

A STUDY OF METAL CHELATION TITRATIONS  
IN 2-PROPANOL

By

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A STUDY OF METAL CHELATION TITRATIONS  
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DEDICATION

To the memory of Dr. Paul Arthur whose guidance  
and understanding made this work possible.

#### ACKNOWLEDGMENT

Appreciation is expressed to Dr. Louis Varga for his help in the final preparation of the manuscript; to Dave Rulison and fellow graduate students for their suggestions and assistance; to my husband Ken who encouraged me to continue my studies; and to Oklahoma State University for financial aid in the form of graduate teaching assistantships.

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## CHAPTER I

### INTRODUCTION

#### Metal Analysis

The determination of metals in trace or larger amounts is a very important industrial analysis. When the metal is present in an aqueous medium, the analysis is usually fairly straightforward. Gravimetric methods and various titrations have long been used. More recently analyses using chelating agents, most commonly EDTA, have come into wide spread use. Polarography, atomic absorption spectroscopy, emission spectroscopy, and numerous other methods find application in metal analysis.

When the metal is present in an organic system, the analysis is usually more complicated. In the usual methods the metal is first separated by burning off the organic phase, followed by ignition of the sample until only an inorganic ash remains. The residue is then dissolved in an acid solution and standard methods of separation and analysis are followed. Another common method of separation is the aqueous acid extraction from the organic phase. Much recent work has been done on the separation of metals using ion-exchange and chromatographic columns (15,29,36,55). In these cases much time is spent in separation, before the actual analysis can proceed.

Some methods have been developed in which the metal can be determined directly in the organic phase, thus eliminating the need for

laborious separations. Polarographic analyses have been developed to determine the concentration of metals directly in the nonaqueous phase. The determination is based on calibration with a standard solution. Both atomic absorption and emission spectroscopy can be used for direct analysis but require standards and rather elaborate equipment. The absorbance of light at a suitable wavelength, by a metal chelate in a nonaqueous solution has been used to determine concentration but again requires a standard solution and may require separations.

Titration methods using an EDTA solution and the metal in an organic or mixed solvent system have been developed. Excess aqueous EDTA is added and the metal determined by back titration with a standard metal solution using Eriochrome Black T as indicator. Turbidity is a problem resulting from the mixture of the aqueous and organic phases and tends to obscure the endpoint.

Very little work has been done using EDTA-type chelating agents as titrants in a completely nonaqueous system, obviously because they are only very slightly soluble directly in organic solvents. It is quite possible that simpler methods of analysis could be developed if more was known about the behavior of these compounds in nonaqueous systems.

#### Possible Industrial Applications for a Nonaqueous Analysis for Metal

There are many places where a completely nonaqueous analysis could be very useful, for example in the paint industry. Paints are mixtures containing various resins, oils and driers. The driers are usually a heavy metal naphthenate, often of lead, cobalt or manganese and sometimes calcium, iron or zinc. The lead, manganese and cobalt resins

are found in some driers and the calcium and zinc resins in varnish resins. The metal concentration is quite critical in the performance of the drier (58). An accepted method of analysis for lead in paint driers is to dissolve the drier in glacial acetic acid, dilute with isopropyl alcohol and water, and treat with excess standard EDTA in water. A back titration with standard  $\text{CuSO}_4$  is performed using PAN indicator (9).

In the petroleum industry too, metals are often present. Some are introduced purposely as additives such as tetraethyl lead in gasoline and some metal sulfonates added as detergents. A standard method of testing for lead in aviation gasoline is to convert the lead alkyl to the lead chloride then to extract it from the gasoline by refluxing with concentrated HCl. The acid extract is evaporated to dryness, any organic material present is removed by oxidation with  $\text{HNO}_3$  and the Pb is then determined either volumetrically or gravimetrically (9).

Metals are often present in petroleum products as impurities introduced in the refining process. An analysis for metals in new and used lubricating oils is given by the American Society for Testing and Materials (9). The organic material is burned off. The residue is digested in  $\text{H}_2\text{SO}_4$  followed by ignition. The metals are separated into groups by routine methods followed by determination of the individual metals by volumetric or gravimetric methods.

In these cases and certainly many others, a simpler method of direct analysis would surely be preferable.

## CHAPTER II

### HISTORICAL

#### Chelating Agents in Aqueous Solution

A metal complex is formed when the solvent molecules surrounding a metal ion are replaced with other ions or molecules called ligands. The simplest type is a monodentate such as  $\text{NH}_3$  which has one point of attachment. These and bidentate as well are not very useful in quantitative analyses as they tend to form a series of stepwise complexes, the number and formulas of which, depend on the concentration of ligand in solution. It frequently happens that the formation of a higher complex begins before the formation of the next lower one is completed. By contrast for ter- and quadridentate ligands, the stabilities of the successive complexes is such that the first is much more stable than the second, thus the 1:1 chelate is formed completely before the next one begins. Thus such compounds as diethylenetriamine (dien) and triethylenetetramine (trien) can be used in metal determination.

Copper(II), zinc(II) and cadmium(II) react with dien to form two complexes and with trien and tetraethylenepentamine to form one complex (13,50,51).

The use of amine titrations is restricted to metals that will coordinate strongly with nitrogen. The alkali and rare earths do not form amine complexes (51).

The most widely used chelating agents are of the EDTA type, con-

taining both amine and carboxylate coordinating groups. EDTA forms chelates with many metals with the general structure shown in Figure 1. The presence of a number of chelate rings tends to make these complexes quite stable. Extensive work has been done with EDTA and books have been written on its uses (23,54,63).

