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COMPARISON OF POLAROGRAPHIC CURVES OBTAINED WITH A ROTATED MICRO-ELECTRODE AND A STATIONARY ELECTRODE.

H.H. Miller and L.B. Rogers

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Comparison of Polarographic Curves Obtained with a Rotated Micro-Electrode and a Stationary Electrode.

H. H. Miller and L. B. Rogers

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The technique and advantages of using stationary platinum electrodes for making automatically recorded measurements with the polarograph have been discussed in a previous report (2). In that paper it was pointed out that because the diffusion current is proportional to the electrode area, larger electrodes are more suitable for the analysis of very dilute solutions than the usual microelectrode. Similarly, Kolthoff and Lingane (1) and Skobets and Kacherova (3) have pointed out that the larger diffusion current resulting from the use of a rotated electrode as compared to a stationary one, gave the former an advantage of greater sensitivity in the analysis of very dilute solutions. It is the purpose of the present paper to compare the data obtained from a dilute solution for a large stationary electrode with those for a rotating microelectrode.

The rotating electrode used in this study was similar to the one Kolthoff and Lingane described with the exception that a set screw was added to the bottom of the shaft so that the platinum wire could easily be replaced. The electrode was coated with ceresin wax several times and the platinum wire scraped to expose about 2.5 mm. of clean wire. The stationary electrode was a 2.1 cm^2 platinum foil sealed in a soft glass tube which was filled with mercury to facilitate electrical contact.

About 30 ml. of solution, which had been deaerated 15 minutes with oxygen-free nitrogen, was polarographed. The potentials in each case were measured against an outside saturated calomel electrode (S.C.E.).

Using 0.1 M HCl, a comparison was made of the residual currents (i.e. blank runs) for the two electrodes by starting at zero potential and proceeding towards negative potentials until hydrogen was evolved. An analogous wave was obtained by starting at zero potential and going toward positive potentials until oxygen was evolved. Composite curves were constructed for each electrode

and these are shown in Figure 1 as curves I and II.

If, instead of starting at zero potential and going negative, one started at a potential where the oxygen was being evolved, the curve for the stationary electrode did not coincide with the one described above. Throughout most of the region of positive potential the residual current in the latter case was opposite in sign but of the same order of magnitude as that current found when the potential was applied in the opposite direction. Curve III in Figure 1 is a representative example. A comparison of curves I and III in Figure 1 illustrates how errors can be introduced into a series of analyses if a new blank is not run when the direction of polarization is changed. The irregularities shown in the curves for the stationary electrodes are common to this type of electrode. The larger size of the electrode and the residual current merely tended to make the irregularities more conspicious.

The sign of residual current for the rotating electrode also depends upon the direction of polarization. However, the differences are less conspicious because the residual current is much smaller, being in the order of one-tenth microampere or less.

Another comparison of the two types of electrodes were made by recording the curves for two ions with each electrode under conditions of an actual analysis. One set of curves for the reduction of silver ion is illustrated by Figure 2. A similar set of curves for a solution of ferric ion is shown in Figure 3. (The curves have not been corrected for IR drop). The figures indicate that although the particular stationary electrode used in this study gave a larger diffusion current than the rotating electrode, the results from the rotating electrode were easier to interpret because of the smaller residual current, the sharper initial break in the deposition curve, and the usual absence of a maximum.

The better overall definition of a curve for the rotating electrode facilitated the determination of the half-wave potential in very dilute solutions.

Figure 1

A comparison of residual currents obtained with a stationary platinum electrode and a rotated platinum microelectrode in 0.1 M HCl.

