INVESTIGATION OF SOME POSSIBILITIES FOR AMPEROMETRIC TITRATION OF CERTAIN METAL IONS WITH OXINE

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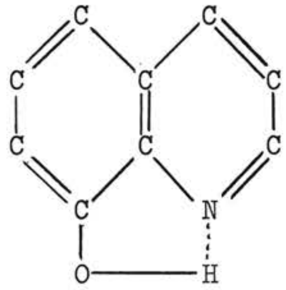
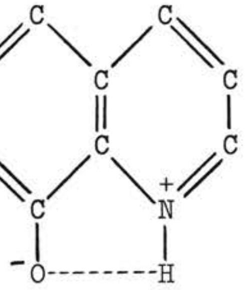
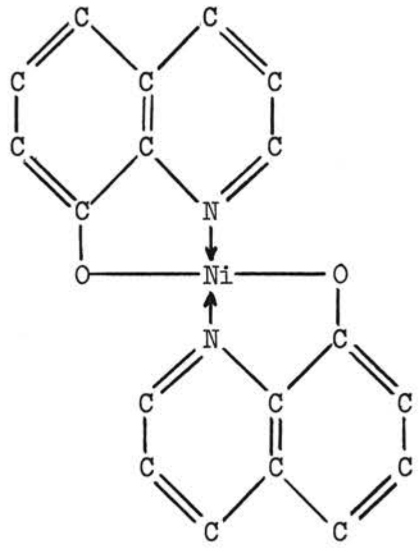
PREFACE

Oxine (8-hydroxyquinoline) is most generally used in analytical chemistry as a precipitant for metals and is known to form water-insoluble chelates with better than thirty metal ions (3). There exists in solutions of oxine a tautomeric equilibrium of the following type:





Chelation of a metal ion involves replacement of the proton and formation of a coordinate bond with the nitrogen to form a stable 5 membered ring compound. Thus nickel, a bivalent cation, would form a compound with the following structure:



The oxinates can be ignited and weighed as such or they may be further ignited to the metal oxides and then weighed. Alternately the oxinates may be dissolved in acid and quantitatively brominated (7).

Considering the number of metal ions that are precipitated by oxine, it seemed that possibly more use could be made of the reagent in volumetric analysis. Comparatively little has been done to utilize oxine for precipitation titrations and, likewise, apparently nothing has been done using soluble oxine chelates in organic solvents.

The primary purpose of this research was to investigate the possibilities of carrying out amperometric titrations in solvent systems involving water and water-miscible organic solvents where it was hoped that most of the chelates of oxine would be soluble and that the polarographic characteristics of the solutions would be suitable. In the event that no such solvent system could be found, an investigation of several possible aqueous amperometric precipitation titrations using oxine should be of equal benefit.

The author wishes to express his deepest appreciation to Dr. Paul Arthur for the help and guidance that he extended during the course of this investigation and also to Continental Oil Company for the support which it rendered both financially and in the way of apparatus and chemicals. The author also wishes to express his gratitude to Oklahoma State University for permitting this research to be done off campus.

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INTRODUCTION

Oxine is reduced at the dropping mercury electrode over the entire pH range but good waves are obtained only in ammoniacal and alkaline solutions (22). Stone and Furman(19) reported two waves for oxine, one at -1.39 volts and another at -1.61 volts vs. the saturated calomel electrode. These waves are probably due to formation of the dihydro and tetrahydro derivatives with the waves at pH 10.0 being the most suitable for polarographic use (16).

Magnesium has been determined by an amperometric precipitation titration in ammoniacal (pH 10.0) solution at an applied voltage of -1.86 volts vs. the saturated calomel electrode (21). At this voltage oxine is reduced and a rapid current increase is obtained with subsequent titrant additions after the end point.

Ishibashi and Fujinaga (9) titrated magnesium under essentially the same conditions with an accuracy of 0.7 per cent and recommend this determination for magnesium in alloys, brines and sea water.

Zanko (22) titrated magnesium in ammoniacal buffer (pH 10.0) and zinc and copper in acetate buffer with oxine. According to him, aluminum can be titrated amperometrically with oxine in either acetate or ammoniacal media.

Gillis, Eeckaut and Standert (6) titrated bismuth with oxine in a tartrate-acetate supporting electrolyte solution at -0.85 volts vs. the saturated calomel electrode. Blackburn and Christian (2) used essentially the same titration to determine bismuth in pharmaceuticals. In this method, a 2 per cent solution of oxine in 1.0 M acetic acid was used as titrant and phenolphthalein in ethanol (0.1 per cent) was used as a maximum suppressor.

Stock (17) performed micro amperometric titrations on copper solutions. Titrations were carried out in both tartrate and acetate buffers containing 0.02 per cent gelatin as a maximum suppressor. Oxygen was removed by bubbling nitrogen gas through the solution and the copper was titrated with oxine at -0.4 volts vs. the mercury pool reference electrode where copper only is reduced. Concentrations of copper as low as 1×10^{-4} M may be titrated successfully by this method.

Zinc and cadmium solutions also were titrated by Stock (18). The cadmium titration was carried out at a pH of 6.0 and at -0.9 volts vs. the mercury pool reference electrode in an acetate buffer while zinc was titrated at a pH of 5.0 at an applied potential of -1.4 volts vs. the mercury pool reference electrode. Stock was able to titrate copper in the presence of both zinc and cadmium at a pH of 6.0 (acetate or tartrate buffer) and at an applied voltage of -0.4 volts vs. the mercury pool electrode.

Vasilev and Marunina (20) titrated zinc amperometrically with oxine after determining copper in the same solution by a thiocyanate precipitation titration.

Polarography

Figure 1 illustrates a simple polarographic circuit. Voltage from the battery is applied across the cell electrodes at a uniform rate by means of a motor driven bridge. The chart of the recorder also moves

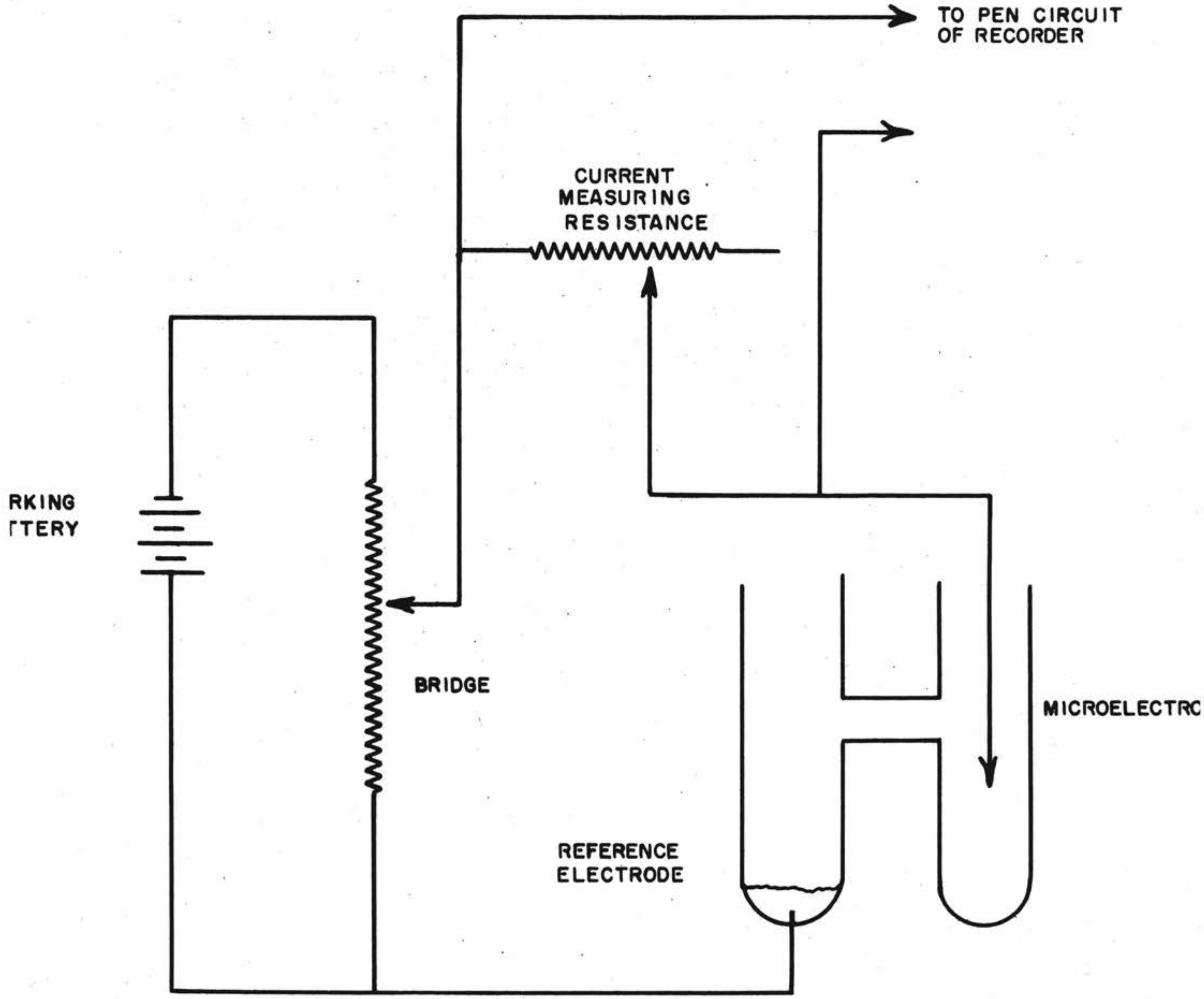

FIGURE I - SCHEMATIC POLAROGRAPH CIRCUIT at a uniform rate while the recorder pen circuit measures current flowing through the cell. The result is a polarogram or current-voltage diagram in which current is plotted as a function of the applied voltage (Figure 2).

