A STUDY OF THE DEAD-STOP ENDPOINT AND THE DETERMINATION OF PRIMARY AROMATIC AMINES

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A STUDY OF THE DEAD-STOP INDICATOR

AND

THE DETERMINATION OF PRIMARY AROMATIC AMINES

By

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PART I

A STUDY

OF

THE DEAD-STOP ENDPOINT

INTRODUCTION

The dead-stop endpoint technique is an electrometric method for determining the stoichiometric point in a volumetric analysis. In contrast to most electrometric methods of analysis, the dead-stop endpoint technique is characterized by the simplicity and ease of noting the endpoint and also by the relative inexpensiveness of the apparatus required. The general method requires the application of a small potential between two platinum electrodes and watching for the appearance or disappearance of a current at the endpoint as noted by a galvanometer attached in series to the circuit. In general, the endpoint in this method is characterized by three different modes of functioning of the galvanometer; (a) the appearance of a small flow of current at the stoichiometric point; (b) the disappearance of a current at the stoichiometric point; (c) the gradual disappearance of the current at the endpoint followed by an increase of current after the endpoint. This last method (c) may require plotting of the relative current near the vicinity of the endpoint in order to determine accurately the stoichiometric point. At first glance, this method would appear to be merely a special case of the normal amperometric method, but as will be shown later, this is not the case.

The dead-stop endpoint technique was originally devised by Foulk and Bawden (7) and applied to the iodine-sodium thiosulfate system, and since that time has found numerous

general applications. Dappinger and Fouik (6) have suggested a number of electrochemical indicators which may be devised in order that this endpoint will function. Of considerable importance is the application by Wernimont and Hopkinson (15) for the determination of the endpoint in the Karl Fischer method for determination of water. This latter application is perhaps by far the most important one. An excellent discussion of most of the applications up to the period of 1942 is contained in a paper by Stock (16). This paper, in addition to giving general descriptive procedures for the methods of application, also discusses the theory as set forth by Foulk and Bowden (7) and contains an excellent bibliography. A more recent application of considerable importance is by Sense, Hansen and Swift (13), who used this technique for indicating the endpoint in a coulometric method for determining thioglycol with electrolytically generated bromine. This method has since been applied by other authors in coulometric work, obtaining excellent results in this manner. Foster, Farrington and Swift (5) have applied it to the determination of iodide while Myers and Swift (12) have made studies in connection with the determination of tripositive arsenic. Dubois and Hogg (4) have applied this technique to the determination of bromine addition numbers for unsaturates with good success. Bruce (2) has modified this technique by the use of mercuric salts to catalyze the addition reaction, greatly speeding up the addition reaction in this manner and

detecting errors due to substitution. Meier, Myers and Swift (11) have applied this endpoint technique in the coulometric titration of chromate and vanadate by means of electrolytically generated cuprous copper while Ferrington and Swift (6) have made a recent study of a coulometric titration using electrolytically generated chlorine, using the dead-stop endpoint technique. Ramsey, Ferrington and Swift (16) have made a further study of this last procedure, using electrolytically generated iodine instead of chlorine for the determination of tripositive arsenic. Schroeder, Hay and Mills have determined amino acids by iodometric titration of their copper salts and have obtained good results, the accuracy of the method apparently being much better than by the starch endpoint. Gale and Mosher (5) have devised a method for the determination of milligram quantities of vanadium in the presence of uranium using the dead-stop procedure.

THEORY

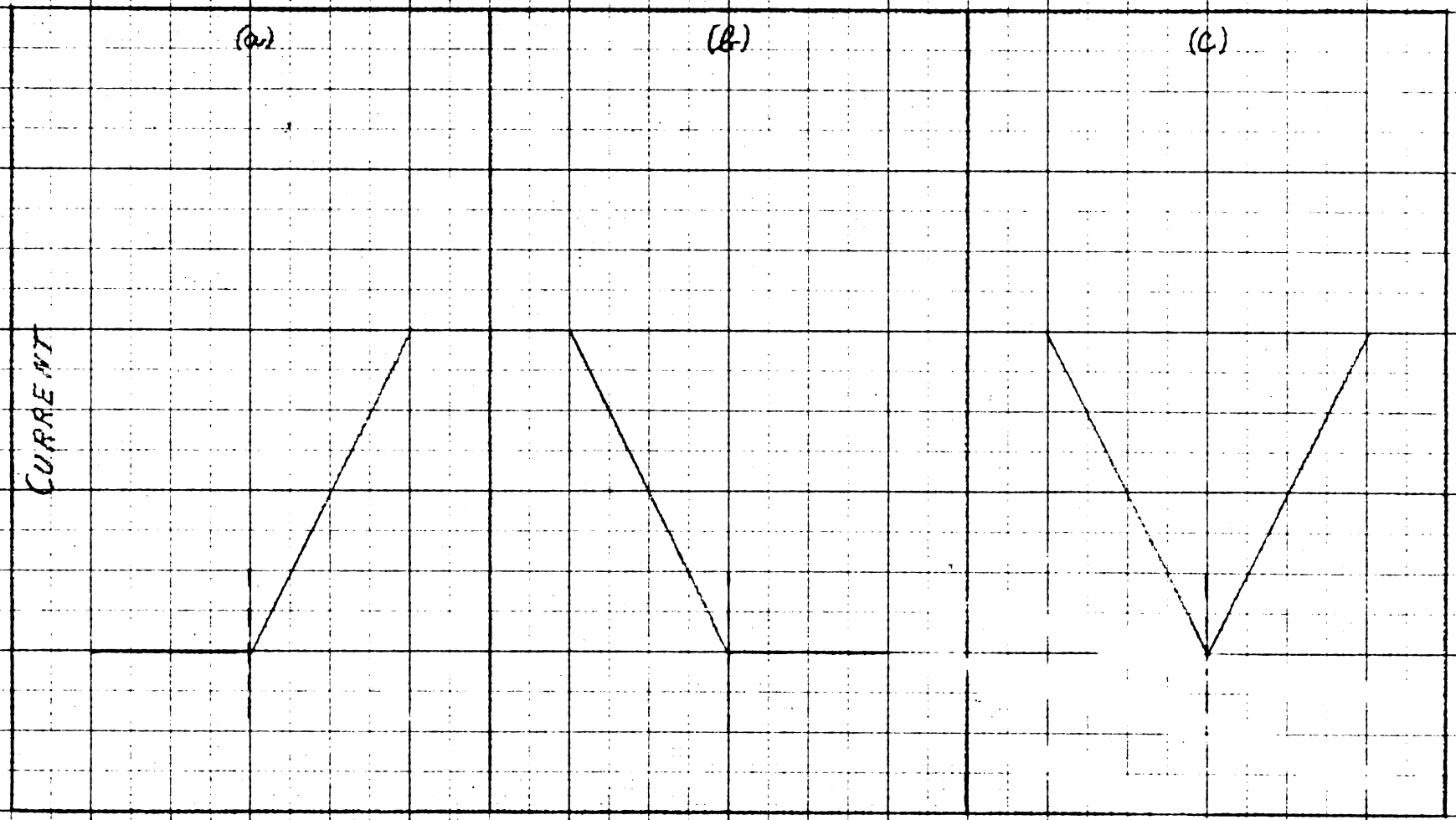
The theory of the dead-stop endpoint technique was originally proposed by Foulk and Bruden (7). They proposed, in the same manner as Willard and Fenwick (18), that metallic electrodes owe their effect in electrometric titrations to gas reaction taking place on the surface of the metal, this phenomenon resulting in the polarization of the electrodes. These authors state that the fundamental requirement for the production of the dead-stop endpoint is the use of so low a

potential between the platinum electrodes that the back electromotive force of polarization balances it and consequently no current flows. Hence, this endpoint will function when a transition from the polarization of at least one electrode to the depolarization of both or vice versa occurs. They assume the polarization is due to oxygen adsorbed on the anodically charged electrode and hydrogen on the cathodically charged electrode and that the anode can be depolarized by a suitable reducing agent and the cathode can be depolarized by a suitable oxidizing agent. These authors proposed that three methods of functioning of the electrodes during a titration can occur. (a) One of the electrodes is polarized up to the endpoint and this electrode becomes depolarized at the first slight excess of the titrating agent while the other electrode remains depolarized during the entire course of the titration. (b) Both electrodes are originally depolarized and one or both become polarized at the endpoint. (c) Both electrodes are originally polarized, due to adsorbed hydrogen on the one and adsorbed oxygen on the other, but become effectively depolarized at the endpoint. Böttger and Forche (1) have taken the view that the amount of applied potential (15 millivolts) is insufficient to cause liberation of either hydrogen or oxygen, and in addition, have shown that when the iodine-thiosulfate titration was carried out in a divided cell, the electrode potential varied with concentration. This being the case, it would appear that the

dead-stop phenomenon is not entirely a polarization effect.

After considerable study, a hypothesis was finally postulated to the effect that merely a reversible oxidation reduction system must be present which will function effectively before or after the endpoint when a small potential is applied across the two platinum electrodes. A further refinement of this proposal was to state that an electrolytic cell must function up to or commence to function at the endpoint. This proposal would then explain the two methods of functioning of the current as follows: (a) an electrolytic cell must commence to function as the stoichiometric point is reached, which would thus result in the appearance of a current; and (b) an electrolytic cell must function until the endpoint is reached, which means a current would flow up to the stoichiometric point and would then disappear. To this may be added a third method of functioning of the current: (c) one reversible electrolytic cell must cease to function as the endpoint is reached and a second reversible electrolytic cell must commence to function at the endpoint. These three different modes of functioning of the current may be shown diagrammatically as in Figure 1. At first glance this would appear to be merely a special case of the normal amperometric titration. However, in this case two half cell reactions are involved and the current flowing between them is measured whereas in the normal amperometric method, only one half cell reaction is important, the amount

FIGURE 1



of oxidation or reduction at the dropping mercury electrode being the important factor. Kolthoff (6) has suggested that, "the term amperometric should be applied only to titrations in which a diffusion-controlled limiting current is measured, to differentiate it from methods such as the 'dead-stop' end-point--".

In order to test the validity of the hypothesis as presented above, various systems were suggested which should react and give an endpoint indicative of the dead-stop technique. Furthermore, if the hypothesis as suggested were correct, the potential of the two platinum electrodes without any potential applied should both be the same, and should give the potential, electrode-solution versus the saturated calomel electrode, whereas the potential of the two electrodes during the entire course of the titration should show a constant difference equal to the potential applied from an outside source across the two electrodes. The systems proposed included the titration of reducing agents such as ferrous sulfate, potassium ferrocyanide, titanous sulfate, hydrogen peroxide and sodium thiosulfate with a variety of oxidizing agents such as ceric sulfate, potassium permanganate, potassium dichromate and iodine. These various systems were merely subjected to a qualitative test rather than to a quantitative one, in as much as the endpoint was being determined both potentiometrically and by the dead-stop technique.

