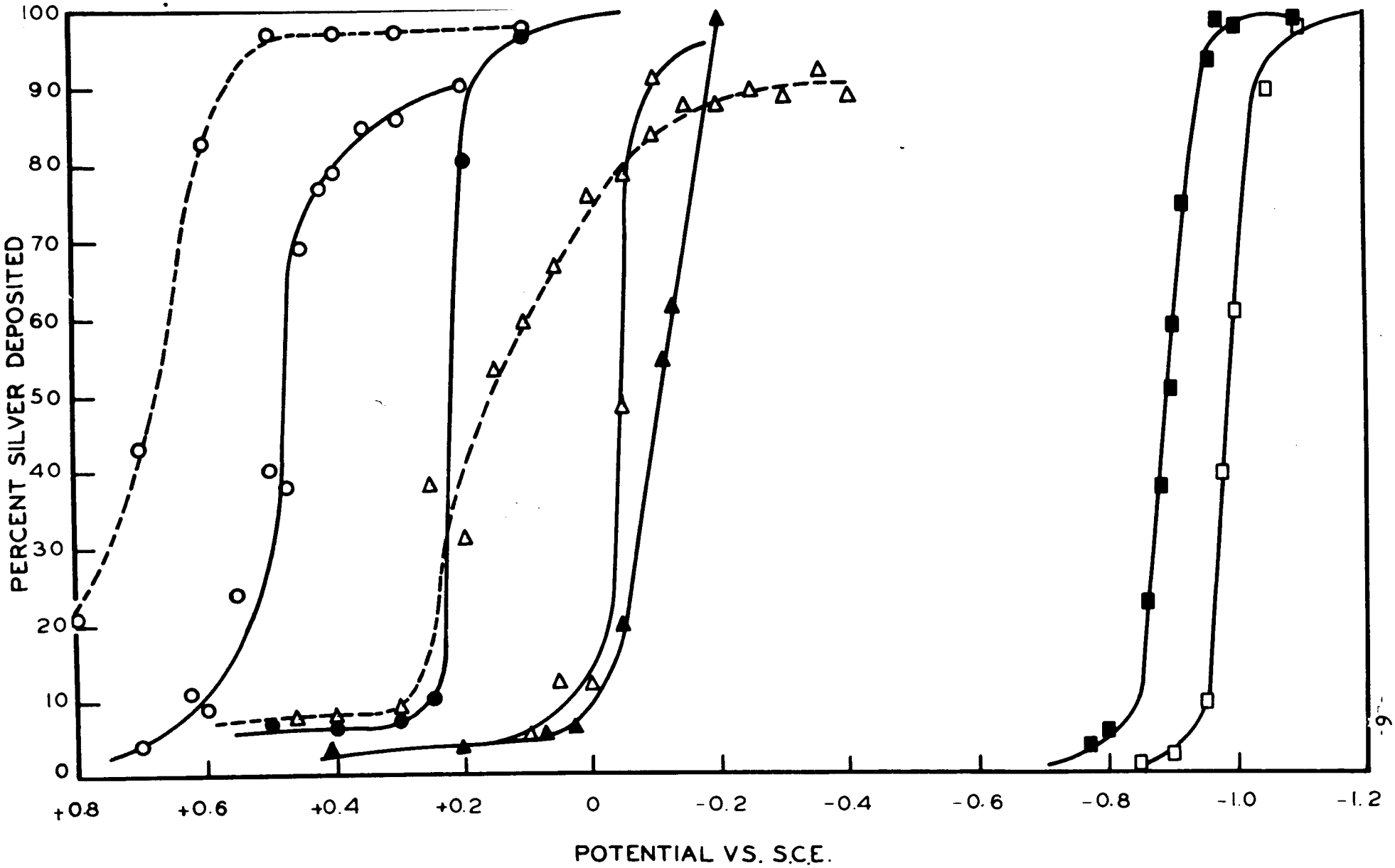


Figure II

Deposition Curves for 10^{-6} M Silver in 0.1 M

KNO_3 pH 4.0

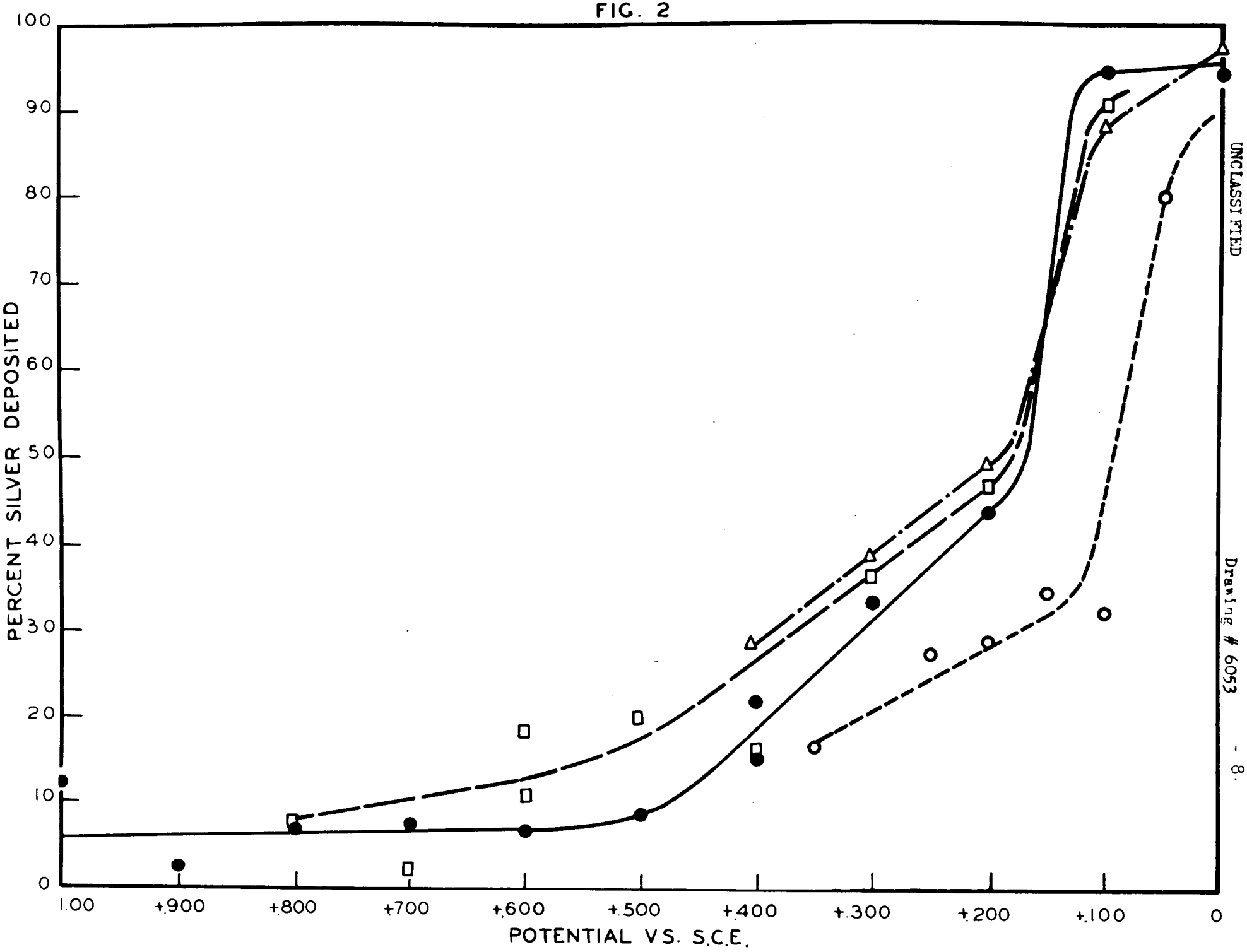
○ - - - - - - - - - - Run No. 1

● ———————————— Run No. 2

□ --- --- --- --- --- Run No. 3

△ --- . --- . --- . Run No. 4

FIG. 2



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Drawing # 6053

Figure III

Deposition Curves for a "Trace" of Silver in 0.1 M KNO_3 (pH 4.0) on Various Electrode Materials