I. Rotated microelectrode with the potentials started at zero; 0.050 cm^2 area, 600 r.p.m.

II. Stationary electrode, 2.1 cm^2 in area, with the potentials started at zero.

III. Stationary electrode with the potential started at approximately 1.3 V.

Drawing # 5950

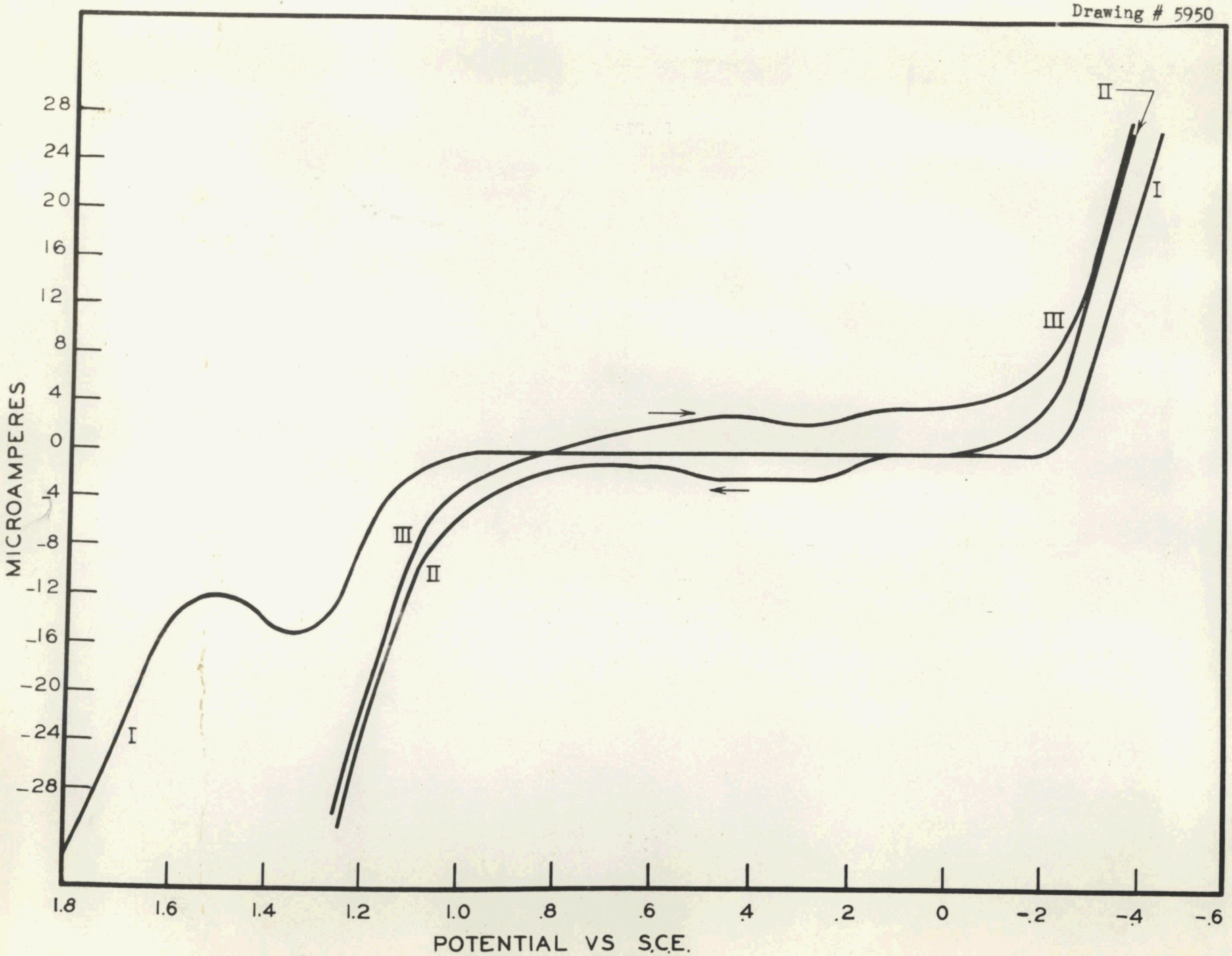

Figure 2

Comparative curves obtained with a stationary platinum electrode and a rotated microelectrode for a solution of 5.0×10^{-5} M $AgNO_3$ in 0.1 M KNO_3 and 0.01% gelatine at pH 4.0.