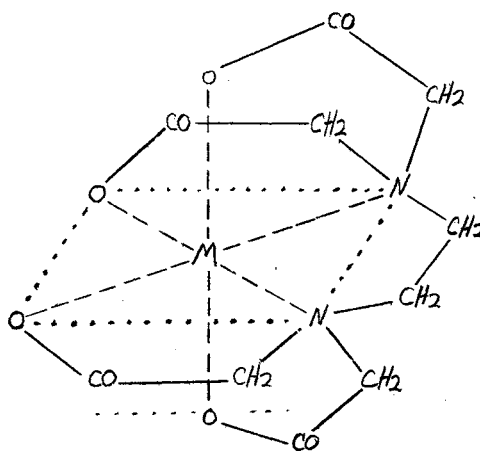


Figure 1. A Typical Metal-EDTA Chelate

An analog of EDTA, ethylenebis (oxyethylenenitrilo) tetraacetic acid (EGTA) has formation constants for most metal chelates that are in general somewhat smaller than those for EDTA. The formation constant (log) for Mg-EGTA is 5.4 and for Ca-EGTA is 10.9 and the main use of EGTA has been in the determination of Ca in the presence of Mg (32,43, 47,52). The equilibrium constants for the dissociation as the acid in  $H_2O$  and the heats of formation of some 1:1 complexes have been determined (10). The stability constants of the complexes of Ag(I), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Mg(II), Ca(II), Sr(II), Ba(II), Cd(II), Hg(II), Zn(II) and Pb(II) have been determined. A comparison of the

relative stabilities of the chelates with those of EDTA and EEDTA suggest that Fe, Co, Ni, Cu, and Sn coordinate through 1 ether and 3 carboxyls while other metals coordinate with 2 ether and 2 carboxyls of EGTA (18).

Many chelating agents are now available and the stability constants for many metal chelates in aqueous solution have been determined. Books have been written on the aqueous chemistry of chelating agents and metal chelates (13,21,24,42,47).

#### Analytical Determinations With Chelating Agents in Mixed Solvent Systems

There has been only a limited amount of investigation of chelating agents in aqueous-organic systems. Usually such medias were chosen to sharpen an indicator color change, increase the solubility of some component, or to make direct determination in an organic solution possible.

Fujinaga and Yamashita (25) determined trace amounts of mercury polarographically as the Hg-diethyldithiocarbamate in a  $\text{CHCl}_3$ - $\text{H}_2\text{O}$  system. 2-methoxyethanol was used as an additive which converted the immiscible phases into a homogeneous solution.

Magnesium has been determined spectrophotometrically as the N,N'-bis (salicylidene)-2-3-diaminobenzofuran complex in a solvent mixture of MeOH, dioxane and  $\text{H}_2\text{O}$  (16).

A determination of Mg(II), Mn(II), and Zn(II) in ferrite has been developed (14). The iron is quantitatively extracted as  $\text{Fe}^{3+}$  with methylisobutyl ketone. A Na diethylthiocarbamate solution added to the aqueous phase forms Mn(II) and Zn(II) complexes, which are extracted with trichloroethylene. Mg(II) is titrated with EDTA and the complexes in the organic phase are mixed with MeOH and back extracted with NaOH

and then titrated with EDTA.

A direct determination of the metals found in the naphthenates in paint dryers has been reported (34). Co(II), Cu(II), Mn(II) and other cations can be determined by titrating with EDTA in an H<sub>2</sub>O - EtOH medium using xylenol orange as indicator.

An analysis for iron applicable to paint driers has been developed (38). Excess EDTA is added, then back titrated with a standard zinc solution. The titration is carried out in 50 - 60% ethanol. Some problems with turbidity were reported.

Calcium(II) and zinc(II) can be determined directly in lubricating oils (26). The sample is mixed with acetone and excess EDTA added which is then back titrated with a standard magnesium solution, with Eriochrome Black T as indicator. Other metals interfere.

The titrations of Cu(II), Zn(II), Cd(II), Ni(II) and Pb(II) with 8-quinoline in dioxane - n-propyl alcohol or dimethylformamide, have been investigated (11). Cu and Zn could be determined with about 2ppt accuracy; the other titrations were unsuccessful. A photometric end-point detection was used.

A spectrophotometric determination of zinc with dithizone in a water-methylcellosolve system has been reported (1). The method was claimed sensitive to 0.1 ppm.

#### Analytical Determinations With Chelating Agents in Nonaqueous Solvents

The most common nonaqueous chelate determinations involve either precipitation of the chelate and dissolution in the organic solvent or extraction of the metal chelate by an organic solvent from the aqueous

phase before analysis. Only a few direct determinations with chelating agents in nonaqueous solvents have been developed.

Copper(II) has been determined as the 8-hydroxyquinolate following extraction with  $\text{CHCl}_3$  from an aqueous buffer (6). After concentration and dilution with  $\text{C}_6\text{H}_6$ , the solution is passed through a column of activated alumina. The Cu chelate is eluted by an 8-hydroxyquinoline solution in 1:1  $\text{CHCl}_3:\text{C}_6\text{H}_6$  while most other metals are retained. Absorbance is measured as 400 m $\mu$ .

Lead, zinc and cadmium have been determined by titration with (1, 2-cyclohexylenedinitrilo) tetraacetic acid in 2-propanol (3). The acid was solubilized by use of ethanolamine. Quantitative results were reported.

Potentiometric titrations of mixtures of metals and the  $\text{di}(\text{Bu}_4\text{N}^+)$  salt of EDTA in tert-butyl alcohol, with tetrabutylammonium hydroxide have been reported (40). Mg(II) could not be determined by titration with the tert-butylammonium salt of EDTA owing to precipitates of various M:EDTA compounds, however the reverse titration of  $(\text{Bu}_4\text{N})_2\text{H}_2\text{EDTA}$  with Mg(II) was successful using Eriochrome Black T indicator and a HAC-tert-butylammonium acetate buffer.