Currents of polarographic magnitude arise from the fact that the micro electrode is easily polarized and therefore controls the cell current. The reference electrode can be any stable electrode that is not easily polarized, such as a saturated calomel electrode.

The dropping mercury electrode is the microelectrode most commonly used because of the large hydrogen overvoltage associated with mercury. Thus it is possible to let the cathode assume fairly high negative potentials without reducing hydrogen ions which would interfere with the reaction of other ions or molecules.

Reacting ions or molecules -- i.e., ions or molecules that are electro-oxidizable or electro-reducible -- can reach the electrode surface through two forces, an electrical force and a diffusion force. The electrical force is proportional to the potential difference between the electrodes and produces what is known as a migration current. The diffusion force is caused by the concentration gradient that exists between the layer immediately surrounding the microelectrode and the bulk of the solution. The magnitude of the diffusion current is proportional to the concentration of the reacting ions or molecules in the bulk of the solution.

To minimize the migration current, a high concentration of some inert salt is added to the cell solution. For example, the potassium ions in a KCl solution are reduced at comparatively high cathode potentials and hence do not interfere with ions or molecules reduced at less negative potentials.

When the cell solution contains ions or molecules that will react at the microelectrode, if the voltage across the cell terminals is uniformly advanced, the rate of current increase is at first small (Figure 2, line AB). This is the residual current line and is the sum of the condenser current and a current due to reduction or oxidation of trace impurities present in the solution. When point B (the decomposition potential) is reached, the slope increases sharply until point C is reached. Along line BC the rate of reaction at the electrode is slower than the rate of replacement of reacting ions or molecules from the bulk of the solution.

When the voltage is advanced sufficiently so as to be at a point along line CD, the limiting current has been reached. Along this line the ions or molecules arriving at the electrode surface from the bulk of the solution react at once and their concentration in the layer immediately surrounding the electrode is virtually zero.

The magnitude of the diffusion current depends on the concentration of ions or molecules in the bulk of the solution and hence can be used as a measure of this concentration. The half wave potential ($E_{\frac{1}{2}}$) is characteristic of the substance reacting.

Effects of High Cell Resistance. In conventional or low resistance polarography, the iR-drop across the cell may be neglected and $E_{applied}$ is for all practical purposes equal to $E_{effective}$. If high cell resistances are to be encountered, the following relationship applies:

$$E_{applied} = E_{effective} + iR$$

If solvent systems of resistance higher than that of the usual water systems are employed, the product iR becomes significant and $E_{applied}$

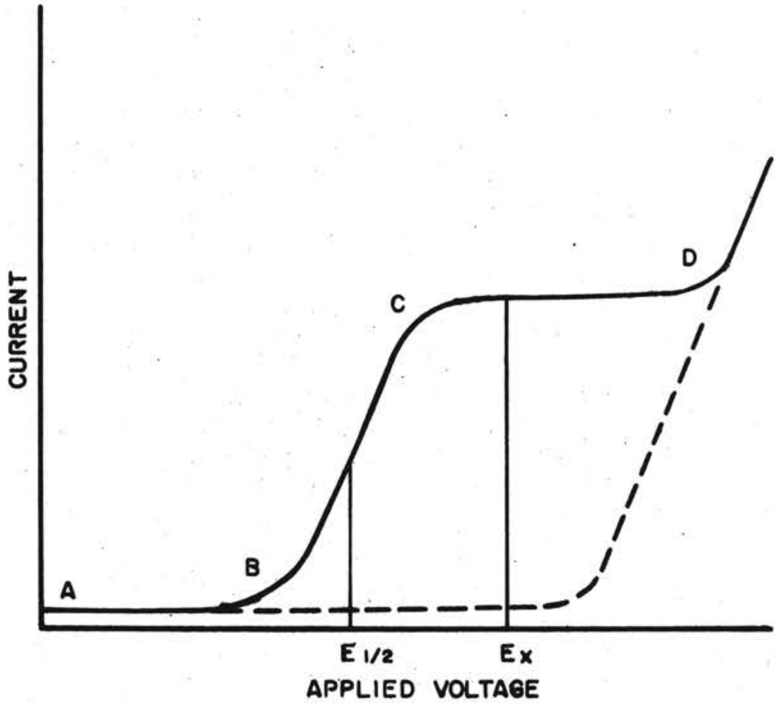

FIGURE 2 - TYPICAL POLAROGRAM

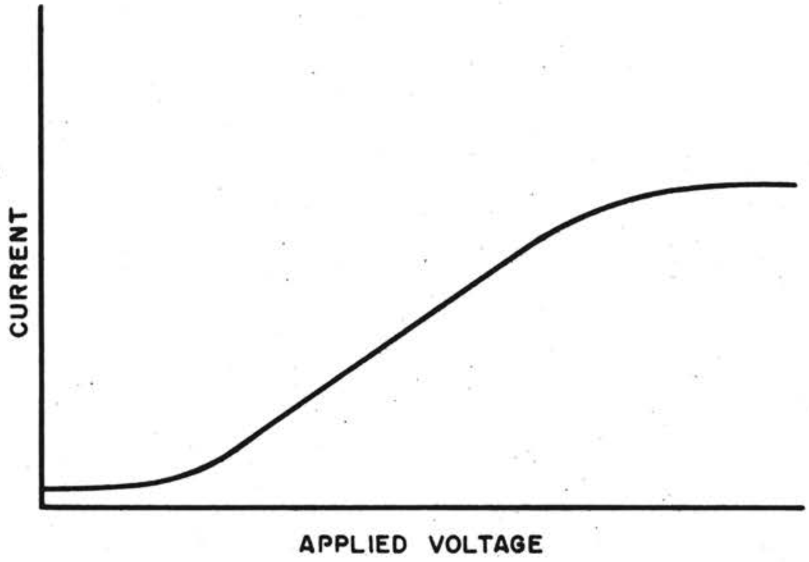

FIGURE 3 - CONVENTIONAL POLAROGRAM WITH HIGH RESISTANCE SYSTEM

is no longer essentially equal to $\underline{E}_{\text{effective}}$. This has the effect of distorting the polarogram (Figure 3), this distortion increasing with increased cell resistance and/or higher current levels. When this situation is encountered, calculated corrections must be applied or special polarographic equipment must be employed.

Amperometric Titrations

In amperometric titrations the current that is produced when an ion or molecule reacts at a microelectrode at a suitable voltage (see $\underline{E}_x$, Figure 2) is plotted as a function of the volume of titrant added. The end point of the titration is the point of intersection of two lines which give the change in current before and after the equivalence point.

In order for an amperometric titration to work, the ion (or molecule) to be determined, or the reagent, or both must react at a microelectrode to produce a current that is directly proportional to concentration. Also the reagent must form either a very stable soluble complex or an insoluble precipitate with the ion.

In the case where a soluble complex is formed, the complex should react at significantly different voltages than the uncomplexed ion. A successful precipitation titration requires that the ion be precipitated rapidly and quantitatively by the reagent and that a minimum of reagent or metal ion be occluded by the precipitate.

The three most commonly encountered types of amperometric titration curves are as follows:

a. If the titrant reacts at the microelectrode at voltage $\underline{E}_x$ but the titrated substance does not, then the current remains essentially constant before the end point and increases when the end point is past (see Figure 4, a).

b. If the titrant does not react at the microelectrode at voltage $\underline{E}_x$ but the titrated substance does, then the current decreases before the end point and remains constant beyond the end point (Figure 4, b).

c. If both the titrated substance and the titrant react at voltage $\underline{E}_x$, then the current decreases before the end point and increases beyond the end point (Figure 4, c).