Apparatus

The apparatus used to determine both the potential of the two electrodes and also the current is shown in Figure 2. This apparatus consists of the Beckman pH meter (Model G), a Beckman calomel electrode and a Fischer Scientific Company Electropode. The dropping mercury electrode was removed from the Electropode and leads from the two platinum electrodes were inserted in its place. The Electropode was then used to apply the potential across the two electrodes and in addition the enclosed galvanometer was used to measure the current flowing. One added advantage in the use of this instrument is the fact that the sensitivity of the galvanometer can be regulated over a wide range. The actual current in this case is not known, but could be calculated after calibration of the galvanometer; however, the absolute current value in terms of microamperes is not required but merely the relative current needs to be known. The potential of each of the two platinum electrodes was measured against the Beckman saturated calomel electrode, the two electrodes being connected one to each pole of a double throw switch, both poles being in turn connected by a single lead to the Beckman pH meter. It should be pointed out that a very inexpensive apparatus for determining the dead-stop endpoint has been devised, the only parts being required consisting of a small battery with a potential of about two volts, two platinum electrodes, a sensitive galvanometer, and a variable resistor for regulating

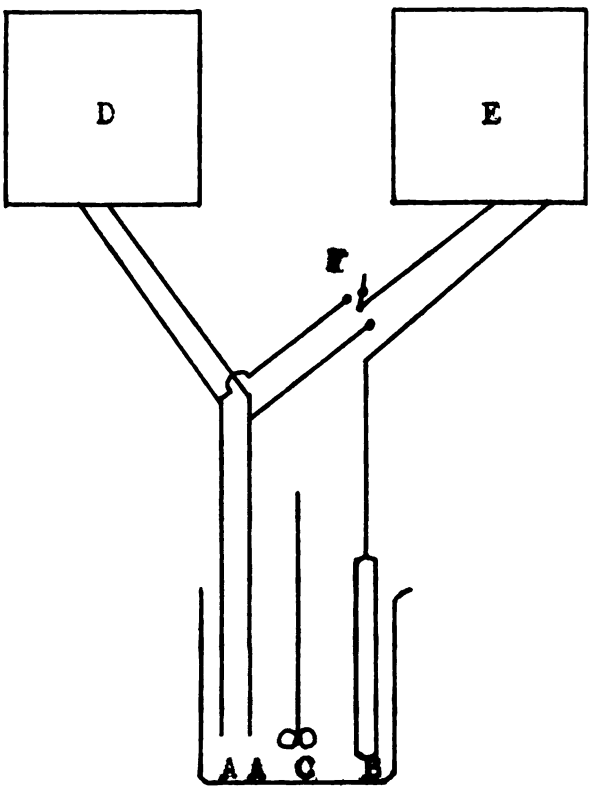


FIGURE 2

APPARATUS

A.-Platinum Electrodes
B.-Saturated Calomel Electrode
C.-Glass Stirrer
D.-Fischer Scientific Company Electropode
E.-Beckman pH Meter (Model G)
F.-Two Way Switch

the applied potential. A full description and diagram of this apparatus is contained in a paper by Kolthoff and Hopkinson (17).

Reagents

Solutions of sodium thiosulfate, iodine with potassium iodide, potassium permanganate, ceric sulfate, ferric ammonium sulfate and sodium metavanadate were prepared in the usual manner. A 0.1000 potassium dichromate solution was prepared by dissolving the appropriate amount of the dried primary standard, reagent grade crystals in a one liter volumetric flask. Ferrous sulfate was prepared by the method of Duke (5). A titanous sulfate solution was prepared by dissolving metallic titanium sponge in dilute sulfuric acid and filtering off insoluble materials. With the exception of the standard dichromate, none of these solutions was standardized in as much as merely a qualitative examination was required, the dead-stop endpoint being compared with the potentiometric endpoint. Certain indicators such as o-phenanthroline ferrous with ceric sulfate, potassium thiocyanate with ferric and the color of permanganate and iodine were found to change color within a few hundredths of a ml. from the potentiometric and dead-stop endpoints.

General Procedure

A 10 ml. portion of the solution to be titrated was

placed in a 400 ml. beaker together with 100 ml. of water and 20 ml. of 1-4 sulfuric acid. In the sodium thiosulfate-iodine titration, 200 ml. of water were used. The platinum electrodes, which had been previously cleaned by allowing them to stand in a potassium dichromate-sulfuric acid cleaning solution for at least one hour, were connected to the Electropode and placed in the solution together with the Beckman saturated calomel electrode and the glass paddle of the mechanical stirrer. A potential had been previously determined at which value a reversible electrochemical cell would function effectively with the ions involved. This potential was applied to the platinum electrodes by means of the Electropode, the stirrer was started, and the reagent was added from a buret in small increments. The current flowing between the electrodes together with the potential of each electrode versus the saturated calomel electrode was measured after each small increment of the reagent had been added with the potential applied and the solution being stirred. In the vicinity of the endpoint the increment of the reagent added was of the order of 0.01-0.05 ml.

RESULTS

Various systems were suggested in which it was thought that this technique might be applied. These systems included the titration of ferrous sulfate with ceric sulfate and potassium permanganate; potassium ferrocyanide with ceric

sulfate and potassium permanganate; titanous sulfate with ceric sulfate and potassium permanganate; hydrogen peroxide with potassium permanganate; pentavalent vanadium with ferrous sulfate; ferric sulfate with titanous sulfate; and sodium thiosulfate with iodine. These various systems were merely subjected to a qualitative test rather than to a quantitative one.

The results are shown in the following tables and graphs. It is interesting to note that in all cases the current break corresponds precisely to the sharp break in the potential of the system and furthermore, during the entire course of the titration the potential changes gradually from the system originally present to the one present after the endpoint. From the nature of the data presented, there can be little doubt that the prime requirement of the dead-stop endpoint technique is merely the functioning of a reversible electrolytic cell.

Consider, for example, the titration of sodium thiosulfate with iodine; both electrodes initially assume the potential of the platinum electrode-tetrathionate solution. After a small potential has been applied, one electrode assumes a more negative potential and the other electrode a more positive potential, the potential difference between the two electrodes versus the saturated calomel electrode being equal to the applied potential. In this titration no current flows until the endpoint is reached. Until the potentiometric break

occurs, the potentials observed are those which would be expected with the thiosulfate-tetrathionate system (10). Since this couple is not reversible no electromotive force will be established and hence no current will flow. After the potentiometric break the potentials which are observed correspond to those characteristic of the iodine-iodide system. Since this couple is easily reversible so that iodine may be oxidized at the more or more positively charged electrode and the iodine may be reduced at the cathode or more negatively charged electrode, an electrolytic cell will function and a current will flow. The reverse titration, the titration of iodine with sodium thiosulfate was made and the changes in potential and current were followed. Initially, both electrodes obtain the potential of the platinum electrode-iodine, iodide solution. After a small potential is applied the one electrode becomes more positively and the other electrode more negatively charged, the potential difference between the two electrodes again being equal to the applied potential. There is a large current flow at the start when the small potential is applied due to the presence of both the iodine and iodide which reacts with the two electrodes as a reversible electrolytic cell. The solution as originally prepared contained an excess of the iodide; consequently, as the thiosulfate is added iodine will be consumed and there will be a steady decrease in the amount of current due to the limiting value of the iodine present. When the endpoint is

reached, all the iodine is consumed and only iodide and tetrathionate remain. This does not constitute a reversible electrolytic cell and consequently no current flows. After the endpoint, thiosulfate is also present but this together with the tetrathionate does not constitute a reversible electrolytic cell and hence no current will flow even after the endpoint.

In the case of the titration of potassium ferrocyanide with ceric sulfate, there is initially present a large amount of the ferrocyanide and a small amount of the ferricyanide, hence a small amount of current will flow. As the ceric is added, more ferricyanide is formed and hence the current increases. The current apparently increases to a maximum when the concentration of ferrocyanide equals the concentration of ferricyanide and further addition of the ceric reagent causes a decrease in the current due to decrease in the concentration of the ferrocyanide, which has now become the limiting component for the amount of current. At the endpoint, there are present only ferricyanide and cerous ions which do not constitute a reversible electrolytic cell and hence no current will flow. Before the endpoint is reached the reversible ferricyanide-ferrocyanide couple is present and a current flows. Up to this point, the potentials observed are those to be expected with the platinum electrode-ferricyanide,ferrocyanide system. It should be pointed out that the consumption of ferrocyanide by electrolytic oxidation

will not affect the accuracy of the titration because the same amount of ferrocyanide will be produced by reduction of the ferricyanide at the other electrode. At the equivalence point only ferricyanide and cerous ions will be present and these do not constitute an electrolytic cell and therefore no current will flow. With the first slight excess of ceric sulfate, the cerous-ceric reversible couple begins to function. The current now flows again by electrolysis and the current increases as the limiting substance, ceric sulfate, is increased, the potential assuming the value of the ceric-cerous system.

Various systems exhibited varying degrees of reversibility as noted by the amount of current flowing at a specific applied potential and a definite concentration of the ions involved. Hence it was necessary to determine in advance a potential at which the couple would function effectively. The iodine-iodide couple and also the ferrous-ferric system function effectively at an applied potential of 50 mv. For the other systems, such as the cerous-ceric, titanous-titanic, a higher applied potential is required, 100 mv. being sufficient. It follows, of course, that up to a certain limit the current flow is proportional to the applied potential.

It should be noted that in all cases which were investigated, the break in the potential curve coincides with the break in the current curve so that the dead-stop technique gives as reliable results as the potentiometric method.

The experimental results for the endpoint region of the sodium thiosulfate-iodine titration are tabulated below and are shown in Figure 3. The experimental results for the other systems are shown graphically in the other diagrams.