I. Stationary platinum electrode, 2.1 cm^2 in area.

II. Blank (residual current) with stationary electrode.

III. Rotated platinum microelectrode, 0.050 cm^2 area, 600 r.p.m.

IV. Blank (residual current) with rotated microelectrode.

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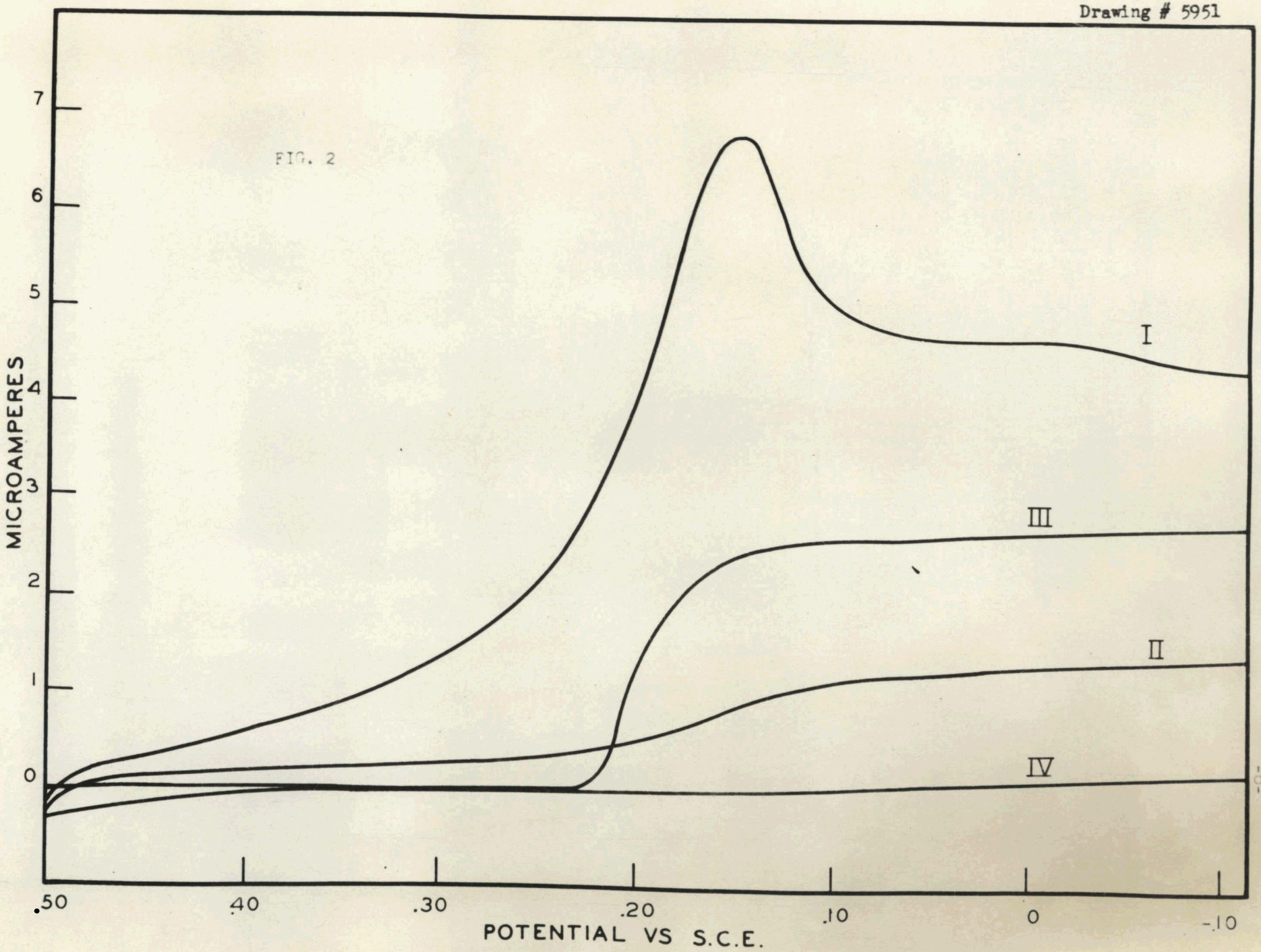


Figure 3

Comparative curves obtained with a stationary platinum electrode and a rotated platinum microelectrode for a solution of 5.0×10^{-4} M ferric chloride in 0.1 M hydrochloric acid.