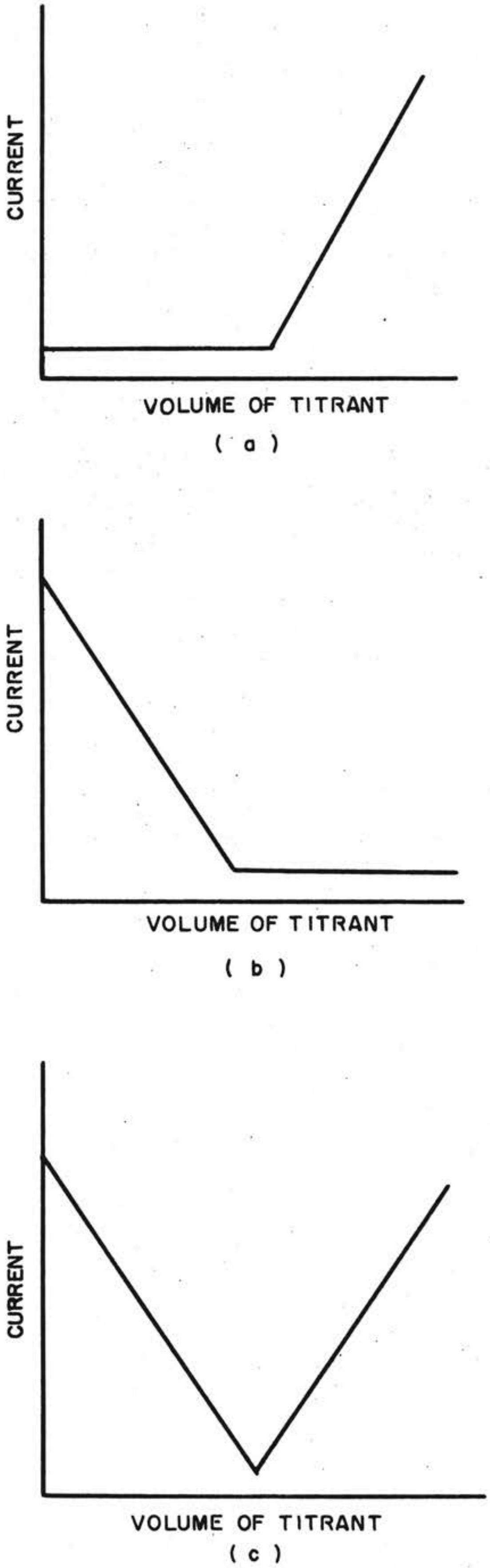

FIGURE 4- TYPES OF AMPEROMETRIC TITRATION CURVES

SCOPE OF WORK

In the research represented by this thesis, the possibility of working with a semiaqueous system was investigated first. A solvent system in which the metal chelates are soluble and whose resistance is low enough for conventional polarography was sought. It was found in general, though, that of the solvents and combinations of solvents investigated, any that would dissolve metal oxinates gave cell resistances much too high for conventional polarography. It appeared that the amperometry of soluble oxine chelates might be successfully performed using a non-aqueous polarographic technique; but since the needed apparatus was not available to this investigator, the non-aqueous approach was abandoned and it was decided to investigate some possible aqueous precipitation titrations.

Several possibilities for precipitation titrations using oxine were investigated. Among these were the titration of copper (II) in ammoniacal medium, the titration of nickel (II) in both aqueous KSCN and aqueous pyridine media, aluminum (III) at a pH of 13.0 (present as aluminate) and lead (II) at a pH of 12.3 (present as a bi-plumbite ion).

REAGENTS

Acetic Acid - Baker reagent grade was used without further purification.

Ammonium Hydroxide - Baker reagent grade containing 28.7 per cent NH_3 was used without further purification.

Ammonium Chloride - Baker reagent grade was used without further purification.

Argon - Linde high purity (99.995 per cent) was purified as described later by passing it through a chromous sulfate scrubber.

Cadmium Chloride - Baker reagent grade $CdCl_2 \cdot 2\frac{1}{2}H_2O$ was used without further purification.

Cupric Acetate - Mallinckrodt reagent grade was used without further purification.

Cupric Chloride - Baker reagent grade was used without further purification.

Chromic Sulfate - Baker reagent grade $Cr_2(SO_4)_3 \cdot xH_2O$ was used without further purification.

1-4 Dioxane - Matheson, Coleman and Bell reagent grade was used without further purification. Melting point was 10-11°C.

Ethanol - U. S. Industrial Chemicals Co. reagent grade was used without further purification.

Gelatin - Knox No. 1 was used without further treatment.

Helium - Bureau of Mines Grade A was purified as described for argon.

8-Hydroxyquinoline - Mallinckrodt reagent grade was used without further purification.

Isopropanol - Baker reagent grade was used without further purification.

Lead Nitrate - Mallinckrodt reagent grade was used without further purification.

Lithium Chloride - Baker reagent grade was used without further purification.

Methanol - Mallinckrodt reagent grade was used without further purification.

Mercuric Chloride - Mallinckrodt reagent grade was used without further purification.

Mercurous Chloride - Fisher Scientific reagent grade was used without further purification.

Mercury - Mallinckrodt reagent grade contained in glass bottles was used without further purification.

Mono-ethanol Amine - Matheson Co. Stock No. 5113 was used without further purification.

Nickelous Nitrate - Baker analyzed $Ni(NO_3)_2 \cdot 6H_2O$ was used without further purification.

Nitrogen - Linde Laboratory Grade, H. P., dry, was purified as described for argon.

Potassium Chloride - Baker reagent grade was used without further purification.

Potassium Thiocyanate - Mallinckrodt reagent grade was used without further purification.

Pyridine - Mallinckrodt reagent grade was used without further purification. Boiling point was 115.2±2.0°C.

Sodium Acetate - Baker reagent grade was used without further purification.

Sodium Hydroxide - Mallinckrodt U. S. P. pellet-form was used without further purification.

Sulfuric Acid - Baker reagent grade was used without further purification.

Zinc Metal - Baker mossy zinc was used without further treatment.

APPARATUS

A Sargent model XXI recording polarograph and a Sargent Ampot composed the polarographic equipment used in this work.

Two different types of cells were used (see Figure 5). One of these was a large-volume titration cell (150 ml capacity) (a) with a saturated calomel reference electrode, while the other was a 20-ml cell (b) using a mercury pool reference electrode.

Most of the work was done using nitrogen for degassing though argon or helium was used in some experiments. In any case the gases were put through a chromous sulfate oxygen scrubber (1) (Figure 6) before they entered the titration cell. A 5-ml micro burette was used in most titrations.