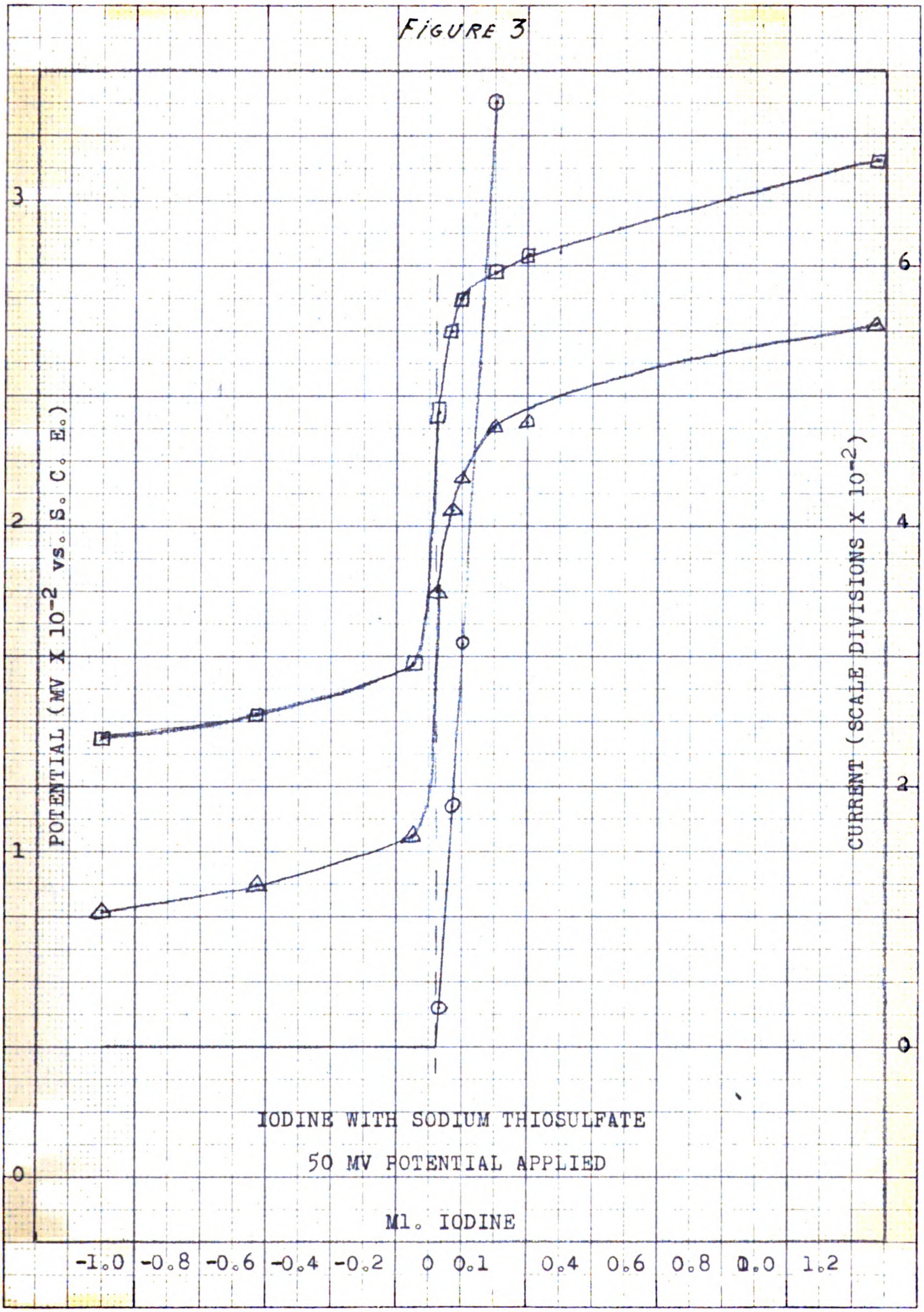
Table I

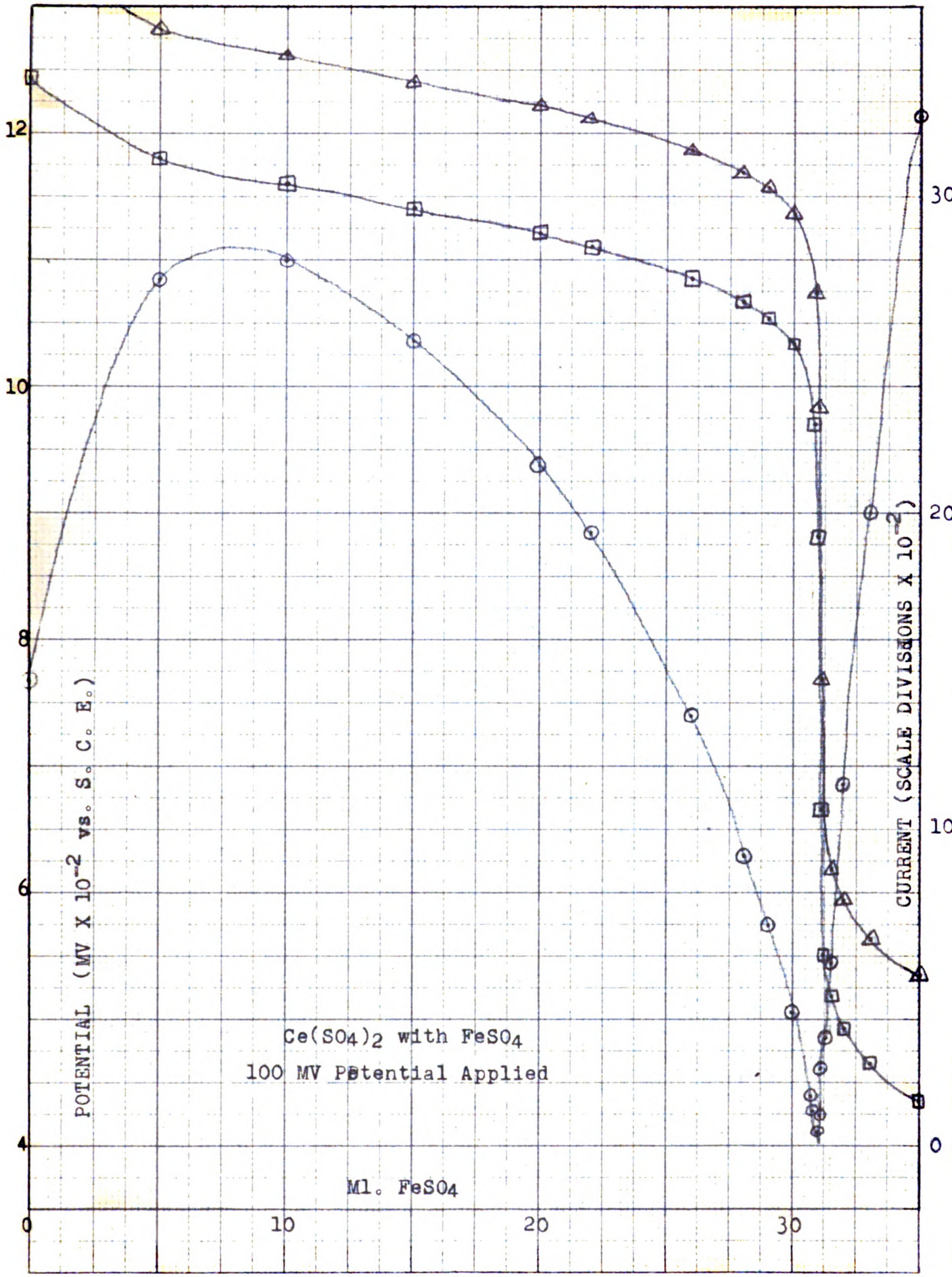
Titration of Sodium Thiosulfate with Iodine

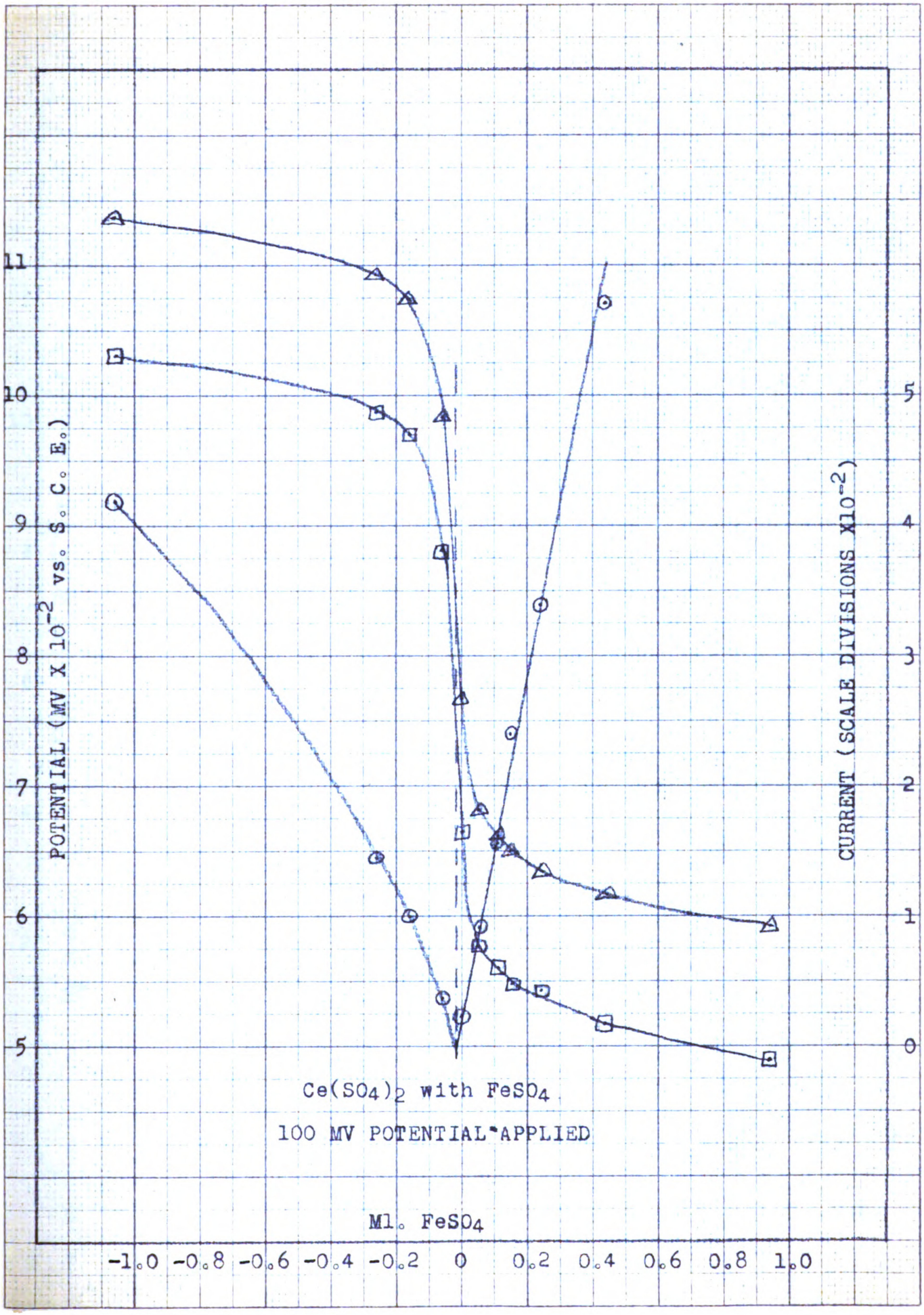
(Endpoint Region)

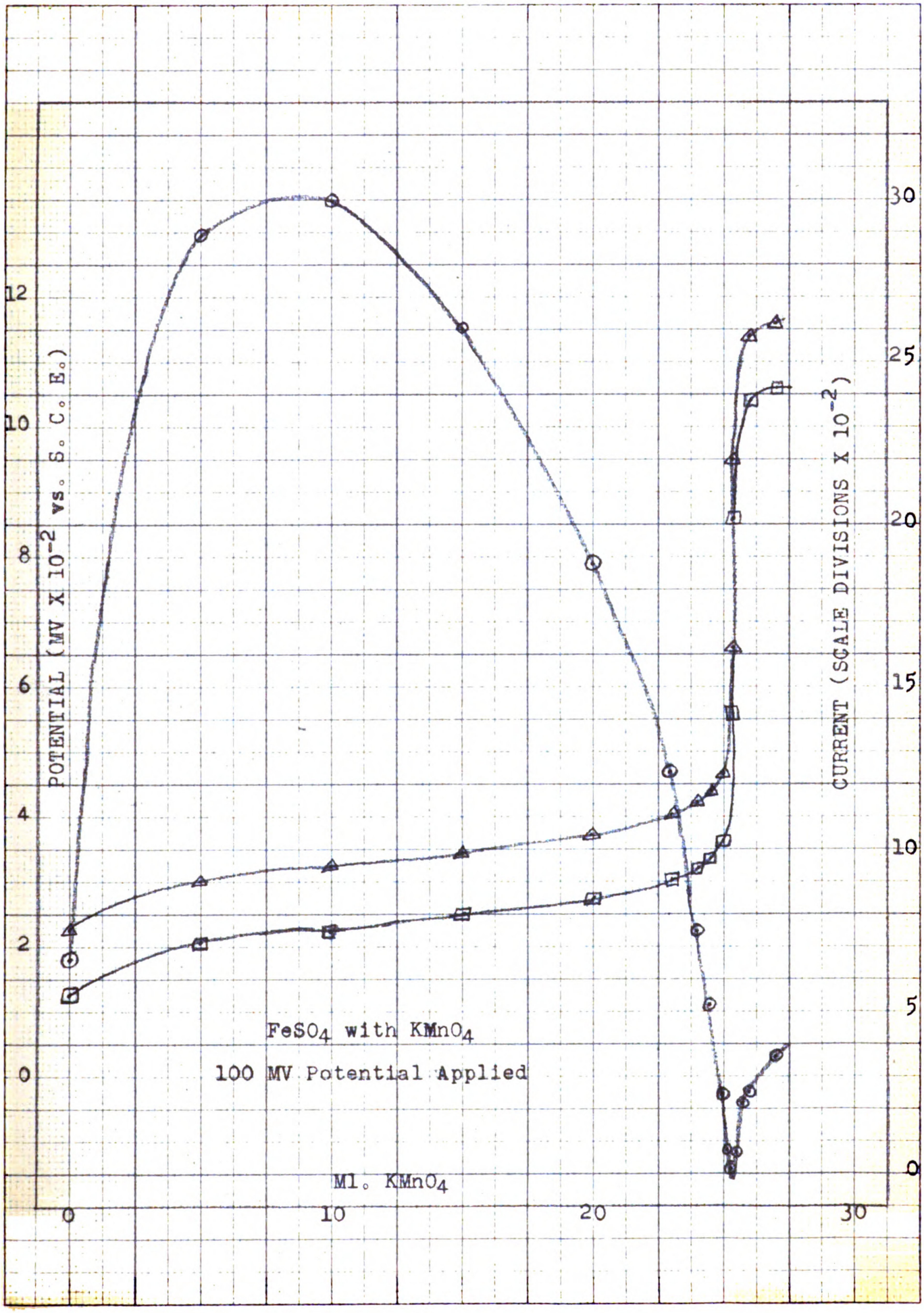
Ml. Iodine	Current Scale Units	$E_{(-)}$ mv.	$E_{(+)}$ mv.
-1.00	0	82	135
-0.53	0	90	142
-0.05	0	105	158
0.00	0		
0.03	30	180	225
0.07	185	205	260
0.10	310	215	270
0.20	725	230	278
0.30	1100	232	283
1.27	5200	262	313