The  $\text{H}^+$  released when metal ions react with chelating agents, can be titrated to determine the metal. Brummet and Hollweg (12) utilized such a titration in 80%  $\text{C}_6\text{H}_6$ - 20% MeOH for an indirect potentiometric determination of Cu (II), Co(II) and Ni(II). Dimethylglyoxime, dithizone, 8-quinolinol and 1-nitroso-2-naphthol were used as chelating agents and standard NaOH as titrant.

Blair and Pantony determined Cr(III) spectrophotometrically as the 8-hydroxyquinolate following dissolution of the precipitate in  $\text{CHCl}_3$  and



dilution with  $C_6H_6$  and a chromatographic separation (6). Absorbance was read at 425 m $\mu$ . Lead has been determined spectrophotometrically as the diphenylthiocarbazone complex following extraction into xylene from an aqueous  $CN^-$  solution (60).

Zinc has been determined directly in lubrication oils (41). The Zn-dithizone complex in a benzene-methanol system was used as the basis of a spectrophotometric determination. It was reported that less than 0.1% zinc in oils can be determined with 1-2% accuracy. Only lead and mercury interfere.

Dimethylglyoxime was used as titrant by Behm and Robinson (5). Micro amounts of Ni(II) and Co(II) were determined in a solution of 1:1  $CHCl_3$ -isopropyl alcohol. Spectrophotometric titrations determined Ni to 3ppt and Co to 2.5ppt.

Takahashi and Robinson used 1-nitroso-2-naphthol for the titration of divalent metals in N,N'-dimethylformamide (56). Spectrophotometric titrations of Cu(II) and Ni(II) were reported with precision of 2ppt. Lead and zinc interfere and the titrant is gradually decomposed by the solvent.

#### Complex Formation in Nonaqueous Solutions

The formation of complexes in nonaqueous solvents has not been widely investigated, though a number of studies have been done and the stability constants determined and solvent effects noted for some systems. The chloro complexes of Fe(III) which exist in N,N'-dimethylacetamide have been examined in dilute solution over the mole ratio range 0-14 moles Cl/mole Fe(III) (20). There was evidence of mono, di and tetra chloro complexes.

Potentiometric and spectrophotometric methods were used by Golub (27) to study nitrite complexes of lead(II) in MeOH and MeOH-H<sub>2</sub>O solutions. Complexes of the formulas  $\text{Pb}(\text{NO}_2)^+$ ,  $\text{Pb}(\text{NO}_2)_2$ ,  $\text{Pb}(\text{NO}_2)_3^-$ , and  $\text{Pb}(\text{NO}_2)_4^{2-}$  were reported.

Manahan and Iwamoto studied the stepwise formation constants of the chloro complexes of Cu(II) and Cu(I) in acetonitrile (39). Both Cu(II) and  $\text{Cl}^-$  are more weakly solvated in acetonitrile than in water and Cu(I) has a much higher solvation energy. By spectrophotometric and potentiometric means it was determined that Cu(I) forms  $\text{CuCl}$  and  $\text{CuCl}_2^-$  complexes and Cu(II) forms complexes of the formulas,  $\text{CuCl}^+$ ,  $\text{CuCl}_2$  and  $\text{CuCl}_3^-$ .

The effect of the solvent on the stability of complex compounds has been studied by Popa (49). Complexes of Ag(I) with pyridine (Py) and its derivatives was examined in acetone-H<sub>2</sub>O and dioxane-H<sub>2</sub>O systems. The instability constants of Ag(I) complexes with Py, 2MePy, and 2,6-diMePy for 10 different concentrations of the solvent from 0-90% were determined. For  $(\text{AgPy}_2)^+$  in 30% Me<sub>2</sub>CO,  $\text{pK} = 4.16 \pm 0.001$ . There was a nonlinear dependence of the instability constants on the proportion of organic solvent.

The formation constants of ten Ag(I)-amine complexes in acetone have been determined (44). A stable diamine complex was indicated for all but one of the amines. The stability constants were two to four orders of magnitude greater than for the analagous complexes in water.

The complexes of Cd(II), In(II) and Sn(II) formed by varying amounts of dimethylformamide in H<sub>2</sub>O, MeOH and acetonitrile solvents have been studied (28). Complexes with formulas of  $\text{In}(\text{DMF})_6^{+3}$ ,  $\text{Sn}(\text{DMF})_6^{+2}$ ,  $\text{Cd}(\text{DMF})_6^{+2}$ ,  $\text{Cd}(\text{H}_2\text{O})_3^{+2}$ ,  $\text{Cd}(\text{H}_2\text{O})_6^{+2}$ , and several solid solvates were observed.

Jantz (33) utilized conductivity, viscosity and density measurements to study  $\text{AgNO}_3$  solutions of varying concentrations in anhydrous acetonitrile and benzonitrile. The formation of ion pairs and aggregates was noted as the concentration increased. The data supported the view that MeCN has a more open solvent structure than either PhCN or  $\text{H}_2\text{O}$ .

The dissociation constants of acetylacetonate and the successive stability constants of the Co(II) and Ni(II) acetylacetonates have been determined at 0, 25 and 40°C in methanol and n-propanol- $\text{H}_2\text{O}$  mixtures (17).

Anodic and cathodic polarographic studies of Hg(II) and Cd(II) cyanide complexes were done by Touller and co-workers (59). The dissociation constants were determined for Hg(II) in 0-100% ethanolamine in  $\text{H}_2\text{O}$  and 0-70% ethylenediamine in  $\text{H}_2\text{O}$ . Data for Cd(II)-CN complexes in 0-25% ethylenediamine in water indicated that the addition of amine lowers the stability of the complexes, especially in dilute solutions of the amine, which solvates the metal more strongly than water.