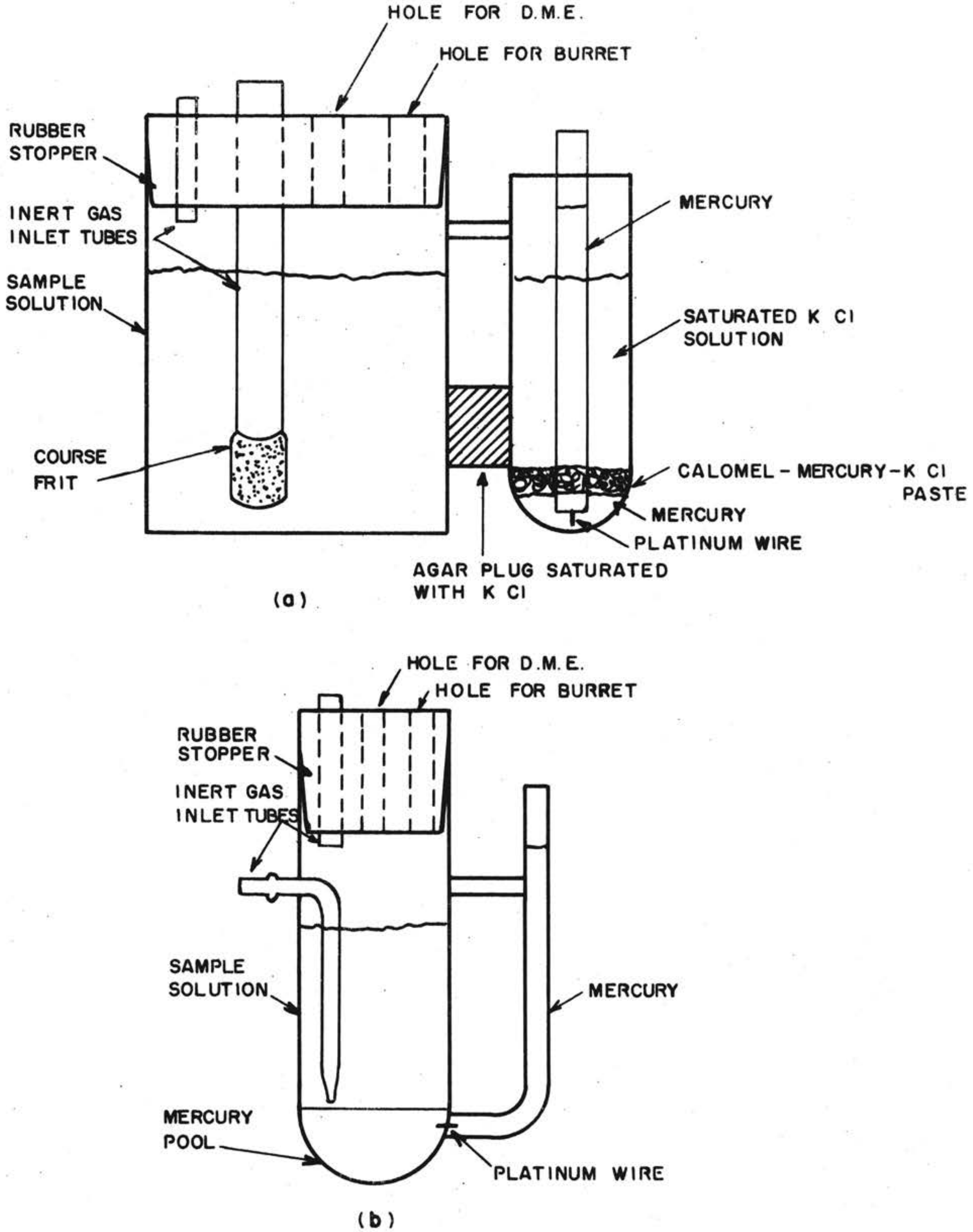

FIGURE 5-AMPEROMETRIC TITRATION CELLS

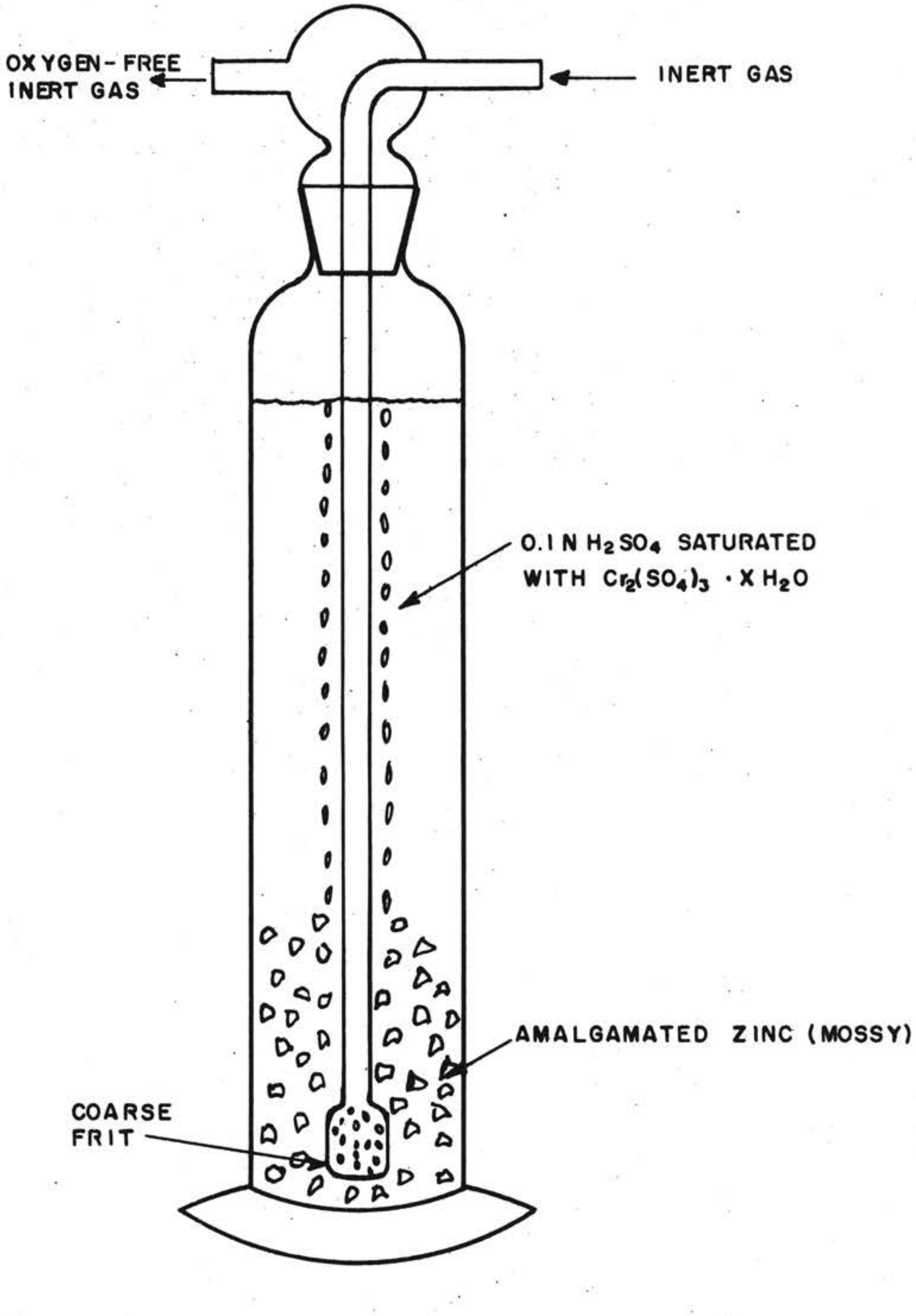

FIGURE 6 - CHROMOUS SULFATE OXYGEN SCRUBBER

EXPERIMENTAL WORK

Mixed Solvents Involving Water

This work was carried out in the hope of finding a solvent system for oxine and some of its chelates which would permit conventional polarograms to be run on both. If such a low resistance system were found, then possibly amperometric titrations could be worked out utilizing the fact that a metal oxine chelate should have a more negative half-wave potential than that of the unchelated metal ion. Three solvent combinations were evaluated.

Dioxane-isopropanol-water Systems. Two different combinations of the above solvents were evaluated. In both cases dioxane-isopropanol (50-50 mixture) was used as the organic portion of the solvent system. Both systems were 0.1 M with LiCl and contained one per cent by volume of mono-ethanol amine. The systems differed in that the first contained one per cent by volume of water and the second contained 11.0 per cent water.

Using the first solvent system (1.0 volume per cent water) the following series of runs were made. The metal ions Cd(II), Zn(II), Cu(II), and Pb(II) were added to the solvent system in amounts to give concentrations of 1×10^{-3} molar. Half as much oxine as would be required to chelate the metal ion completely was also added.* A typical

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* Two moles of oxine are required to chelate a bivalent metal ion, three moles for a trivalent metal ion, etc. In all cases neutral (uncharged) chelates are formed.

solution was made in the following way:

1 ml of 0.10 M oxine in dioxane-isopropanol
1 ml of mono-ethanol amine
1 ml of 0.1 M Me(II) (aqueous)

Dilute this mixture to 100 ml with dioxane-isopropanol that is 0.1 M with LiCl.

Polarograms of the above solutions were very gradual waves with no indication of the two waves representing chelated and unchelated metal ions. Cell resistance was undoubtedly too high for the current levels encountered here.

The second solvent system (11.0 volume per cent water) was evaluated next. Instead of working with all of the bivalent metals mentioned previously, cadmium was selected as an ideal representative of the metals because of the reasonably high formation constant of cadmium oxinate (5) and the good polarographic characteristics of cadmium solutions. A solution was made as follows:

1 ml of 0.1 M oxine in dioxane-isopropanol
1 ml of mono-ethanol amine
1 ml of 0.1 M Cd(II) (aqueous)
10 ml of distilled water

This mixture was diluted to 100 ml with dioxane-isopropanol that was 0.1 M with LiCl. A polarogram of electrolyte solution and one of the solution containing Cd(II) were run, two very distorted waves corresponding to Cd(II) and Cd(II) oxinate being obtained for the latter. The polarogram of the electrolyte solution showed no waves in this region. The distortions of the curves were such as to make it appear that the resistance is still too high even with the increased water content of this system.

The solutions were allowed to stand overnight and precipitates formed during this time. Evidently chelate solubility drops to a point where precipitation begins when 11 per cent water is present. Since the system still had a resistance too high for the current levels encountered, it was decided that this solvent was unsuitable for the purpose intended.

Methanol-water System. A medium of ammoniacal methanol that was 30 per cent water was tried next. Cd(II) (5×10^{-3} M) plus oxine (5×10^{-3} M) in this solvent produced no wave at all. A precipitate formed after the solution stood for only a short time indicating that this medium does not possess the desired solvent properties. This is reasonable since methanol is more polar than the dioxane-isopropanol system and also more water was present than in the case of either of the two dioxane-isopropanol evaluations.

Precipitation Titrations

Titrations of Copper (II). In order to gain practice and learn of any difficulties that might be encountered, the work of Stock (17) in which he titrated Cu(II) in acetate buffer at -0.40 volts vs. the saturated calomel electrode was repeated and his results confirmed. The medium used was the same as that of Stock except that 30 ml of 2.49×10^{-3} M Cu(II) solution was titrated instead of 10 ml. The molarity of this solution was determined by iodometric titration. The titrant was 1×10^{-2} M oxine in ethanol-water (50-50) and one ml of a 0.3 per cent gelatin solution was added as a maximum suppressor. The solution was degassed with nitrogen for three minute intervals between titrant additions. The Sargent Ampot was used for the titration at an applied voltage of -0.4 volts and the large-volume cell with saturated calomel reference electrode was the titration vessel used.

Figure 7 was produced when current was plotted against volume of titrant. Plotted values are corrected for volume changes but still a slight curvature is noticeable. If the end point is taken as the intersection of the gradual curve (pre-end point) and the residual current line (post-end point) then this value (14.62 ml) agrees to within 2.2 per cent of the theoretical titer value of 14.94 ml.

A titration of Cu(II) in ammoniacal medium should work as well as one in acetate buffer since Cu(II) oxinate is also insoluble in this medium. Cu(II) has two well defined waves in ammoniacal medium (10).

An ammoniacal Cu(II) solution was made as follows:

13.5 ml of concentrated NH_4OH
19.3 gms. of NH_4Cl
0.3260 gms. of $CuCl_2 \cdot 2H_2O$

This mixture, diluted to 1 liter with distilled water, gave a solution 0.20 M with NH_4OH, 0.36 M with NH_4Cl and 2.44×10^{-3} M with Cu(II). The molarity of this solution was determined by iodometric titration as before. Thirty milliliters were added to the large volume cell with the saturated calomel reference electrode and a polarogram was run using the Sargent Model XXI polarograph. Two excellent waves for copper were obtained, their half-wave potentials being -0.10 and -0.37 volts vs. the saturated calomel electrode. An applied voltage of -0.70 volts vs. the saturated calomel electrode should be ideal for amperometric titrations since it is located on a very level plateau.