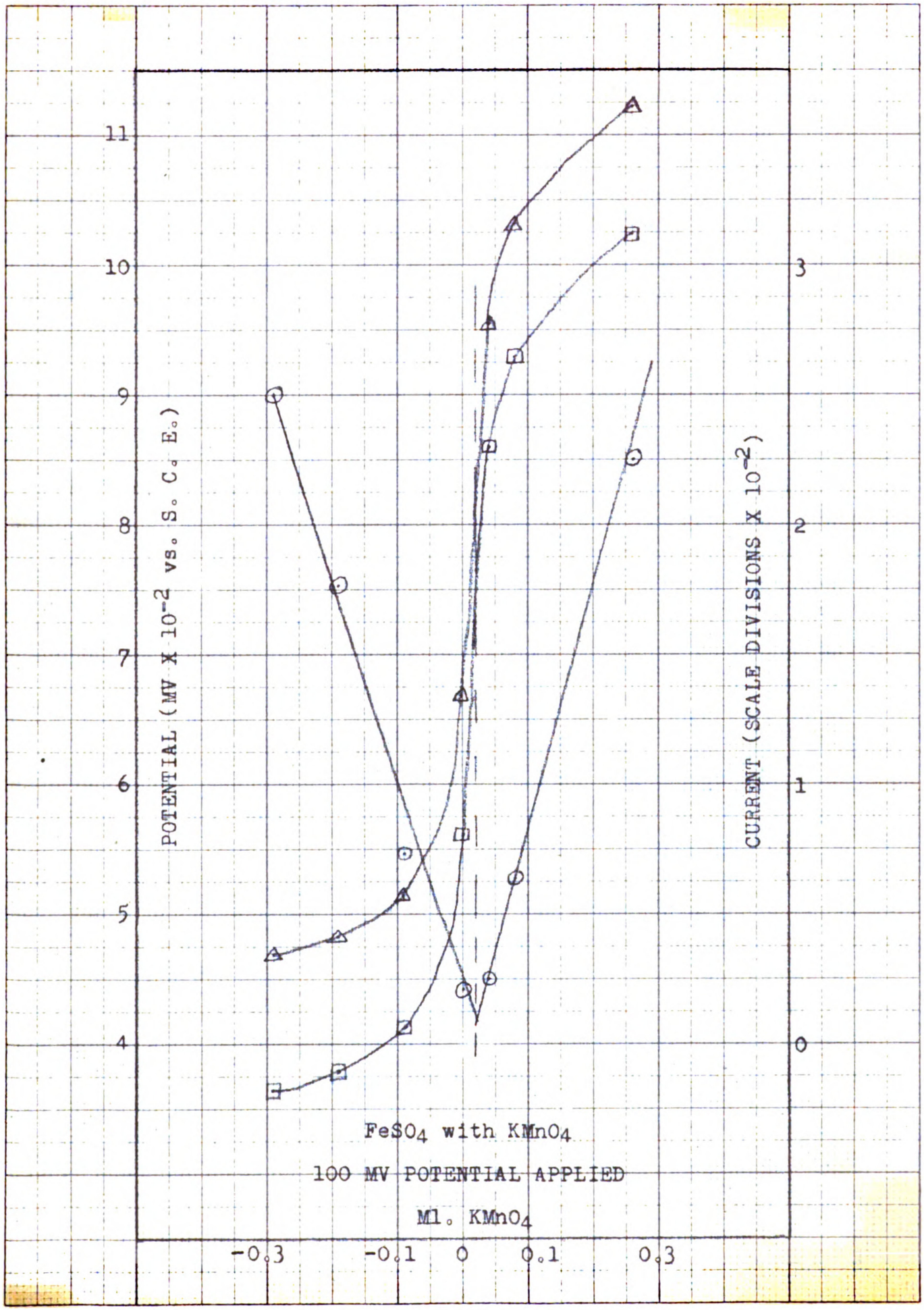
FIGURE 3

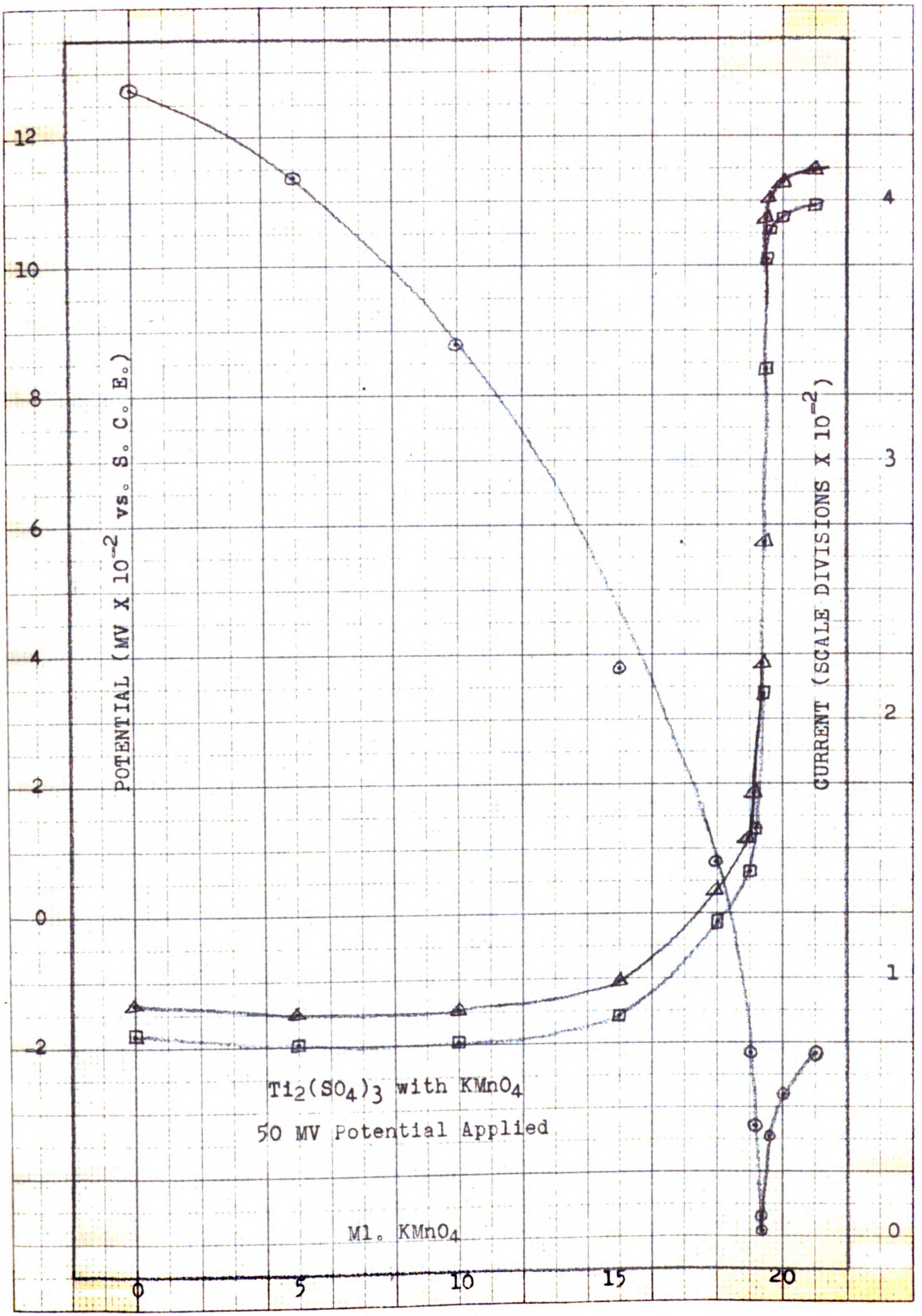

POTENTIAL (MV X 10-2 vs. S. C. E.)
CURRENT (SCALE DIVISIONS X 10-2)
3
2
1
0
6
4
2
0
IODINE WITH SODIUM THIOSULFATE
50 MV POTENTIAL APPLIED
Ml. IODINE
-1.0 -0.8 -0.6 -0.4 -0.2 0 0.1 0.4 0.6 0.8 1.0 1.2


POTENTIAL (MV X 10^{-2} vs. S. C. E.)
CURRENT (SCALE DIVISIONS X 10^{-2})
Ce(SO4)2 with FeSO4
100 MV Potential Applied
Ml. FeSO4
12
10
8
6
4
0
10
20
30
30
20
10
0

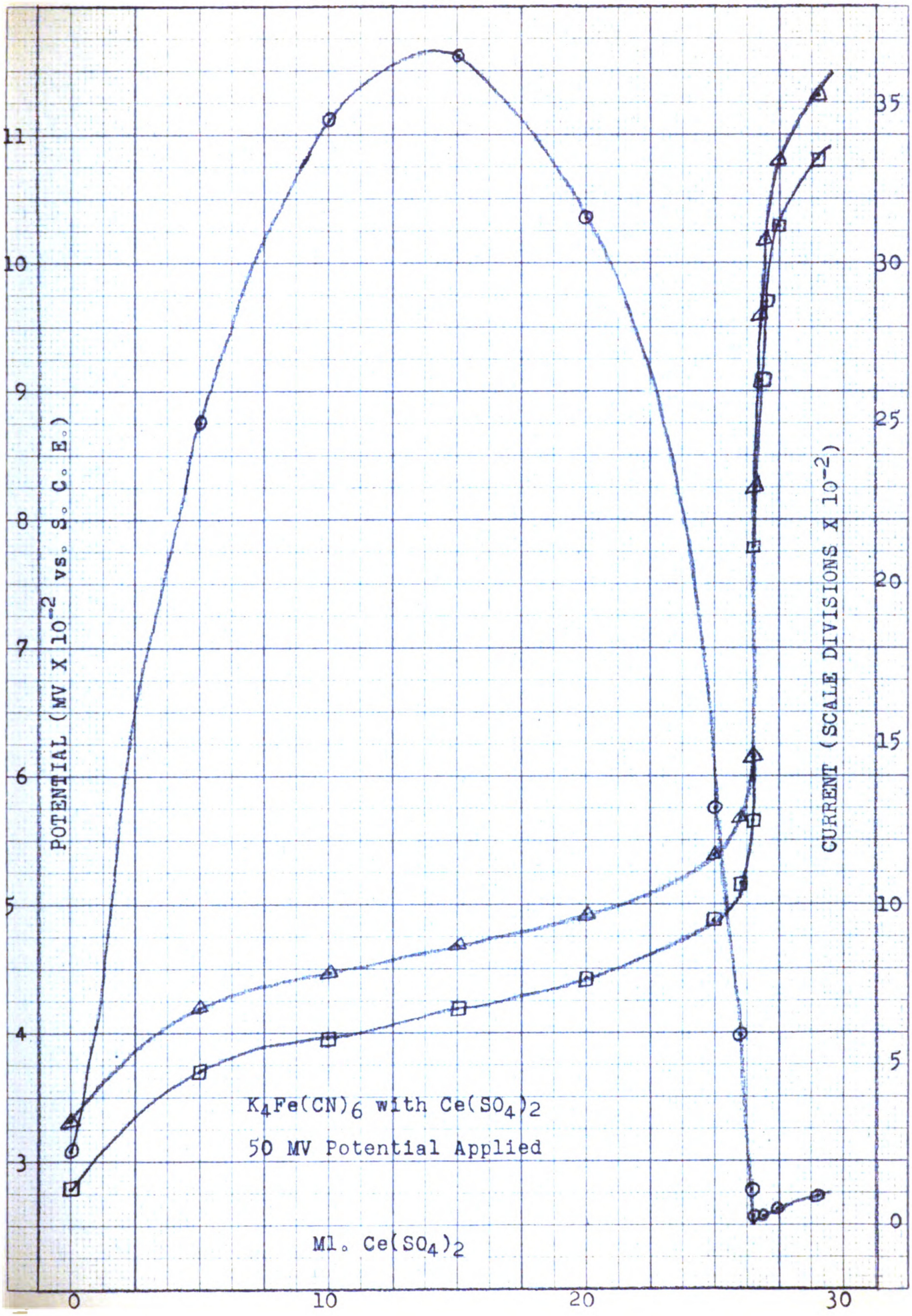

POTENTIAL (MV X 10^{-2} vs. S. C. E.)
CURRENT (SCALE DIVISIONS X10^{-2})
11
10
9
8
7
6
5
5
4
3
2
1
0
Ce(SO4)2 with FeSO4
100 MV POTENTIAL APPLIED
Ml. FeSO4
-1.0 -0.8 -0.6 -0.4 -0.2 0 0.2 0.4 0.6 0.8 1.0