Savedoff studied the conductance of a number of lithium (I) and tetrabutylammonium salts in anhydrous acetone (53). It was reported that for LiCl, the unsolvated ions are in contact while in LiBr, the ion pairs are formed from fully solvated ions.

The formation of Cd(II) complexes with thiourea in aqueous-EtOH solutions (0, 5, 25, 55, 77, 91 and 100%) was studied polarographically by Migal and Tsipliyakove (45). With increased EtOH concentration, both size and stability of the complexes increased. A sudden increase in stability was observed at 77% alcohol because EtOH was substituted for  $\text{H}_2\text{O}$  in the solvate shells.

A similar study of Cd-SCN complexes in aqueous EtOH was done by Bondarenko (8). As the per cent alcohol in the solvent increased, the stability of the complexes increased.

The individual formation constants  $k_1$ - $k_6$ , have been determined for aquo-Cu(II) complexes in MeNO<sub>2</sub> (37). Comparison with similar data using EtOH as solvent showed the constants to be larger in MeNO<sub>2</sub>.

Polarographic studies of the chloro complexes of Cd(II) in H<sub>2</sub>O, H<sub>2</sub>O-MeOH, MeOH and H<sub>2</sub>O-EtOH were done by Turyan (61). In H<sub>2</sub>O, CdCl<sup>+</sup>, CdCl<sub>2</sub>, and CdCl<sub>3</sub><sup>-</sup> are present and in mixed and nonaqueous media, CdCl<sub>4</sub><sup>-2</sup> and CdCl<sub>5</sub><sup>-3</sup> are also formed. The stabilities of the complexes increase with decreasing dielectric constant.

Ablov and Nazarova (1) did a spectrophotometric study of the pyridinates of Ni(II) and Co(II) in MeOH, EtOH, PrOH, BuOH and Me<sub>2</sub>CO. The monopyridine complexes were reported most stable in Me<sub>2</sub>CO and in the alcohols the stability increased from MeOH to BuOH. The addition of a small quantity of H<sub>2</sub>O to the solvents, significantly decreased the stabilities of the complexes.

The polarographic behavior of the quinolates of Al(III) and Fe(III) in dimethylformamide has been studied (19).

## CHAPTER III

### SCOPE OF INVESTIGATION

Previous studies (3,31) have led to the development of a titration method for directly determining metals in organic solvents. This technique does not require the separation of metal from nonaqueous phase as do most such analyses. The current work was to continue the development and expansion of this method.

It had been discovered that EDTA-type chelating agents could be dissolved in 2-propanol (or methanol or ethanol) with the use of an organic amine. The amine complexes of numerous metal ions were also soluble. Thus direct titrations could be performed. Titration studies of (1,2-cyclohexylenedinitrilo) tetraacetic acid (CDTA) complexed with ethanolamine in 2-propanol had been done for Cd(II), Pb(II) and Zn(II) (31). The endpoints were determined amperometrically. CDTA quantitatively complexed all three metals.

The present investigation was undertaken to develop the methods for the determination of metals using a different chelating agent and some different metals. The  $\text{LiNO}_3$  carrier electrolyte used in the amperometric determinations caused some interference and a substitute was sought. Also it was hoped that a visual means of endpoint detection could be found.

## CHAPTER IV

### APPARATUS AND POLAROGRAPHIC TECHNIQUES

All polarographic data was collected by the use of a Sargent Model XXI polarograph and a Sargent Model A IR compensator. The polarographic cell used is shown in Figure 2 and the circuit in Figure 5. The basic steps used in performing the experimental amperometric titrations are as follows;

1. Place a known volume of the metal ion-supporting electrolyte solution in the cell.
2. Degas the solution for about 30 minutes.
3. Fill the T-tubes with supporting electrolyte.
4. Fill the electrode compartments with saturated acetone calomel solution.
5. Start the mercury flow in the electrode. Rinse the electrode with the solvent, wipe dry and lower into the cell.
6. Obtain a polarogram of the metal in solution.
7. Insert the buret tip (specially constricted) into the cell and add a small amount of titrant. Repeat, obtaining a polarogram after each addition.
8. After completing the titration, remove the electrode from the solution, rinse with solvent, immerse the tip in solvent and stop the mercury flow.