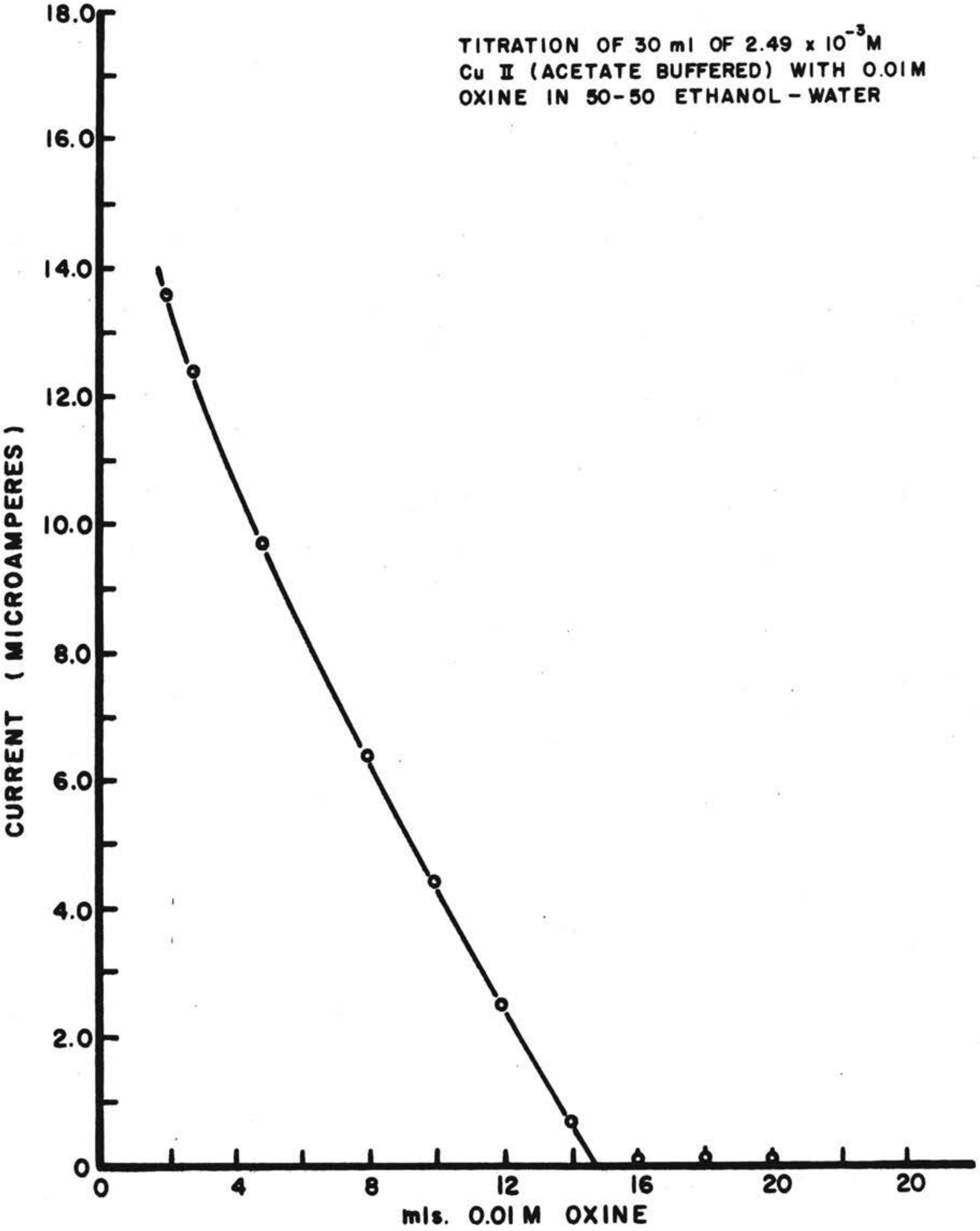


FIGURE 7 TITRATION CURVE OF 2.49 x 10^{-3}M Cu (II) IN ACETATE MEDIUM

At this point the leads to the cell were switched to the Sargent Ampot and the solution was titrated with 1×10^{-2} M oxine in ethanol-water (50-50) at an applied voltage of -0.70 volts. Current values were corrected for volume changes and plotted against the volume of titrant added (Figure 8). As in the case of the Cu(II) titration in acetate medium, a slight pre-end point curvature is noticed. If the gradual pre-end point curve is extended to intersect the residual current line (post-end point), a titer of 14.61 ml is obtained. Compared to the theoretical titer of 14.64 ml, this represents an error of about 0.2 per cent.

Titration of Nickel (II). According to Fleck and Ward (4) the useable pH range for complete precipitation of Ni(II) oxinate is 4.33 to 14.5. Ni(II) produces a well defined wave ($E_{\frac{1}{2}}$=-1.06 volts) in an ammoniacal medium in the presence of 0.005 per cent gelatin (14). In view of this it seemed that an amperometric titration of ammoniacal Ni(II) solution with oxine, based on Ni(II) reduction or both Ni(II) and oxine reduction, should have possibilities. Ni(II) oxinate was found to be quite soluble, however, and several milliliters of 0.10 M oxine solution (50-50 ethanol-water) had to be added to an ammoniacal Ni(II) solution to induce precipitation.

Ni(II) oxinate is quite insoluble in acetate medium (pH=5.0) requiring very little of the 2.5×10^{-2} M oxine (in 50-50 ethanol-water) to induce precipitation from a dilute Ni(II) acetate-buffered solution. Ni(II) in acetate medium, however, produces a poorly defined wave which is irreversible (15). In view of this an amperometric titration based on the reduction of Ni(II) in acetate medium did not appear to be feasible.

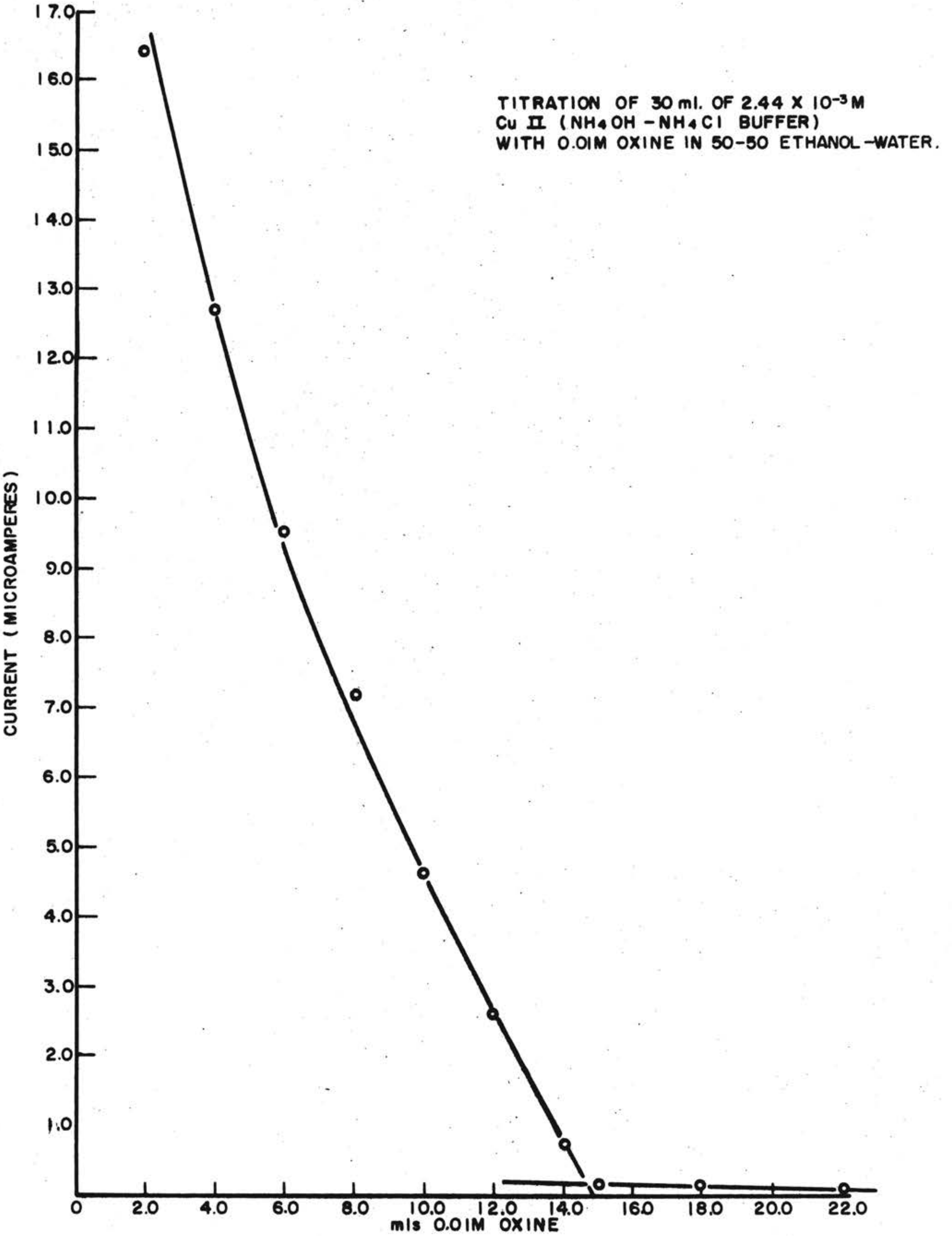


FIGURE 8 - TITRATION CURVE OF 2.44 X 10^{-3}M Cu (II) IN AMMONIACAL MEDIUM

In an article by Lingane and Kerlinger (15), the authors showed that Ni(II) produced well defined waves both in aqueous KSCN and in aqueous pyridine media. According to them, Ni(II) had an $E_{\frac{1}{2}}$ value of -0.70 volts vs. the saturated calomel electrode in 1.0 M aqueous KSCN and an $E_{\frac{1}{2}}$ value of -0.78 volts vs. the saturated calomel electrode in a 0.05 M aqueous pyridine solution that was 1.0 M in KCl. They used a 0.05 per cent gelatin solution as maximum suppressor.