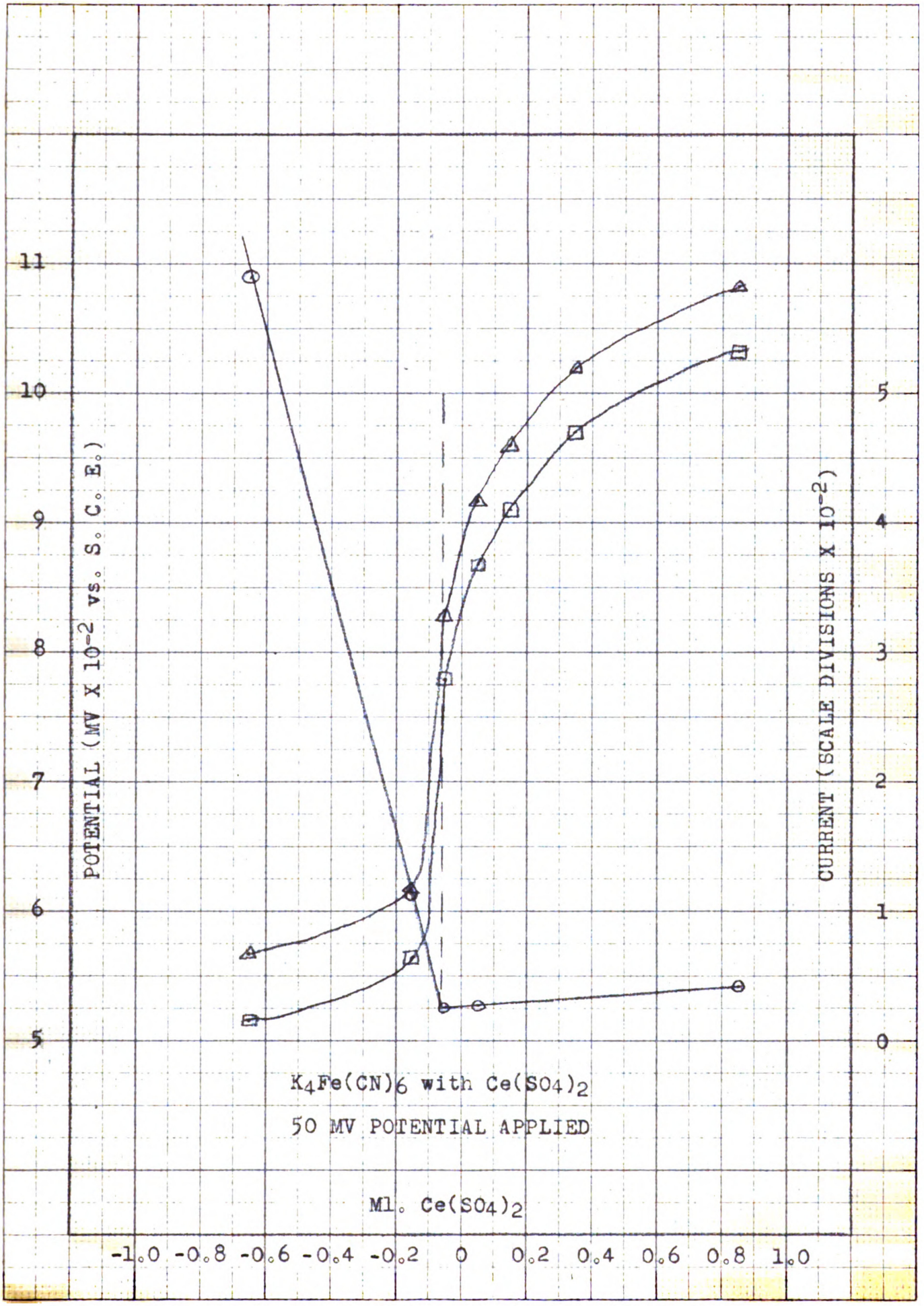

POTENTIAL (MV X 10^{-2} vs. S. C. E.)
CURRENT (SCALE DIVISIONS X 10^{-2})
FeSO$_4$ with KMnO$_4$
100 MV Potential Applied
Ml. KMnO$_4$
0
2
4
6
8
10
12
0
5
10
15
20
25
30
0
10
20
30

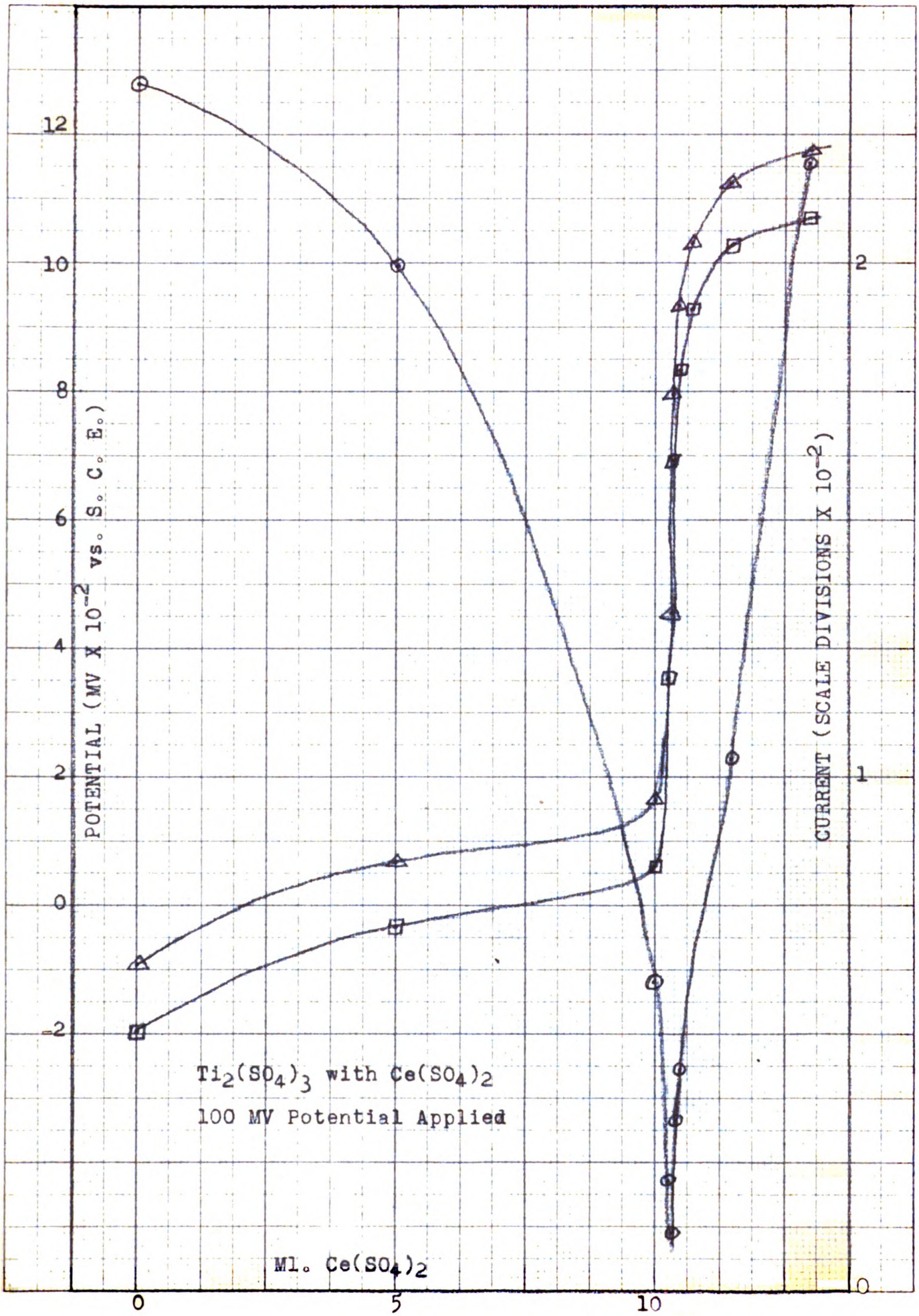

POTENTIAL (MV X 10-2 vs. S. C. E.)
CURRENT (SCALE DIVISIONS X 10-2)
11
10
9
8
7
6
5
4
3
2
1
0
-0.3
-0.1
0
0.1
0.3
FeSO4 with KMnO4
100 MV POTENTIAL APPLIED
Ml. KMnO4

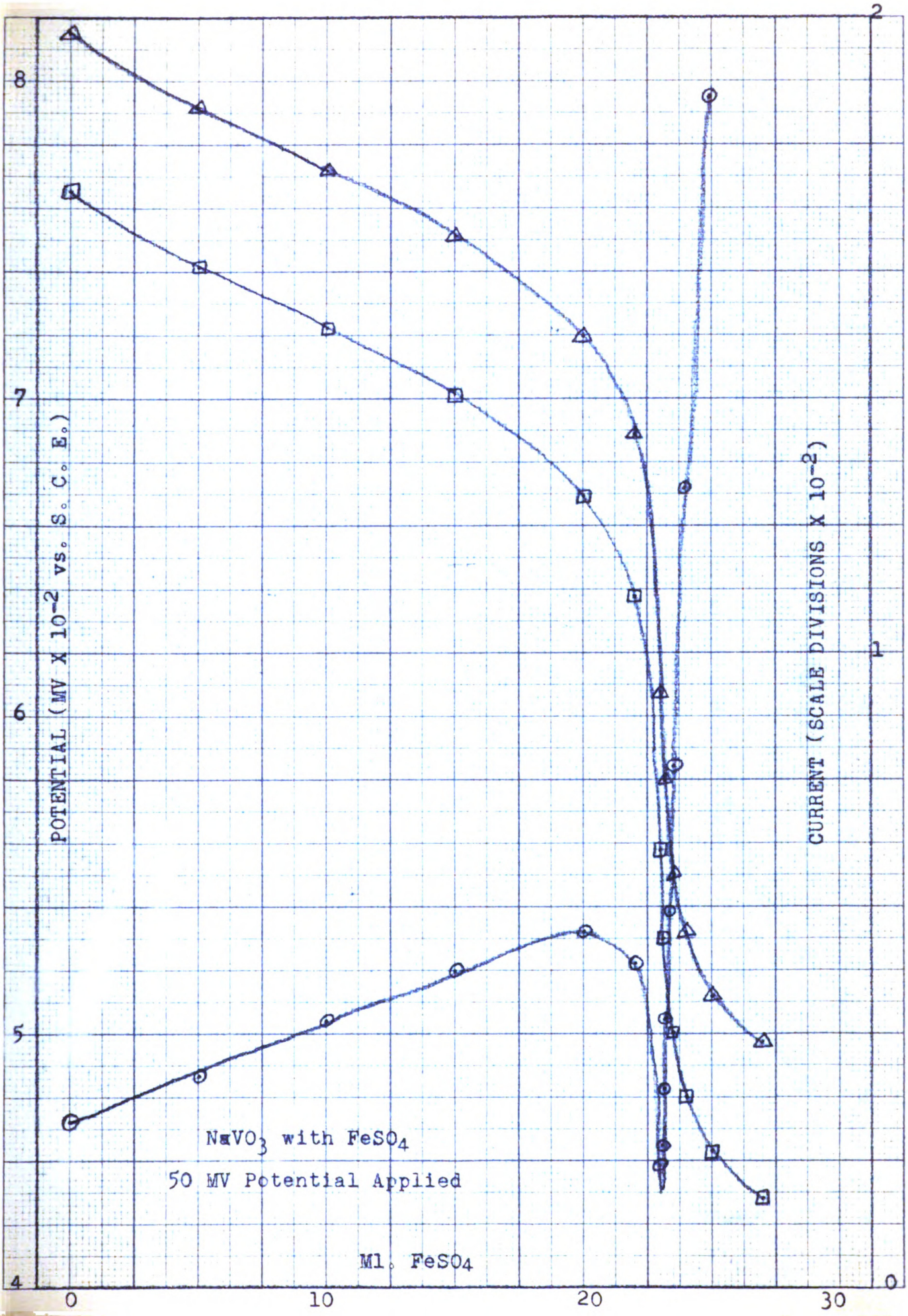

POTENTIAL (MV X 10^{-2} vs. S. C. E.)
CURRENT (SCALE DIVISIONS X 10^{-2})
12
10
8
6
4
2
0
-2
4
3
2
1
0
0
5
10
15
20
Ml. $KMnO_4$
$Ti_2(SO_4)_3$ with $KMnO_4$
50 MV Potential Applied