A complete polarogram was obtained in each step to provide infor-

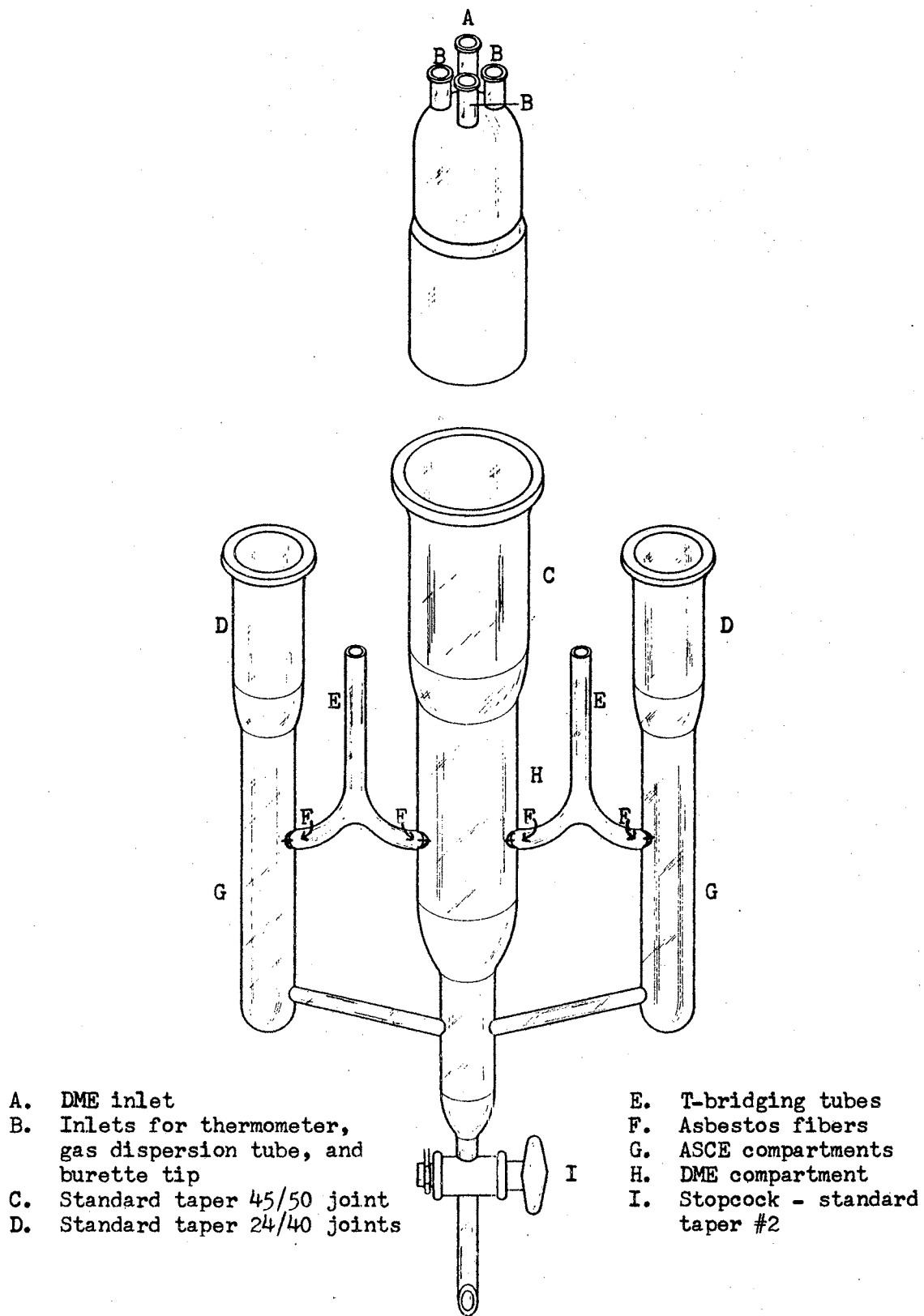


Figure 2. Polarographic cell

mation on complex formation, and to allow selection of the best voltage for current measurement.

The half-wave potential ( $E_{1/2}$ ) of a species being reduced at the dropping mercury electrode is characteristic and can be used for identification. Normally when a metal ion forms a complex, the  $E_{1/2}$  of the complex is found at a more negative potential than the simple ion (See Figure 3).

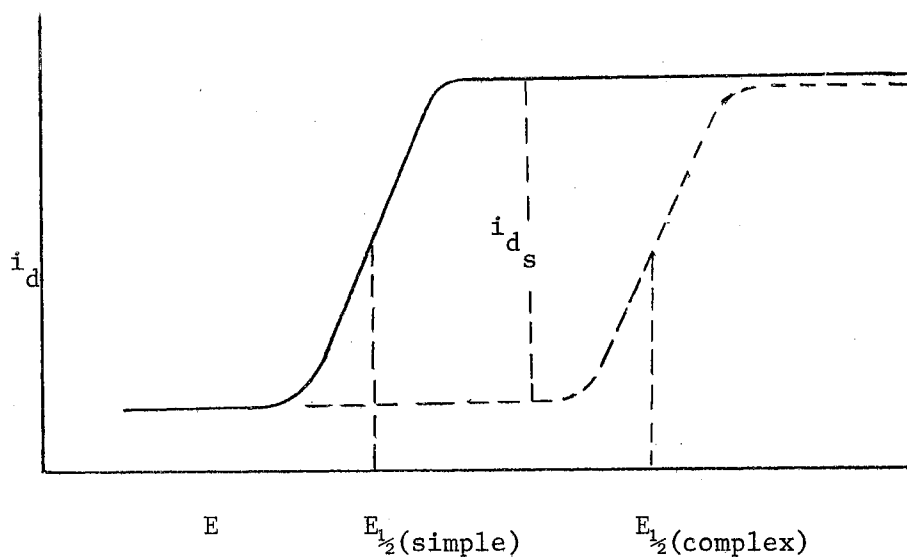


Figure 3. A Typical Polarogram

The extent of this shift is an indication of the stability of the complex. The wave height (diffusion current) is proportional to the concentration of the species being reduced. For each titration, plots were made of diffusion current (Figure 31) at the chosen potential, versus milliliters of titrant added (See Figure 27,28). Dilution corrections in the current were made as follows:



$$I_{d(\text{corrected})} = I_{d(\text{measured})} \left( \frac{V_{\text{titrant}} + V_{\text{original solution}}}{V_{\text{original solution}}} \right)$$

For successful titrations, curves were obtained as shown in Figure 4.