A polarogram was made using a mixture of 30 ml of a 2.5×10^{-3} M Ni(II) solution that was 1.0 M with KSCN, with 1 ml of a 1.0 per cent gelatin solution. A wave that rose normally then dropped fairly rapidly at higher voltages was obtained. The apparent half-wave potential was -0.690 volts, this agreeing fairly well with the -0.70 volts vs. saturated calomel electrode found by Lingane and Kerlinger.

This solution was then titrated at an applied potential of -0.80 volts using the Sargent Ampot. A 2.5×10^{-2} M oxine solution in 50-50 ethanol-water was used as titrant. Although a decrease in diffusion current was produced by additions of the titrant, it was an erratic decrease and the current was reduced to low values rapidly and considerably before the theoretical end-point titer value of 6.0 ml had been reached.

Next, 30 ml of a solution 2.5×10^{-3} M with Ni(II) and 0.05 M with pyridine was added to the titration cell. A small amount of solid KCl was added to act as inert electrolyte and 1 ml of a 1.0 per cent gelatin solution was added as maximum suppressor. A polarogram run on this solution yielded an excellent wave with an $E_{\frac{1}{2}}$ value of -0.74 volts vs. the saturated calomel electrode, this agreeing fairly well with the -0.78 volts vs. the saturated calomel electrode obtained by Lingane and Kerlinger. This same solution was titrated with 2.5 x 10^{-2} M oxine in 50-50 ethanol-water at -0.82 volts vs. the saturated calomel electrode using the Sargent Ampot. The same rapid, erratic decrease in current was noticed as in the titration of Ni(II) in KSCN medium. The current dropped to a value only one-ninth of the initial current when only 1.2 ml of titrant had been added. The theoretical titer value was 6.0 ml.

A second polarogram was run after 0.5 ml of titrant had been added, two waves being obtained. The first had an $E_{\frac{1}{2}}$ value of -0.76 volts vs. the saturated calomel electrode -- essentially the same $E_{\frac{1}{2}}$ value as the initial polarogram. The second wave had an $E_{\frac{1}{2}}$ value of -1.04 volts vs. the saturated calomel electrode. Both waves had sprawling wave fronts, and the titration voltage now was partly on the wave front of the first wave. The whole Ni(II) wave, however, was abnormally small.

Apparently the Ni(II) wave is reduced in size by the addition of oxine but the rate of decrease in current is much too rapid to give a theoretical current-volume relationship.

As a check the work was repeated using fresh reagents and an applied voltage of -1.0 volts vs. the mercury pool electrode. A 10.0 ml sample of a 12.5 x 10^{-3} M Ni(II) solution that was 0.05 M with pyridine and 0.1 M with KCl was titrated with 0.05 M oxine hydrochloride. The diffusion current decreased rapidly and erratically and as before, gave a premature end-point.

The oxine hydrochloride reagent was made by adding excess concentrated HCl to 14.5200 grams of Mallinckrodt reagent grade oxine and evaporating to dryness on a steam bath. The oxine hydrochloride formed was diluted to 1 liter with water to give a 0.1 M solution of the reagent. This was done to produce an aqueous titrant of minimum acidity which is desirable in unbuffered or slightly buffered systems where pH is critical. Alternatively, the oxine would normally need to be dissolved in an acid solution to get this concentration. Since this solution contains no ethanol, it has less tendency to dissolve the oxinates formed during the titration.

The precipitate formed in all these titrations differed greatly in appearance from that of typical flocculent oxinate precipitates, looking more like the hydroxide of the metal. Also, as well as could be estimated, instead of corresponding to a 1:2 Ni(II)-oxine chelate, it has the approximate ratio of 1:04 Ni(II) to oxine. Whether a new complex or mixture of complexes is formed in these media is not known; however, the wave produced by Ni(II) in aqueous pyridine medium disappears long before its expected titer value indicates it should.

<u>Titration of Lead (II)</u>. According to Goto (8) the pH range for complete precipitation of Pb(II) as the oxinate is 8.4 to 12.3. Pb(II) exists as the biplumbite ion, $HPbO_2^-$, in alkaline solutions from pH 12.0 to pH 14.0 (10) and is reduced reversibly at the dropping mercury electrode (13) according to the equation:

$$HPbO_2^- + 2e + H_2O + Hg \rightleftharpoons Pb(Hg) + 3OH^-$$

$E_{\frac{1}{2}}$ for this reaction is -0.60 volts vs. the saturated calomel electrode at a pH of 12.1 (0.012 N NaOH) (10). In view of these properties it seemed possible that a precipitation titration of Pb(II) using oxine could be worked out.

If the pH of a solution of Pb(II) is kept in the range 12.0 to 12.3 initially and during titration, then Pb(II) will exist as the biplumbite ion and oxine should serve to precipitate Pb(II) from this medium. Oxine alone is quite soluble in this medium.

A polarogram of 2.54×10^{-3} M Pb(II) in 0.1 N NaOH run on the Sargent model XXI polarograph gave an excellent wave. From this polarogram it appeared that an applied voltage of -0.85 volts should be a suitable potential at which to carry out the proposed amperometric titration.

The molarities of all Pb(II) solutions were determined by a gravimetric sulfate procedure and also by a chelometric titration employing diphenylthiocarbazone as indicator and cyclohexanediamine tetraacetic acid as titrant.

Titration of Pb(II) Based on $HPbO^{-}_{2}$ Reduction. Ten milliliters of a 2.54×10^{-3} M Pb(II) solution with NaOH added to give a pH of 12.3 and 1.0 ml of 0.3 per cent gelatin solution were added to the 20 ml titration cell. This solution was titrated with 0.01 M oxine hydrochloride after degassing with nitrogen for three minutes before readings were taken and was degassed for three minute intervals between titrant additions.

A polarogram was run after 3 ml of 0.01 M oxine titrant was added. The wave was seen to be reduced in height considerably from what it was before titration. Figure 9 is the titration curve produced when current was plotted vs. millititers of 0.01 M oxine hydrochloride added. It shows an initial curvature up to 1.8 ml probably caused by the solubility of Pb(II) oxinate. The short but straight portion of the curve that follows extrapolates to intercept the residual current line at 5.01 ml compared to a theoretical titer of 5.08 ml. The large curved portion of the curve in the vicinity of the end point is no

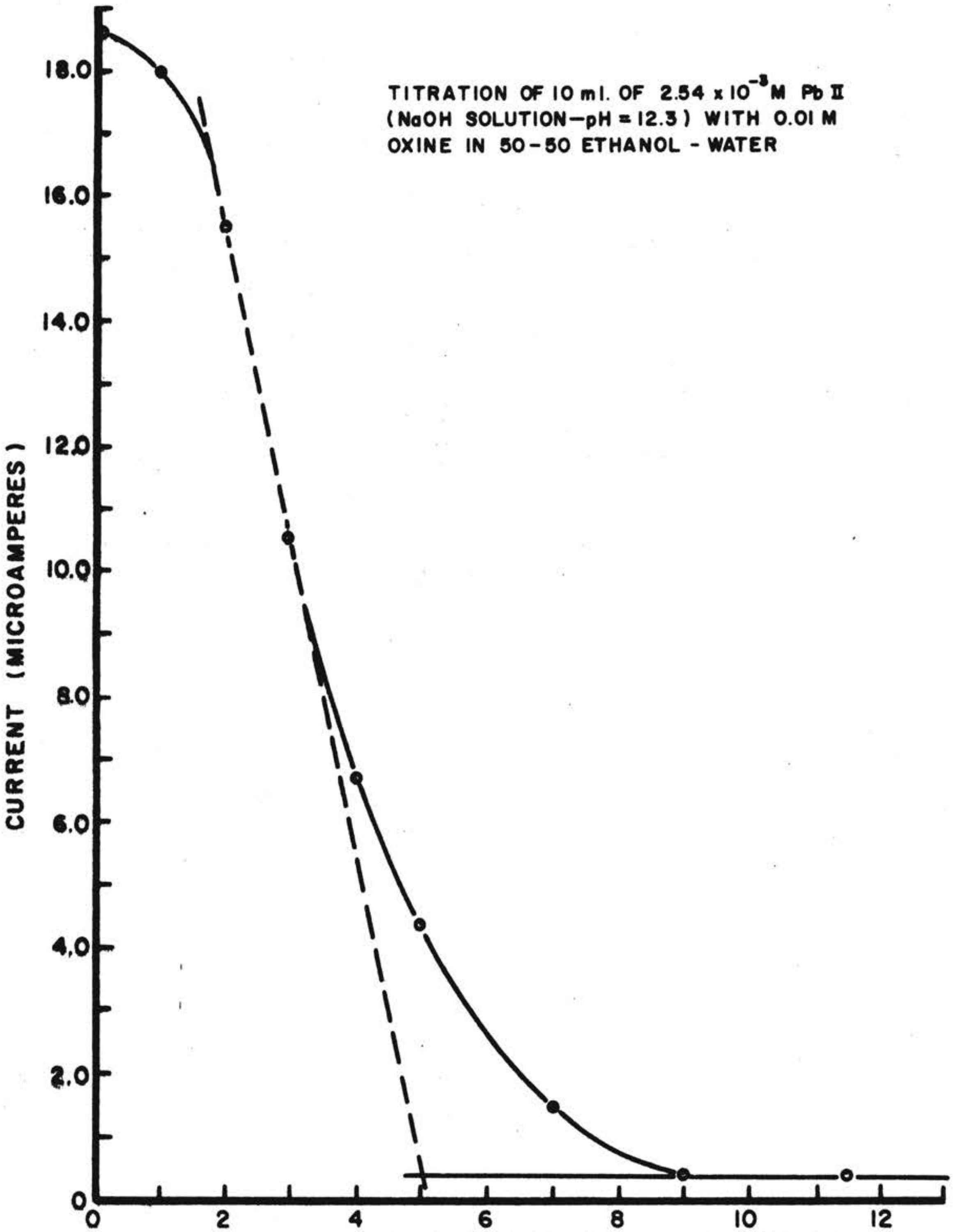


FIGURE 9 TITRATION CURVE OF 2.54×10^{-3}M Pb (II) IN NaOH SOLUTION.

doubt also due to the solubility of Pb(II) oxinate.