- □ Gold
- ■ Platinum
- ▲ Tungsten
- △ Rhodium
- ○ Palladium
- ● Tantalum

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FIG. 3

Drawing # 6054

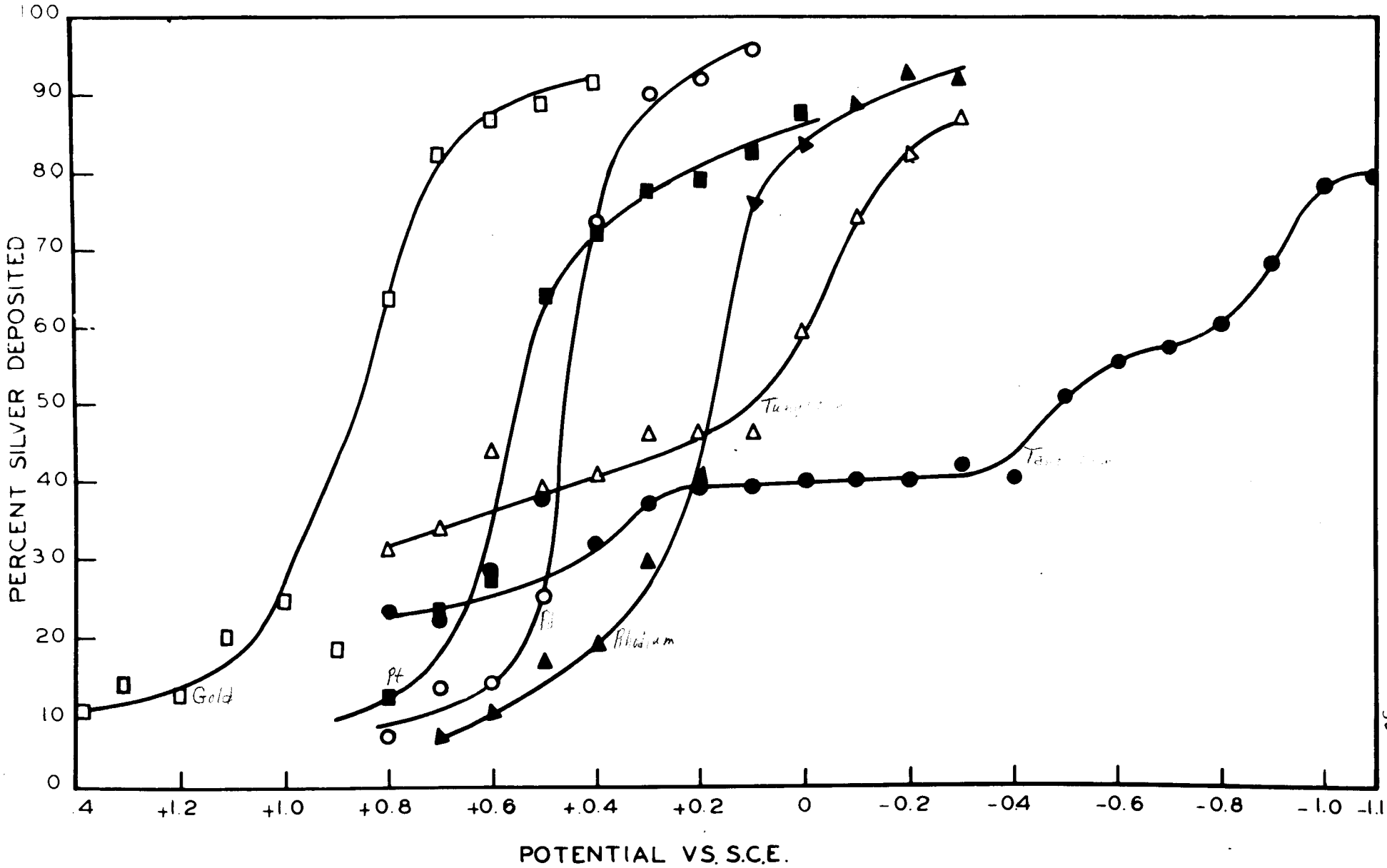

Figure IV

Stripping Curves for a "Trace" of Silver on Various Electrode Materials in 0.1 M KNO_3 pH 4.0