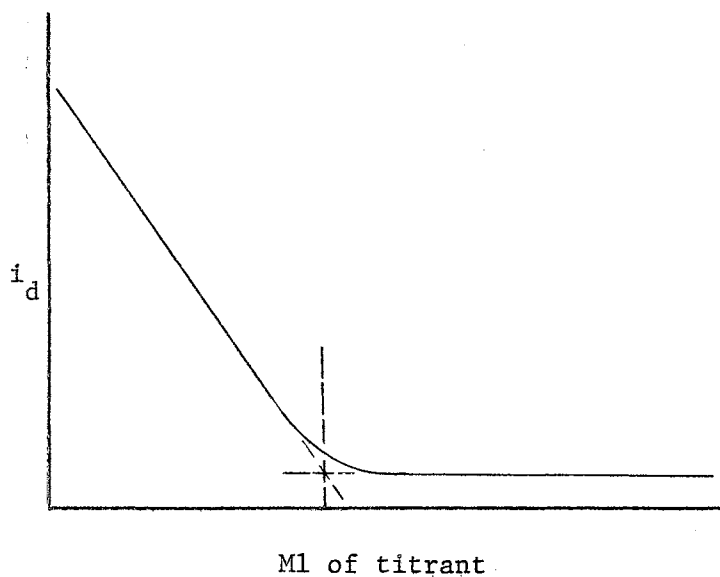


Figure 4. Amperometric Titration Curve

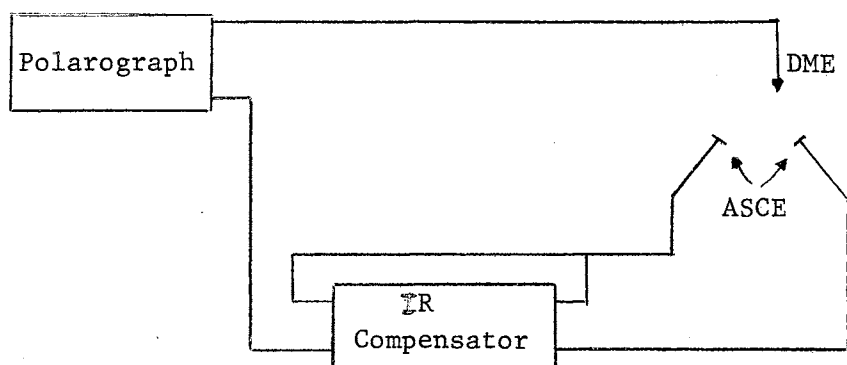


Figure 5. Circuit Diagram

## CHAPTER V

### REAGENTS

Acetone. J. T. Baker reagent grade was used without further purification.

2-Aminoethanol. Eastman Organic Chemicals white lable grade was used without further purification.

Ammonium Chloride. J. T. Baker reagent grade was used without further purification.

n-Butylamine. Matheson, Coleman and Bell White lable grade was distilled under nitrogen before use.

Calcium Chloride. J. T. Baker reagent grade was used without further purification.

Calcium Nitrate Tetrahydrate. J. T. Baker reagent grade was used without further purification.

Cadmium Nitrate Tetrahydrate. Fisher Scientific reagent grade was used without further purification.

Copper(II) Nitrate Trihydrate. Fisher Scientific reagent grade was used without further purification.

Diethylamine. Eastman Organic Chemicals white lable grade was distilled under nitrogen before use.

Diethylenetriamine. Eastman Organic Chemicals technical grade was distilled at low constant pressure. The fraction distilling at 83 - 88° C was used.

Disodium Ethylenedinitrilotetraacetate. J. T. Baker reagent grade was used without further purification.

Diphenylthiocarbazono. Eastman Organic Chemicals, was used without further purification.

Eriochrome Black T. J. T. Baker was used without further purification.

95% Ethanol. U. S. Industrial Chemical U. S. P. grade was used without further purification.

Ethylene-bis (oxyethylenenitrilo) tetraacetic Acid, Eastman Organic Chemicals white lable grade was used without further purification.

Ethylenediamine. Eastman Organic Chemicals white lable grade was used without further purification.

Hydrochloric Acid. Fisher Scientific reagent grade was used without further purification.

Lead(II) Nitrate. J. T. Baker reagent grade was used without further purification.

Lithium Chloride. J. T. Baker reagent grade was used without further purification.

Lithium Nitrate. J. T. Baker reagent grade was oven dried at 120°C before use.

Magnesium Nitrate Hexahydrate. J. T. Baker reagent grade was used without further purification.

Mercury. Bethlehem Instrument triple distilled mercury was used without further purification.

Methanol. Fisher Scientific reagent grade was used without further purification.

Nitric Acid. J. T. Baker reagent grade was used without further

purification.

Nitrogen. Linde laboratory grade nitrogen was used after purification by the method described by Arthur (2).

Perchloric Acid. J. T. Baker reagent grade was used without further purification.

2-Propanol. J. T. Baker reagent grade was distilled under nitrogen before use.

Pyrocatechol Violet. K and K Laboratories, was used without further purification.

Silver Nitrate. J. T. Baker reagent grade was used without further purification.

Tetra-n-butylammonium Bromide. Southwestern Analytical Chemicals, was used without further purification.

Tetraethylammonium Bromide. Eastman Organic Chemicals white lable grade was used without further purification.

Tetramethylammonium Chloride. Eastman Organic Chemicals white lable grade was recrystallized by the method of Moran (46).

Triethylamine. Eastman Organic Chemicals white lable grade was distilled under nitrogen before use.

Triethylenetetramine. Fisher Scientific reagent grade was vacuum distilled and the fraction boiling around 90° was used.

Tributylamine. Eastman Organic Chemicals white lable grade was used without further purification.

Zinc Nitrate Hexahydrate. J. T. Baker reagent grade was used without further purification.

## CHAPTER VI

### EXPERIMENTS AND DISCUSSION

#### Exploratory Studies

##### Exploratory Studies With Diphenylthiocarbazone

Dithizone has been used to determine zinc directly in a nonaqueous solvent system (41), so some qualitative studies of its behavior in 2-propanol under varying solvent conditions were done. Zinc(II), Cu(II), Pb(II), Bi(III), Mg(II) and Ca(II) were used. Concentrations of 0.001M were tried since the interest was in relatively low amounts of metal. Bismuth and lead were not soluble to this extent so were used at unknown lower concentrations. Dithizone in neutral isopropanol gave an intense green color and the metal chelates were pink, except for Cu which was yellow. In an acid solution Zn(II), Pb(II), and Bi(III) gave pink chelates as did Mg(II) after standing a few minutes. Ca(II) gave no change from the green and Cu(II) was yellow.