In an attempt to minimize the curved portions of the current volume graph, the concentration of Pb(II) was increased along with the concentration of the oxine hydrochloride titrant. Ten milliliters of 12.75×10^{-3} M Pb(II) solution (pH=12.3 with NaOH) and 1.0 ml of 0.3 per cent gelatin solution were added to the 20 ml mercury pool reference cell. This solution was titrated with 5×10^{-2} M oxine hydrochloride at -0.85 applied volts using the Sargent Ampot. A graph of current vs. volume is shown in Figure 10. The initial and end point curvatures were reduced considerably by increasing the Pb(II) and oxine hydrochloride concentrations, and the straight portion of the curve (pre-end point) extrapolates to intercept the residual current line (post-end point) at 5.10 ml. The theoretical titer value is 5.10 ml.

In order to get some idea of how high a Pb(II) concentration is necessary to give an acceptable titration curve, a 6.38×10^{-3} M Pb(II) solution (pH=12.3 with NaOH) was titrated with oxine hydrochloride. Ten milliliters of the Pb(II) solution with 1.0 ml of 0.3 per cent gelatin solution were used with the mercury pool reference cell. The solution was titrated with 5×10^{-2} M oxine hydrochloride at an applied voltage of -0.85 volts using the Sargent Ampot.

The current volume curve produced (Figure 11) has a fairly long straight portion (pre-end point) that extrapolates to meet the residual current line (post-end point) at a value of 2.54 ml. Since the theoretical titer value is 2.55 ml, the results are about 0.5 per cent low.

It appears that the titration works well at this concentration level and that solutions down to 2.54×10^{-3} M Pb(II) produce reasonable results but that the straight, pre-end point portion of the