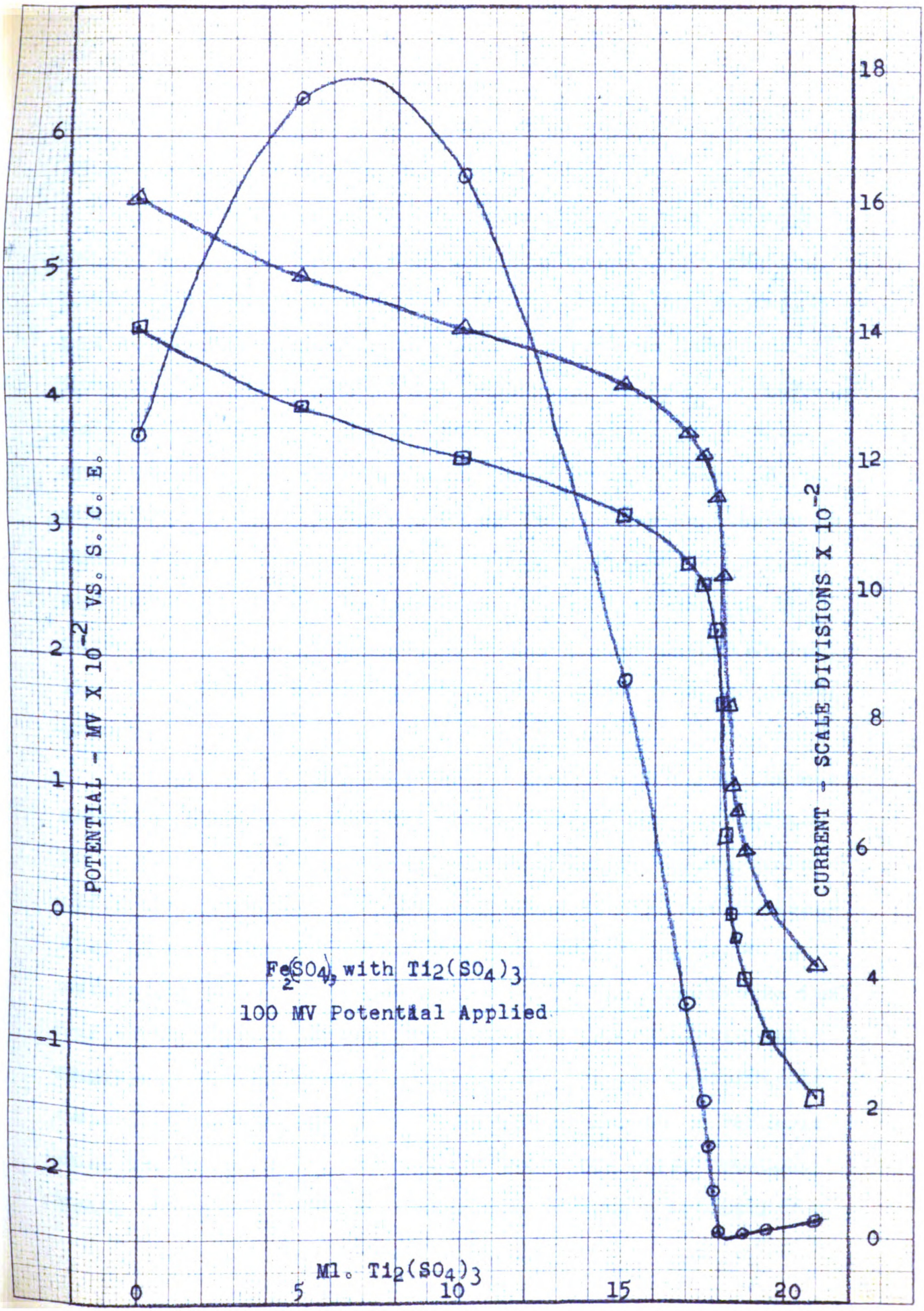

POTENTIAL (MV X 10^{-2} vs. S. C. E.)
CURRENT (SCALE DIVISIONS X 10^{-2})
12
10
8
6
4
20
15
10
5
0
0
5
10
15
20
25
H_2O_2 with $KMnO_4$
50 MV Potential Applied
Ml. $KMnO_4$


POTENTIAL (MV X 10^{-2} vs. S. C. E.)
CURRENT (SCALE DIVISIONS X 10^{-2})
$K_4Fe(CN)_6$ with $Ce(SO_4)_2$
50 MV Potential Applied
Ml. $Ce(SO_4)_2$
0
10
20
30
3
4
5
6
7
8
9
10
11
0
5
10
15
20
25
30
35


POTENTIAL (MV X 10-2 vs. S. C. E.)
CURRENT (SCALE DIVISIONS X 10-2)
11
10
9
8
7
6
5
5
4
3
2
1
0
K4Fe(CN)6 with Ce(SO4)2
50 MV POTENTIAL APPLIED
Ml. Ce(SO4)2
-1.0 -0.8 -0.6 -0.4 -0.2 0 0.2 0.4 0.6 0.8 1.0


POTENTIAL (MV X 10^{-2} vs. S. C. E.)
CURRENT (SCALE DIVISIONS X 10^{-2})
12
10
8
6
4
2
0
-2
2
1
0
0
5
10
$Ti_2(SO_4)_3$ with $Ce(SO_4)_2$
100 MV Potential Applied
Ml. $Ce(SO_4)_2$


POTENTIAL (MV X 10-2 vs. S. C. E.)
CURRENT (SCALE DIVISIONS X 10-2)
NaVO3 with FeSO4
50 MV Potential Applied
Ml. FeSO4
8
7
6
5
4
2
1
0
0
10
20
30


POTENTIAL - MV X 10^{-2} VS. S. C. E.
CURRENT - SCALE DIVISIONS X 10^{-2}
Ml. $Ti_2(SO_4)_3$
$FeSO_4$ with $Ti_2(SO_4)_3$
100 MV Potential Applied
6
5
4
3
2
1
0
-1
-2
18
16
14
12
10
8
6
4
2
0
0
5
10
15
20

CONCLUSIONS

It is evident from the results of this set of experiments that the dead-stop endpoint is at least in part an electrolytic cell phenomenon, not discounting the fact that gas reactions may play a part in the electrode reactions. However, if this endpoint technique were entirely a polarization phenomenon resulting from adsorbed gases, then the two electrodes should not show a constant difference of potential; the difference of potential of the two electrodes should vary from the amount which was applied from an outside source. In these experiments, as has been shown, the potential difference did not vary to any significant degree, the small variations being within the limits of experimental error.

It is obvious that the dead-stop endpoint technique has many and varied applications. The applications are limited in so far as an electrolytic cell must function prior to or after the endpoint. The electrolytic cell need not necessarily be a reversible one; it furthermore need not involve merely two oxidation states of one ion, but can involve two different species of ions, as long as an electrolytic cell functions to some degree. It is felt that the electrolytic cell formed from potassium permanganate is not a reversible one, but forms two different reactions, the anode reaction being the oxidation of manganous ion to manganese dioxide

and the cathode reaction involving the reduction of potassium permanganate to potassium manganate or manganese dioxide.

It appears that certain definite types of analyses can be advantageously performed by the dead-stop procedure. As an example, consider the determination of an iodine-iodide solution. It would be possible to reduce the iodine with a sodium thiosulfate solution to determine the amount of iodine present and then oxidize all the iodide with a suitable oxidizing agent to determine the total iodine present. Another example would be the determination of two reduced ions which are preferentially oxidized by a suitable oxidizing agent. In such a case, the current would rise to a maximum and then decrease to a minimum, this minimum being the endpoint in the selective oxidation of the first component. A second maximum should then occur followed by a decrease to or near the zero current which corresponds to the oxidation of the second component. Although this latter procedure has not been applied, it should be applicable to the oxidation of a ferrous-titanous mixture.

An attempt was made to determine fluorine by this method. In this case, a known amount of ferric sulfate solution was used together with a small amount of ferrous ion. The fluoride solution was added from a buret, and fluoro-ferric complex thus being formed. As ferric is removed from the system by complex formation, a decrease in current should result. This did occur, but the decrease was linear only for

about two thirds of the amount of fluorine required for hexafluoride formation; the current then decreases quite slowly even after a large excess of fluorine is present. The extrapolated straight line portion of this curve to zero current gave a result which was on the order of 1-2[illegible] high.

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PART II

DETERMINATION

OF

PRIMARY AROMATIC AMINES

Introduction

One of the more popular analytical methods for the determination of primary aromatic amines is the diazotization procedure. This method has been extensively studied by numerous authors, resulting in two methods of application, a direct method and a back titration method.

When a solution of sodium nitrite is added to a solution of a primary aromatic amine containing an excess of acid, a quantitative reaction occurs in most cases as follows:

$$NaNO_2 + H^+ = HNO_2 + Na^+$$

$$ArNH_2 \cdot HCl + HNO_2 = ArN_2Cl + 2H_2O$$

These are the basic reactions concerned in the diazotization method. There are numerous inherent difficulties in this method, including slowness of reaction, loss of nitrous acid and in some cases incompleteness of reaction resulting perhaps from the slow rate of reaction of the amine and nitrous acid. Another inherent difficulty is the method for determining the endpoint, the normal method requiring the use of starch-iodide paper as an external indicator.

The original direct method required the addition of a standard solution of sodium nitrite to the acid solution of the primary aromatic amine and after waiting for a short period of time, testing some of the solution with the starch-iodide paper, the test being spotted after each addition until the paper turned a permanent blue-black.

Phillips and Lowy (5) used an excess method for slow reacting mono, di and trisamines, back titrating the excess nitrous acid with a standard aniline hydrochloride or sulfanilic acid solution. These authors however found that a blank determination for loss of nitrous acid has to be subtracted from each determination, the blank varying with the excess amount of sodium nitrite used and also with the amount of acid present. Previously, Lee and Jones (4) applied the back titration to the determination of dehydrothio-p-toluidine sulfonic acid successfully and also to aniline and its homologs. They also found that, in the excess method, the excess nitrous acid was stabilized considerably by the presence of nitric acid. The expression commonly given for the decomposition of nitrous acid

$$3HNO_2 = HNO_3 + 2NO + H_2O$$

suggested the use of nitric acid for suppressing the loss of nitrous acid in titrations. Best results in their work were obtained by allowing the solutions to stand for 30-45 minutes before back titrating with a standard solution of p-nitroaniline. It was necessary in this case however to cool the solution to approximately 5°C in order to further stabilize the excess nitrous acid.