Since there was interest in amines as complexing agents, diethylenetriamine (dien) was chosen to test the behavior of dithizone in a basic system. Dithizone in a dien:2-propanol system was orange. Mg(II) in this medium gave a pink color that became orange at higher amine concentrations. On standing, a white precipitate formed with a colorless solution. A solution of Zn(II) added to the dithizone-dien-isopropanol system gave much white precipitate and a pink solution. A repeat with-

out the dithizone gave the precipitate. Cu(II) plus dien in 2-propanol yielded a precipitate also. Some roughly qualitative tests were performed to see if an endpoint could be detected when a dien solution was added to a metal-2-propanol-dithizone solution. In each case, the pink complex color gradually faded into orange and was accompanied by precipitate formation in most cases. Since the main interest was in basic solution and dithizone showed little promise, no further work was done with it.

#### Polarographic Studies With Triethylenetetraamine (trien)

Trien is readily soluble in 2-propanol and is known to have chelating abilities so its usefulness as a complexing agent was investigated next. Cadmium was chosen as the metal for study. Trien was made approximately 0.01M for use as the titrant. Fifty ml of 0.001M Cd(II) with 0.1M LiNO<sub>3</sub> as supporting electrolyte were used. Acetone saturated calomel electrodes (ASCE) were used as reference electrodes (4). The Cd solution gave one polarographic wave at about -0.18V vs ASCE (Figure 6). After the first titrant addition, the polarogram showed a steeply rising wave and a separate level wave (Figure 7). The first wave was probably a combination wave due to uncomplexed cadmium and a Cd:trien complex, and the second wave that of a higher complex. After the second addition, there were definitely three waves (Figure 8). The first, at the  $E_{1/2}$  for uncomplexed Cd, had decreased in height but still was steeply rising and overlapping the second very steep wave. The third wave was separate and level. After addition of enough titrant for a 1:1 trien to Cd ratio, only the second two waves were present (Figure 9) and the solution was cloudy. After enough trien had been added to allow the

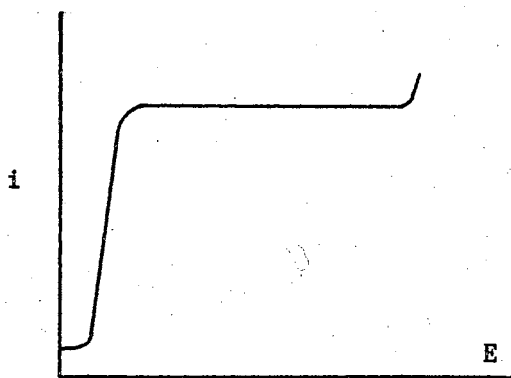


Figure 6.  
Polarogram of 0.001M Cd

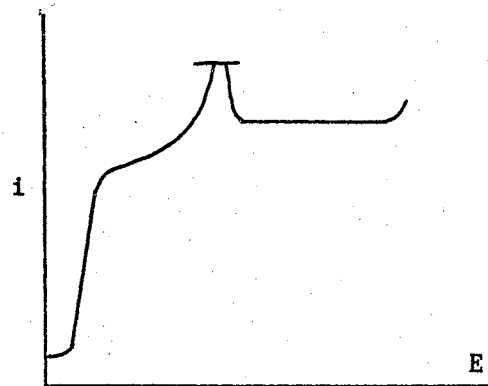


Figure 7.  
Polarogram of 0.001M Cd after  
first addition of 0.01M trien

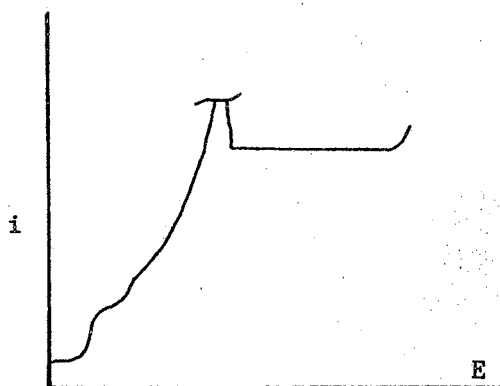


Figure 8.  
Polarogram of 0.001M Cd after  
second addition of 0.01M trien

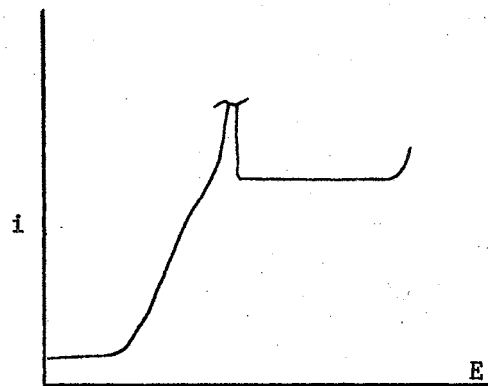


Figure 9.  
Polarogram of 0.001M Cd after  
addition of trien for 1:1 com-  
plex

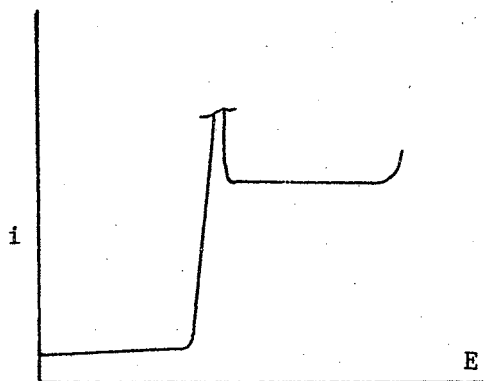


Figure 10.  
Polarogram of 0.001M Cd after  
addition of trien for 2:1 com-  
plex

formation of a 2:1 trien to Cd complex, (Figure 10) only the third wave was present. It had a maximum as it did on all the previous polarograms. It appeared that two complexes were forming: a 1 to 1 that was relatively unstable and a 2 to 1 that was more stable. Whatever the complexes were, the polarograms could not be used for titration curves due to the overlapping waves that made the wave height impossible to measure.