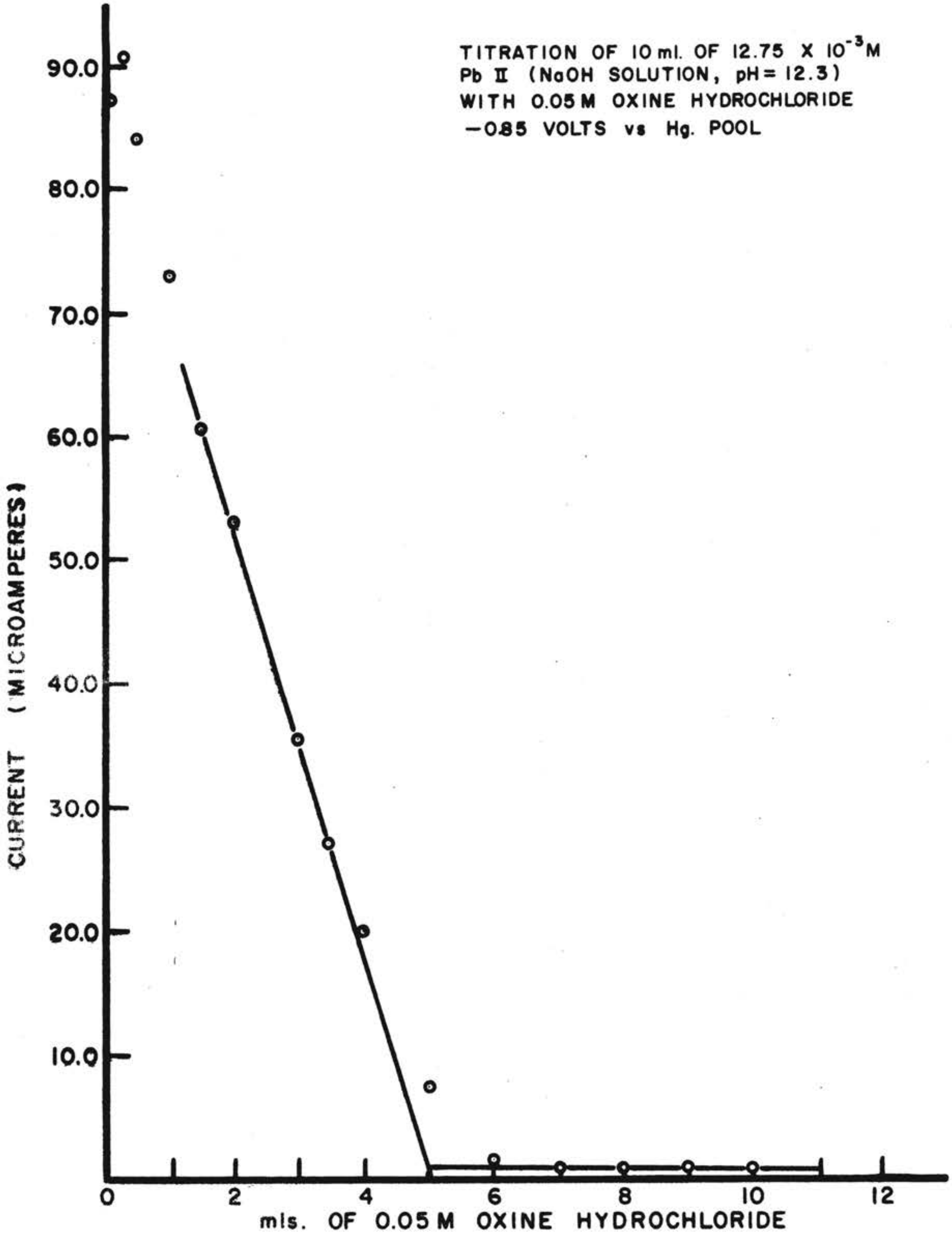


FIGURE 10 TITRATION CURVE OF 12.75 x10^{-3} M Pb(II) AT −0.85 VOLTS vs Hg. POOL

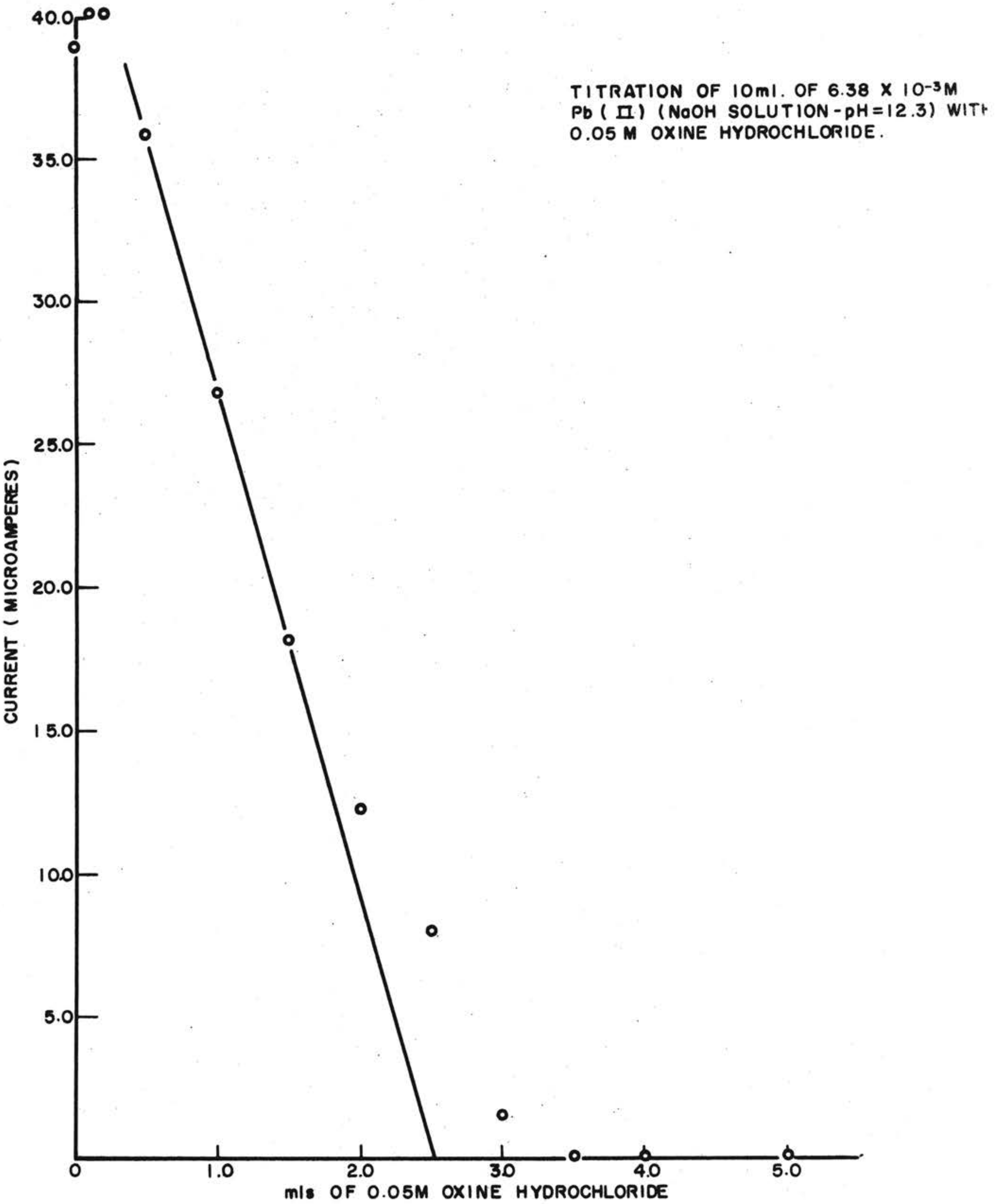


FIGURE 11 - TITRATION CURVE OF 6.38 X 10^{-3} M Pb (II) IN NaOH SOLUTION

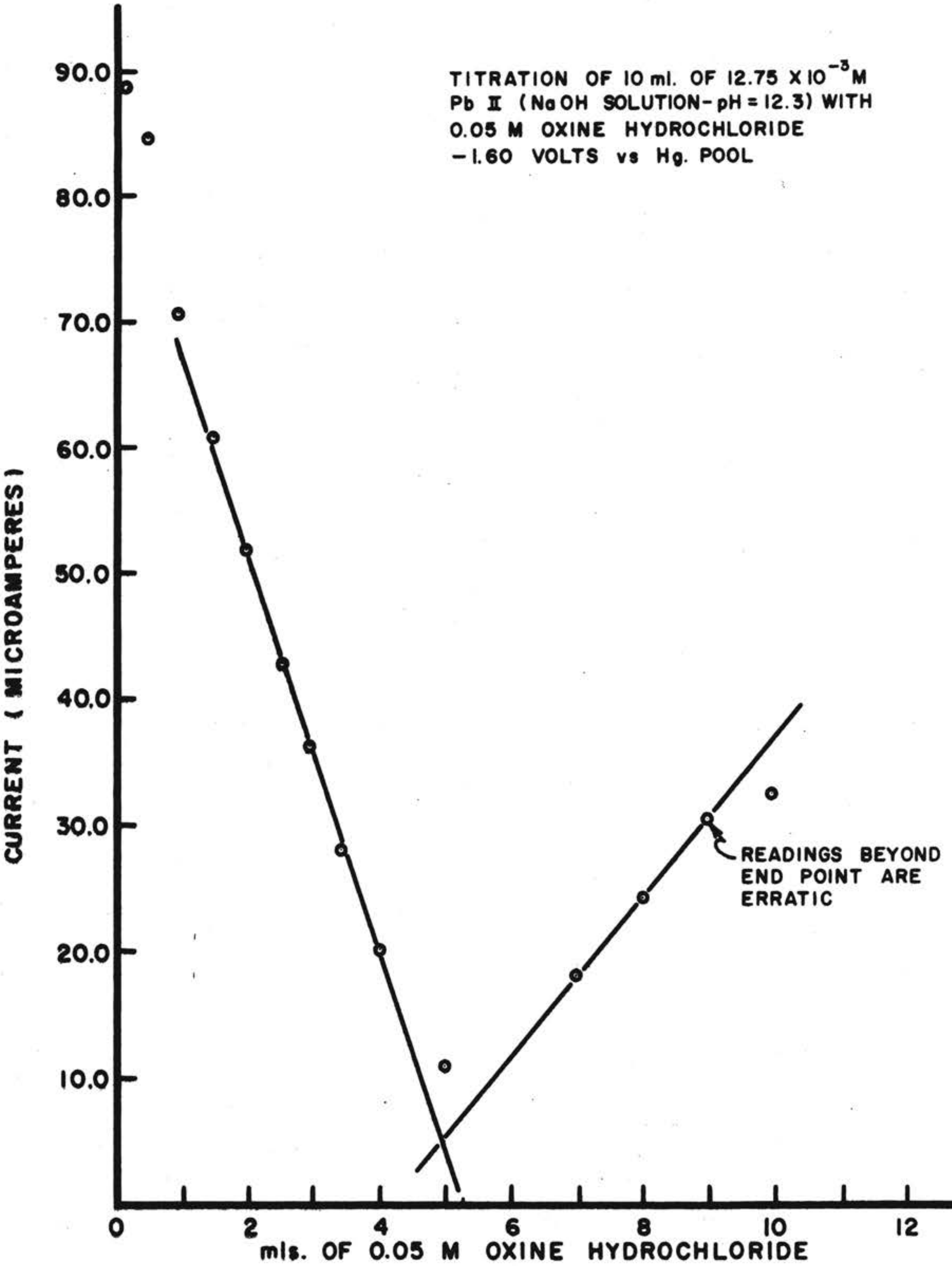
curve becomes shorter at lower concentration levels.

Titration Based on $HPbO_2^-$ and Oxine Reduction. Polarograms made with oxine in NaOH solution (pH=12.3) containing 0.03 per cent gelatin gave excellent curves with an $E_{\frac{1}{2}}$ value of -1.41 volts. From these curves, a voltage of -1.60 volts vs. the mercury pool was chosen as a suitable potential at which to carry out titrations based on oxine reduction.

Ten milliliters of 12.75×10^{-3} M Pb(II) solution (pH=12.3 with NaOH) and 1.0 ml of 0.3 per cent gelatin solution were added to the 20 ml mercury pool reference cell (e). This solution was titrated with 5×10^{-2} M oxine hydrochloride solution at -1.60 volts vs. the mercury pool.

Figure 12 shows the kind of results obtained. The post-end point values represent the current increase due to excess oxine after the end-point is reached. Only three meaningful points on this line were obtained, further additions giving erratic currents. This may be due to oxine being occluded by the Pb(II) oxinate present since the current readings tended to decrease in value on repeated standing and degassing and since oxine is known to be occluded by oxinate precipitates (12). Although the straight post-end point portion of the curve in Figure 12 intersects the pre-end point line at a value very close to theory, owing to the fact that the post-end point readings tend to be unstable, the titration of Pb(II) based on oxine reduction should not be trusted unless timing between additions of titrant and other factors are very carefully controlled.

Titration of Aluminum (III). According to Goto (8), the pH range for complete precipitation of Al(III) oxinate is 4.2 to 9.8; however,



TITRATION OF 10 ml. OF 12.75 X 10^{-3} M Pb II (NaOH SOLUTION - pH = 12.3) WITH 0.05 M OXINE HYDROCHLORIDE -1.60 VOLTS vs Hg. POOL

READINGS BEYOND END POINT ARE ERRATIC

FIGURE 12 TITRATION CURVE OF 12.75 x 10^{-3} M Pb (II) AT -160 VOLTS vs Hg. POOL tests with Al(III) in 0.1N NaOH medium (Al(III) present as aluminate ion) indicated that Al(III) oxinate might possess the desired insolubility for a precipitation titration. Very little 0.1 M oxine hydrochloride was required to precipitate Al(III) as the oxinate from dilute Al(III) solution in 0.1N NaOH. In view of this, it was decided to try an amperometric precipitation titration of such solutions.

Ten milliliters of a 2.5×10^{-3} M solution of Al(III) in 0.1N NaOH containing 1 ml of 0.3 per cent gelatin solution were added to the mercury pool reference cell. This solution was titrated with 5×10^{-2} M oxine hydrochloride. The theoretical titer value is 1.50 ml; however, no precipitate was visible when 1.50 ml of titrant had been added. Titrant was added beyond this point to see where precipitation would be noticeable and 8.8 ml of the oxine titrant were required to produce the first permanent haze of yellow Al(III) oxinate.

Obviously the Al(III) oxinate is much too soluble in 0.1N NaOH to favor a precipitation titration at these low concentrations.

SUMMARY AND CONCLUSIONS

An initial reason for carrying out this research was to find a solvent system of low enough resistance and in which most of the metal oxinates would be soluble so as to permit the use of conventional polarographic techniques. Such a system would then permit the investigation of amperometric titrations based on the reduction of oxine and its soluble chelates. As it turned out, however, when a solvent or combination of solvents was found that would keep the metal oxinates in solution, the cell resistances were much too high to permit the use of conventional polarographic equipment.

It seems reasonable that the oxine chelates could be successfully investigated using organic solvents and high-resistance polarographic techniques. It is also possible that a system such as benzene-methanol would possess the desired characteristics for low resistance polarography.

Precipitation titrations offered the next most promising approach and investigation of various possibilities in this area composed the major portion of this research.

Of the titrations tried, that of Cu(II) in ammoniacal medium was successful, showing an error of about 0.2 per cent in the determination of amounts of Cu(II) at the 5 mg. level. The Ni(II) titration, for reasons that are not readily apparent, did not prove workable, while the titration of Pb(II) at pH 12.3 gave good results in the concentration range from 2.5×10^{-3} M to 1.25×10^{-2} M with average errors of 0.1 per cent or less. Aluminum oxinate proved to be too soluble at pH 12.3 and therefore the titration of aluminum was abandoned.

It is felt that Zn(II) and Cd(II) in ammoniacal medium and Ag(I) in acetate medium might lead to workable amperometric titrations with oxine but these were not investigated because of the time involved.

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