A later refinement of the direct method (7) involved the addition of potassium bromide to the solution of the amine in hydrochloric acid. This procedure is apparently especially adaptable to amines which diazotize slowly, as

it greatly increases the diazotization rate in some cases. Perhaps the answer to this phenomenon can be found in the report of Saunders (6) in which the following points concerning diazotization reactions have been established:

1. The velocity of diazotization increases when the concentration of hydrochloric acid rises from 0.5N to 4N.

2. The speed of diazotization is 3-4 times greater at 10°C than at 0°C.

3. Substituents affect speed in the order Cl > COOH > SO_3H > NO_2.

4. Substituents in the ortho position have most effect, while those para or meta have less. Alkyl and alkoxy-groups have no effect.

5. The speed of diazotization is much greater with hydrobromic acid than with hydrochloric acid, while with nitric acid, sulphuric acid, and naphthalene-1,5-disulphonic acid the speed is less.

Hence, the addition of potassium bromide in the presence of a large amount of hydrochloric acid appears to be equivalent to the addition of hydrobromic acid. It has been found in this work that the rate of consumption of sodium nitrite with potassium bromide present is much more rapid than in its absence, and no appreciable change in results occurs.

Singh and Ahmed (8) apply essentially the same technique to amines using a potentiometric endpoint, obtaining excellent

results in this manner.

As was previously mentioned, one of the inherent difficulties of this method is the determination of the endpoint. The normal procedure requires the removal of a minute amount of the solution after each addition of sodium nitrite and placing it on a piece of starch-iodide paper. When a slight excess of nitrous acid is present, this paper turns a permanent blue-black within a few seconds. Consequently, this requires a short waiting period after each addition of sodium nitrite in order to give time for the nitrous acid to fully react. This is rather a cumbersome method, requires a great deal of time, and is not too accurate. Furthermore, the more dilute the sodium nitrite, the more difficult it becomes to determine the precise endpoint. On the other hand, with a more concentrated solution of sodium nitrite, a much larger error is likely to result due to loss of nitrous acid.

It was felt that since nitrous acid is able to undergo both oxidation and reduction quite readily, a second reagent might be found which would serve essentially to form a reversible or irreversible electrolytic couple and hence the dead-stop endpoint technique might be applied. However, in attempting to devise a suitable electrolytic couple which did not poison the electrodes, it was found that sodium nitrite itself when added to a sufficiently acid solution behaves as an electrolytic cell when the two platinum electrodes are inserted into the solution and a small potential is applied

across the electrodes.

Although the exact mechanism of the electrode reaction is not known, it is felt that the small applied potential causes an oxidation and reduction of the nitrous acid, resulting in the formation of minute amounts of nitrate ions and one of the lower valence nitrogen oxides. There was no experimental evidence for this idea and furthermore, no observable gas formation existed at either electrode. In assuming an oxidation and reduction reaction at the electrodes, it would appear then that nitrous acid would be consumed for other than the diazotization reaction. Even though this may be the case the current which flows is such that little of the nitrous acid would be consumed in this manner. For the most part, with a fairly slow rate of addition of the sodium nitrite solution (approximately 1 ml. per 4 sec), the current remains steady in the vicinity of zero until the endpoint is approached. In the vicinity of the endpoint, each drop of sodium nitrite added causes large momentary deflections of the galvanometer which rapidly returns to the neutral position. This phenomenon is particularly advantageous as it signals the approach of the endpoint. At the endpoint, a permanent deflection of the galvanometer occurs. Within a limited region after the endpoint (about 2 ml. of sodium nitrite), the amount of deflection is linear with the amount of excess sodium nitrite used. Of particular advantage in the use of this technique in determining the endpoint is the fact

that a visual means is available which enables one to adjust the rate of addition of the sodium nitrite solution in such a fashion that an excess of nitrous acid is not formed in the reaction solution. Any excess nitrous acid is immediately apparent as shown by large galvanometer deflections. Stopping the flow of sodium nitrite immediately causes the galvanometer to rapidly return to the neutral or zero point.

As the diazotization rate depends on the temperature, the acid strength and the acid used, it was decided to subject to analysis one amine at varying temperatures and various acid strengths in order to determine optimum conditions for these variables.

In as much as little information is available concerning the stability of a sodium nitrite solution, it was decided to prepare a large quantity and determine its relative stability in the pure state and also of solutions to which had been added substances which might stabilize the solution. Knowing that a nitrous acid solution is unstable, it would appear that if the sodium nitrite solution were also unstable, it would possible be due to hydrolysis, sodium nitrite being the salt of a weak acid and a strong base. Consequently, if this were the case, the product of hydrolysis would be nitrous acid and sodium hydroxide,

$$NaNO_2 + HOH = HNO_2 + NaOH$$

and the instability would then possibly arise due to the decomposition of the nitrous acid. If this were true, any sub-

stance added to the solution which would suppress the hydrolysis should increase the stability. With this thought in mind, sodium carbonate was added to two solutions which were then standardized periodically.

A large choice of primary aromatic amines is available which could be subjected to analysis by the diazotization method. It was decided to choose for this work only amines which could be readily analyzed by some other procedure making use of another functional group. As a consequence, those primary amines were chosen which had a mono-basic group attached to the aromatic nucleus. The choice of amines included sulfanilic acid, o-aminobenzoic acid, m-aminobenzoic acid, and p-aminobenzoic acid. It would thus be possible to determine the degree of purity of these amines by titrating the acid functional group with a standard base.

APPARATUS

The same apparatus was used in these experiments as in Part I, except that the potentiometric apparatus was not required. The electrodes were sensitized frequently by placing them in a potassium dichromate-sulfuric acid solution for a period of about one hour. In all cases, a 0.4 volt potential was applied by means of the Fischer electrodes and the current change was measured with the microampere galvanometer. A calibrated 25 ml. buret was used for measuring the amount of sodium nitrite added.

RESULTS

A standard potassium permanganate solution was required to standardize the sodium nitrite solution. This potassium permanganate solution was prepared in a four liter quantity by dissolving the required amount of potassium permanganate crystals (C.P. Grade) to make a 0.2 M solution. This mixture was then heated to effect dissolution of the crystals, and after allowing to stand for a short period of time, the solution was filtered into a five liter suction flask using a large sintered glass buchner type funnel, applying a partial vacuum by means of a water aspirator.

The sodium nitrite solution originally used for titrating the amines was prepared in a two liter quantity by dissolving the appropriate amount of sodium nitrite crystals (Merck, Granular, Reagent Grade) to make approximately a 0.1 M solution. Later a seven liter solution of approximately the same strength was prepared. In order to test the stability of a sodium nitrite solution, a five liter solution approximately 0.1 M was prepared. This solution was divided into five portions as follows:

1. One liter of pure solution contained in a clear bottle.

2. 0.2 gram of sodium carbonate (Anhydrous, Reagent Grade) added to one liter of solution contained in a clear bottle.

3. 0.4 gram of sodium carbonate added to one liter of solution contained in a clear bottle.

4. One liter of pure solution contained in an amber bottle.

5. 0.5 gram of sodium hydroxide (Reagent Grade) added to one liter of solution contained in an amber bottle.

Sulfanilic acid was available in such a high state of purity that no further purification was deemed necessary; however, this amine was oven dried for one day at 105°C. The anthranilic acid was student preparation quality and so it was recrystallized from a hot water solution after treating a boiling water solution with norite and filtering through a Büchner funnel. It was subsequently dried for one day at 75°C. The m-aminobenzoic acid (White Label, Eastman Kodak #633) and also the p-aminobenzoic acid (White Label, Eastman Kodak #P14) were both recrystallized from a hot water solution after treating a boiling water solution with norite and filtering through a Büchner funnel. They were then oven dried at 73°C for one and one-half days.

Primary Standard sodium oxalate (Bakers Analyzed-Reagent Grade) was used for the standardization of the potassium permanganate and a standard solution was also required for the standardization of the sodium nitrite solutions. The required amount of oxalate, which had previously been dried at 105°C for one day, was used to prepare a two

liter standard solution in a Bureau of Standards volumetric flask.

PROCEDURE

The original standardization of the potassium permanganate solution was made against the 0.1000 N primary standard sodium oxalate solution. In this procedure, 40ml. of the sodium oxalate solution were added to a 150 ml. Erlenmeyer flask containing 5 ml. of (1-4) sulfuric acid; this solution was heated to 85°C and titrated with the permanganate solution. In subsequent standardizations of the potassium permanganate solution, weighed samples of the sodium oxalate were used and the sodium oxalate solution was then standardized with the newly standardized permanganate. This sodium oxalate solution was then used in the standardization of the sodium nitrite solutions.

The sodium nitrite solutions were standardized according to the method as given by Furman (8). This procedure is as follows: A ten percent excess of the permanganate solution is added to a flask containing ten ml. of 1-4 sulfuric acid. Twenty ml. of the 0.1 N sodium nitrite solution is added dropwise while the flask is continuously rotated and is then heated to 90°C. A measured excess of the standard sodium oxalate is then added and this excess is titrated with the permanganate solution to the faint pink endpoint.

The purity of sulfanilic acid, o-aminobenzoic acid,

m-aminobenzoic acid, and p-aminobenzoic acid was determined by titrating weighed samples dissolved in water with a sodium hydroxide solution which had been standardized against weighed samples of primary standard potassium acid phthalate, previously dried at 105°C overnight.

As has been noted, various difficulties are encountered in accurately determining primary aromatic amines by diazotization methods. Consequently, it was decided to determine optimum conditions of temperature, acidity and rate of addition of the sodium nitrite solutions. The best conditions found were the following. (1) The best rate of addition of the sodium nitrite solution is not a constant value, but varies for the different amines. The rate of addition is best controlled by regulating it to maximum rate of flow such that the galvanometer remains at or in the immediate vicinity of the neutral point. In this manner, no excess nitrous acid will build up in the solution and hence loss of nitrous acid is avoided. (2) The normal procedure requires that the amine solution be cooled to approximately 0°C by the use of ice. However, it has been found that there is no error introduced in working at room temperatures when operating with dilute solutions (2). This is readily understood when we consider that although the diazo compound may decompose at a more rapid rate at room temperature, it has no effect on the amount of sodium nitrite necessary for complete diazotization, the amount used depending only on the amount of amine present

and that due to loss of nitrous acid. At temperatures above 40-50°C, high results are obtained. (d) The diazotization rate varies considerably both with the acid used and also with the acid concentration. According to Saunders (6), the rate is fastest with hydrobromic acid; however, due to the nature of this acid it is more feasible to use hydrochloric acid plus sodium bromide. A set of samples of the same approximate weight were diazotized at various acid concentrations. An optimum condition is obtained by adding 25 ml. of concentrated hydrochloric acid and 10 gr ms of sodium bromide per 2-3 milliequivalents of the amine in a 300 to 400 ml. solution. At higher acid concentrations high results were obtained whereas at low acid concentrations the rate of consumption of sodium nitrite was exceedingly slow.

Another important effect noticed concerned the manner of addition of the sodium nitrite solutions. In practically all cases, much better results were obtained when the tip of the buret was slightly under the surface of the solution, an effect which has previously been noted by Siggia (7).