I. Stationary platinum electrode, 2.1 cm^2 in area.

II. Blank (residual current) with stationary electrode.

III. Rotated platinum microelectrode, 0.050 cm^2 area, 600 r.p.m.

IV. Blank (residual current) with rotated microelectrode.

FIG. 3

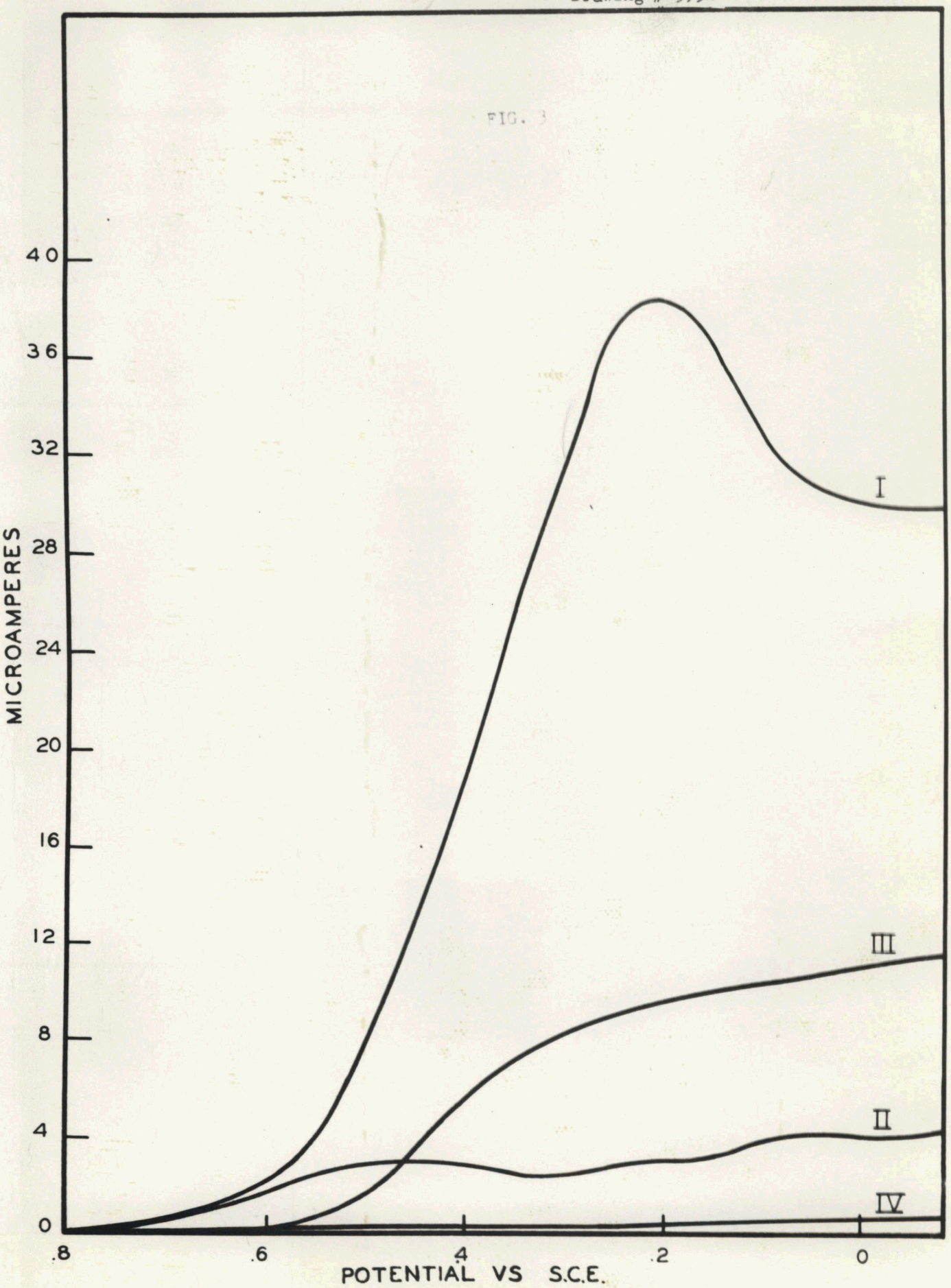
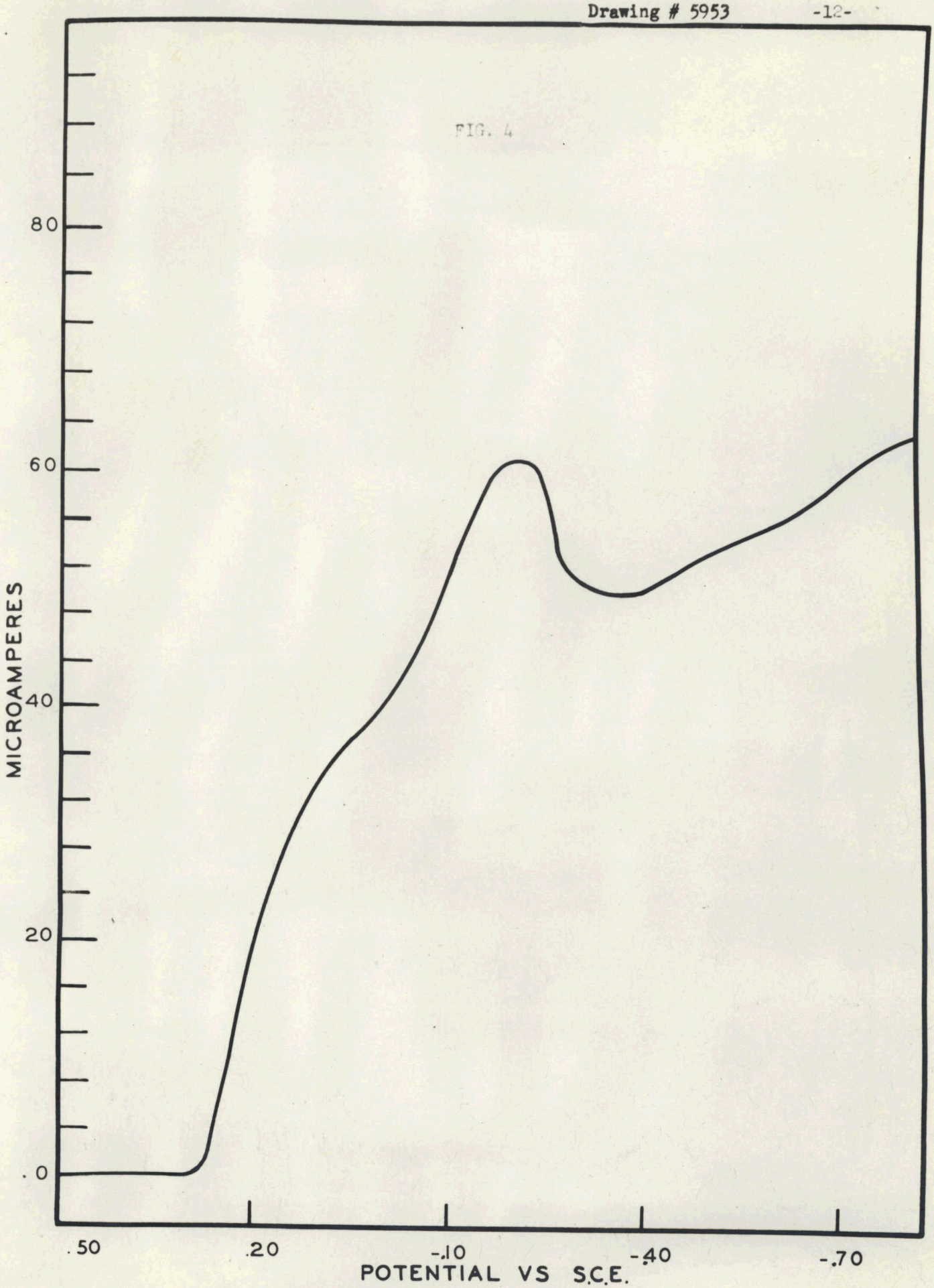