- ▢ Gold
- ■ Platinum
- △ Tungsten
- ▲ Rhodium
- ○ Palladium
- ● Tantalum

FIG. 4

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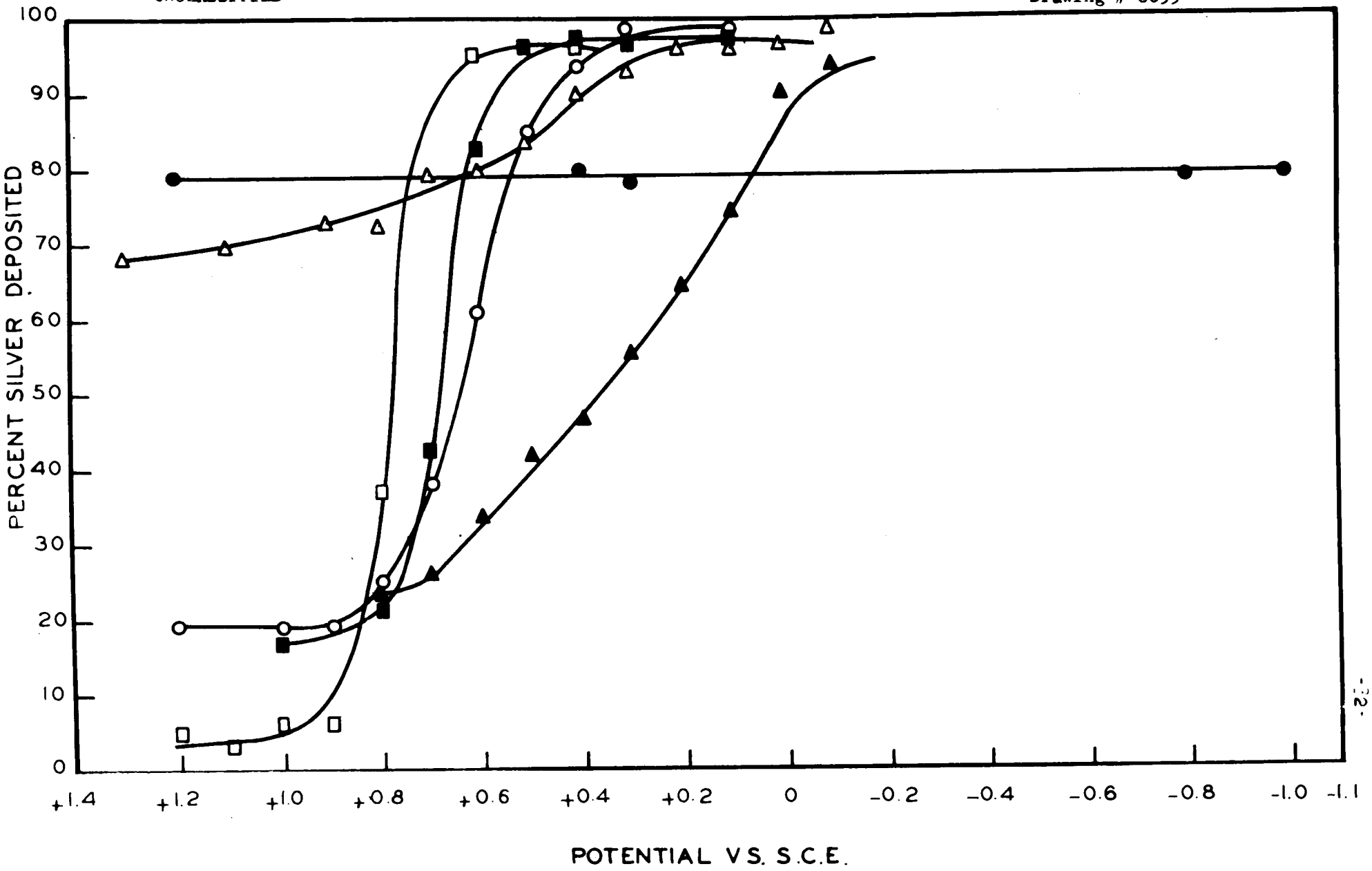
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