The sensitivity of the dead-stop endpoint is related directly to the sensitivity of both the galvanometer and the platinum electrodes. The instrument used in this work, the Fisher Electropode, has a galvanometer with adjustable sensitivity. It is important in all cases that this galvanometer be adjusted to maximum sensitivity and still keep the pointer within the scale limits. It is likewise important to maintain

the electrodes in a condition of maximum sensitivity which is best obtained by placing the electrodes in a potassium dichromate-sulfuric acid solution for at least one hour. It has been found that one set of electrodes retain their sensitivity for at least six titrations over a period of four hours. The entire general procedure may be summarized as follows: A weighed sample of the amine of such size as to require 20-25 ml. of the 0.1 M sodium nitrite solution was weighed on an analytical balance. This sample was dissolved in approximately 300-400 ml. of water to which had been added 25 ml. of concentrated hydrochloric acid and 5 to 10 grams of potassium bromide. The two platinum electrodes together with the stirrer were then placed into the solution; the stirrer was started and a 0.4 volt potential was applied across the electrodes by means of the Electropede. The galvanometer at this point may show an initial large deflection but it returns quite rapidly to near the zero point when the sensitivity is adjusted to a maximum. The standard sodium nitrite solution is added from a 25 ml. buret, the tip of which is submerged in the solution, and the reagent is added at such a rate that the galvanometer remains at or in the vicinity of the zero point. As the endpoint is approached, temporary deflections may occur due to momentary localization of unreacted nitrous acid around the electrodes. When this occurs, the rate of addition is decreased somewhat so that little or no deflection occurs. Near the immediate vicinity of

the endpoint, the tip of the buret is removed from the solution and is rinsed off with water. The nitrite solution is then added dropwise, each drop causing large temporary deflections of the galvanometer. Consequently, a second drop of the nitrite is not added until the galvanometer returns to the zero reading. At the endpoint, a permanent deflection occurs, the magnitude of the deflection varying directly with the amount of excess sodium nitrite added. As the amount of deflection of the galvanometer is approximately constant for each drop of excess sodium nitrite, a correction to the precise endpoint can be applied by noting the deflection units between the zero reading and the reading at the endpoint. The amount of deflection per drop of nitrite solution is then determined. As the volume of a drop off the buret is almost constant at 0.05 ml., the correction can be applied as follows:

$$\frac{\text{Deflection units at endpoint}}{\text{Deflection units per drop}} \times 0.05 = \text{ml. to subtract from buret reading at the endpoint}$$

[illegible]

Stability of Sodium Nitrite Solutions: The stability of the sodium nitrite solutions was determined by standardization against potassium permanganate. The results of the series of standardizations are shown in Table I.

Table I

Stability of Sodium Nitrite Solutions

Date	Solution No. 1	2	3
7/27/50	0.1048N	0.1040N	0.1046N
8/8/50	0.1044N	0.1038N	0.1050N
8/18/50	0.1050N	0.1050N	
9/27/50	0.1047N	0.1050N	0.1040N

1. Pure solution
2. 0.1g./l. of sodium carbonate added
3. 0.5g./l. of sodium carbonate added

From the values shown in the table above, it can be seen that a dilute sodium nitrite solution appears to be completely stable for at least a two month period of time, both with and without sodium carbonate added, when the solution is not unduly exposed to the atmosphere. This is in complete agreement with Vieth (8) and Cook and Roe (1). These solutions will be standardized at future dates by other workers to see if any appreciable changes occur.

Stability of Potassium Permanganate Solution: The potassium

permanganate solution used in the standardization of the sodium nitrite solutions was checked frequently with sodium oxalate. The results are shown in Table II.

Table II

Stability of Potassium Permanganate Solution

Date	Normality
7/27/50	0.1056N
8/2/50	0.1054N
8/16/50	0.1054N
8/28/50	0.1056N
9/16/50	0.1054N

The values given in Table II suggest that a properly prepared potassium permanganate solution is completely stable over a two months period of time (1). The slight variations can be accounted for as no correction was applied for volume changes due to differences in temperature at the various times of standardization.

Evaluation of Standardization Methods for Sodium Nitrite: Phillips and Lowy (5) found a considerable difference of normality in standardizing sodium nitrite against amines and potassium permanganate. In standardizing an approximate 0.1N sodium nitrite solution against aniline hydrochloride, sulfanilic acid and potassium permanganate, they obtained results of 0.1055 N, 0.1055 N and 0.1101 N respectively. This is

consistent with results obtained in this work where the standardization against potassium permanganate gave an average value of 0.1100N with a precision of approximately one percent from high to low value compared to a value of 0.1087N against sulfanilic acid using the dead-stop technique where the precision range was approximately 0.5% between high and low values. Table III summarizes these results.

Table III

Evaluation of standardization methods for sodium nitrite

Potassium permanganate		Sulfanilic acid	
N of Na	Deviation from average	N of Na	Deviation from average
0.1085N	-0.0011	0.1081N	-0.0006
0.1115N	0.0019	0.1086N	-0.0001
0.1130N	0.0014	0.1091N	0.0004
0.1080N	-0.0019	0.1080N	-0.0001
0.1102N	-0.0004	0.1085N	-0.0002
		0.1088N	0.0003
0.1106N	0.0010	0.1087N	0.0003

In view of these results, it appears that the average value based on sulfanilic acid is much more reliable. The samples used in this work which first subjected to analysis, all gave high results of the order of approximately one percent when titrated with sodium nitrite which had been standardized against the potassium permanganate solution. Later analysis

of these amines using the value of the normality of the sodium nitrite based on the sulfanilic acid gave much more accurate results, which further enhances the idea that the normality of sodium nitrite based on sulfanilic acid is a more reliable value.

Purity of Amines: As all the amines contained a mono-basic functional group, the purity was determined by titrating with a standard sodium hydroxide solution. The sodium hydroxide was standardized against weighed samples of primary standard potassium acid phthalate; the results are shown in Table IV.

Table IV

Standardization of NaOH against Potassium Acid Phthalate

Weight of Phthalate	Ml. NaOH	N of NaOH
0.4785g	24.56	0.09540N
0.4700g	24.27	0.09542N
0.4533g	23.28	0.09555N
0.4040g	20.74	0.09541N
0.4278g	21.98	0.09528N
Average		0.09540N

The results obtained for the purity of the amines on the basis of the sodium hydroxide titrations are shown in Table V.

Table V

Titration of Amines with 0.08540 N NaOH

Weight of Amine	Ml. NaOH	Purity
	Sulfanilic Acid	
0.4087g	24.44	100.02%
0.3733g	22.80	100.14%
0.3511g	21.48	100.18%
0.4068g	24.66	100.15%
Average		100.12%
	Anthranilic Acid	
0.3089g	20.47	100.38%
0.2738g	20.04	100.13%
0.2712g	20.02	100.14%
Average		100.20%
	m-Aminobenzoic Acid	
0.3061g	18.46	100.23%
0.3137g	24.05	100.30%
0.2805g	21.40	99.81%
0.3088g	23.14	99.85%
Average		100.07%
	p-Aminobenzoic Acid	
0.3071g	23.57	100.41%
0.3148g	24.21	100.61%
0.2863g	22.17	100.58%
0.3015g	23.16	100.50%
Average		100.52%

The average result for sulfanilic acid, anthranilic acid and m-aminobenzoic acid is within the limits of experimental error and hence these are considered pure compounds. The value for p-aminobenzoic acid is slightly high, hence the results obtained by the titration method should vary somewhat, probably giving slightly low results.

Determination of amines: Originally the amines were analyzed using the sodium nitrite solution which had been standardized against potassium permanganate. The results obtained were all high, being of the order of 1%. In as much as the precision is much better using sulfanilic acid to standardize the sodium nitrite solution, the value obtained in this manner is used for reporting the analysis of the amines. Consequently, no absolute value can be reported for sulfanilic acid. However, a tabulation of the precision of the method is of value and is shown in Table VI.

Table VI

Precision Using Sulfanilic Acid

Sample Weight	ml. Conc. HCl	Grams KBr	ml. NaNO	M of NaNO	Deviation from Average
0.3815g	25	10	20.08	0.1041M	-0.0003
0.4048g	25	10	21.42	0.1048M	-0.0001
0.4387g	25	10	24.13	0.1046M	0.0002
0.3850g	25	0	20.40	0.1048M	-0.0001
0.4008g	25	0	21.10	0.1048M	-0.0001

Table VI (Con't)

Precision Using Sulfanilic Acid

Sample Weight	Ml. Conc. HCl	Grams KBr	Ml. $NaNO_2$	M of $NaNO_2$	Deviation from Average
0.4380g	15	0	24.20	0.1045M	0.0001
0.3638g	15	0	20.28	0.1038M	-0.0006
0.3684g	15	0	19.88	0.1050M	0.0006
0.3842g	15	0	21.12	0.1048M	0.0004
0.4078g	15	0	22.47	0.1045M	0.0004
0.4245g	15	0	23.48	0.1044M	0.0000
0.4364g	15	0	24.12	0.1048M	0.0001
Average				0.1044M	0.0002

0.4 volt potential applied in each case

The results listed in Table VII are on the basis of the 0.1044M sodium nitrite, standardized against sulfanilic acid.

Table VII

Analysis by Diazotization

Sample Weight	Ml. Conc. HCl	Grams KBr	Ml. $NaNO_2$	Calc. Weight	Deviation Parts Per 1000	
			Analysis of Anthranilic Acid			
0.2785g(a)	20	5	19.68	0.2818	8	100.8
0.3062g(a)	25	9	21.68	0.3104	4	100.3
0.3154g(a)	20	9	22.10	0.3178	5	100.4
0.3367g(b)	27	5	23.48	0.3389	-2	99.8
0.2805g(b)	25	5	19.52	0.2795	-4	99.6

Table VII (Con't)

Analysis by Diazotization

Sample Weight	Ml. Conc. HCl	Grams KBr	Ml. $NaNO_2$	Calc. Weight	Deviation Parts per 1000	
0.3027g(b)	15	5	11.10	0.3041	-2	99.8
0.3230g(b)	15	5	11.48	0.3211	-6	99.4
Average deviation					4	100.0±0.4

(a) sodium nitrite added dropwise from buret
(b) tip of buret in solution

Analysis of m-Aminobenzoic Acid

0.1814g	15	5	15.53	0.1861	11	101.1
0.3013g	15	5	11.12	0.3020	5	100.5
0.3175g	15	5	11.27	0.3183	4	100.4
0.3511g	15	10	14.58	0.3511	0	100.0
0.1918g	15	10	10.47	0.1901	-1	99.9
0.3345g	15	10	12.34	0.3341	-1	99.9
Average deviation					4	100.3±0.3

(tip of buret in solution in all cases)

Analysis of p-Aminobenzoic Acid

0.1843g	15	5	11.53	0.1853	4	100.4
0.1850g	15	5	11.18	0.1847	-1	99.9
0.3303g	15	5	13.00	0.3302	-3	99.7
0.3544g	15	5	14.81	0.3545	5	100.5
0.3115g	15	5	11.75	0.3107	-3	99.7
Average deviation					3	100.0±0.3

(tip of buret in solution in all cases)

CONCLUSIONS

It has been shown that the dead-stop endpoint technique can be successfully applied to the analysis of primary aromatic amines. The method is believed to have a number of advantages over those previously reported; the presence of dark colored materials causes no interference; errors due to loss of nitrous acid are reduced to a minimum; and the method is fairly rapid and particularly well suited for routine analysis. The results obtained by this procedure appear to be much more accurate than would have been attained by using the starch-iodide endpoint method. The precision in this procedure is also very good. In addition, the rate of consumption of the sodium nitrite solution can be followed very readily allowing the rate of addition to be regulated in such a fashion that a loss of nitrous acid is avoided.

There is yet much work to be done if this method for determining primary aromatic amines is to be perfected. More work needs to be done on the limiting quantities of amines which can be accurately determined in a given volume of solution by this procedure. In this work between 2-4.5 milliequivalents of the amine in a final volume of 350-400 ml. were determined. The acid concentration which gives good results should be about 10 ml. of concentrated hydrochloric acid per milliequivalent of the amine and the amount of potassium bromide added can vary between 5-10 grams, a better endpoint

occuring by using the larger quantity.

Interferences in this method will obviously be substances which can either oxidize or reduce nitrous acid and also those substances which can combine with it.

An experiment which suggests itself as leading to a better understanding of the electrode reactions would consist of two cells containing a sodium nitrite solution added to an acid solution, both cells containing identical quantities of reagents. These cells could be connected by an agar salt bridge and a source of potential applied for a period of time across platinum electrodes in the solutions, after which the various constituents of the cells could be analyzed. A control consisting of merely one cell with identical constituents would necessarily have to be set up.

This procedure has also been applied to the analysis of one sample of amino guanidine, giving a result of better than 1% accuracy.

In all respects, the use of the acid-step endpoint technique in conjunction with the titration procedure appears to be a simple and accurate method for quantitatively determining primary aromatic amines. Furthermore, this method using sulfanilic acid apparently is superior to the permanganate method in standardizing sodium nitrite solutions.

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