40
36
32
28
24
20
16
12
8
4
0
MICROAMPERES
.8
.6
.4
.2
0
POTENTIAL VS S.C.E.
I
II
III
IV

Figure 4

Polarographic maximum obtained with a rotated platinum microelectrode in a solution containing 5.0×10^{-5} M $AgNO_3$ in 0.1 M KNO_3 and 0.01% gelatine at pH 4.0. Rate of polarization was 4.65 mv/sec.

FIG. 4



The values listed in Table I for different concentrations of silver were in fair agreement with those predicted from earlier data.

Table I

Half-Wave Potentials for the Reduction of Silver Ion in 0.1 M KNO_3 at pH 4 Obtained with a Rotated Electrode.

Conc. of $AgNO_3$	$E_{1/2}$ v. (vs. S.C.E.) Calc.	Exp.
5.0×10^{-4} M.	0.30	0.31 0.31
5.0×10^{-5} M.	0.24	0.24 0.25
5.0×10^{-6} M.	0.18	0.17 0.16

In conclusion, it is interesting to note that during the course of the above study maxima unexpectedly appeared in some of the curves of the rotating electrode. Many of the maxima were relatively large and they were often immediately preceded by an inflection in the polarographic wave. See Figure 4. Although the maximum may be due indirectly to the discharge of silver it is more probably the result of a brief discharge of hydrogen. Support for that type of process is Curve II in Figure 1 which shows a similar but less striking maximum that was found in the oxygen wave.

References

1. Kolthoff, I. M., and Lingane, J. J., "Polarography", p. 444, New York, Interscience Publishers, 1941.

2. Rogers, L. B., Miller, H. H., Goodrich, R. B., and Stehney, A. F., MonC-236, November 13, 1947.

3. Skobets, E. M., and Kacherova, S. A., Zavodskaya Laboratoriya 13, 133-137 (1947).