Next an attempt was made to find a media in which only one complex, presumably the more stable 2 to 1, would form. This was tried using ethanolamine to complex the Cd, then titrating with trien. It was hoped that the formation of a Cd-ethanolamine complex would provide a useful complex wave and prevent the formation of the 1 to 1 trien to Cd complex. A 0.001M Cd solution which was also 0.1M in ethanolamine was titrated with trien (Figure 11). Two rather irregular waves appeared. The first wave was narrow and somewhat sloping and the second was preceded by a large maximum (Figure 12). The small first wave decreased with addition of titrant (Figure 13), and on the assumption that it was due to a Cd-ethanolamine complex, titration curves were plotted. The curves showed an approximately linear decrease in wave height (Figure 14), but the disappearance did not coincide with the known endpoint based on either a 1:1 or a 2:1 trien to Cd complex.

There was some doubt as to the purity of the trien and difficulties were encountered in purifying it. Since the interest was in the development of a straightforward analysis, and not the study of complex formation, no further work was done with trien.

#### Studies of Ethylenebis (oxyethylenitrilo) tetraacetic acid (EGTA)

The EDTA-type chelating agents are not soluble to any appreciable



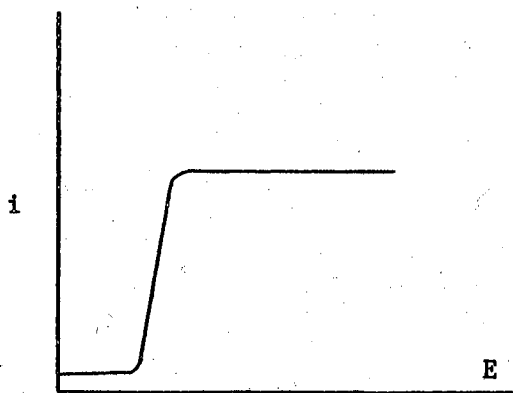


Figure 11.

Polarogram of 0.001M Cd,  
0.1M in ethanolamine

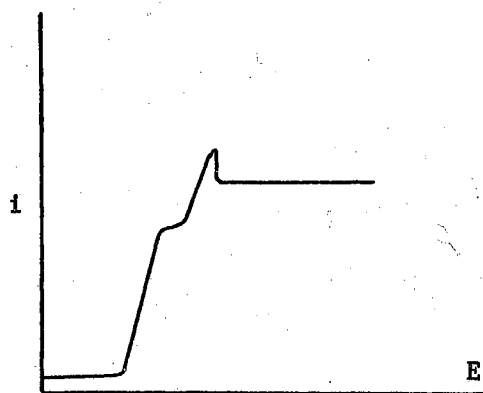


Figure 12.

Polarogram of 0.001M Cd, 0.1M  
in ethanolamine, after first  
addition of trien

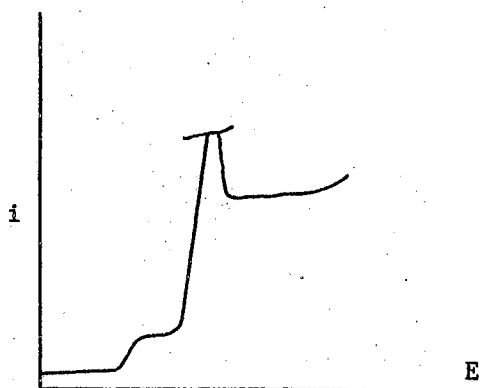


Figure 13.

Polarogram of 0.001M Cd, 0.1M  
in ethanolamine, after addition  
of trien for a 1:1 complex

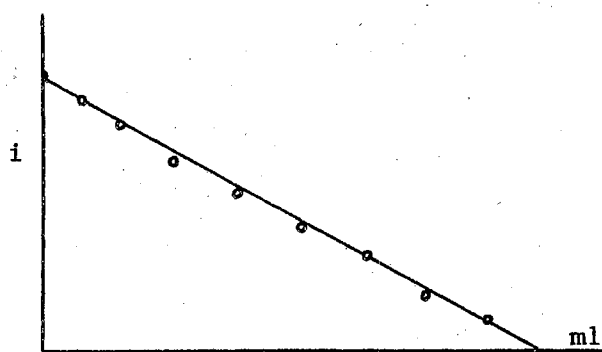


Figure 14.

Titration curve for 0.001M Cd, 0.1M  
in ethanolamine, titrated with 0.01M  
trien

extent in 2-propanol or ethanol. However this type compound can be dissolved in these solvents with the use of an organic amine.

It was determined that EGTA would dissolve 0.01M in isopropanol that was also 3M in ethanolamine (EA), and would go 0.1M in ethanol that was 0.5M in n-butylamine (nBA). It was also soluble to the extent of 0.1M in isopropanol that was also 0.5M in nBA. Diethylamine (DEA) 0.15M would dissolve 0.01M EGTA in 2-propanol. These were the solubilities that could be reached with reasonable effort, shaking by hand at room temperature. No attempt was made to determine maximum solubilities in various amine concentrations. An EGTA solution of 0.01 - 0.1M in 0.1 - 1.0M amine was desired and when a system was found soluble in this range, no effort was made to determine the minimum amount of amine necessary to hold the EGTA in solution. Previous work had shown that in some amine solutions a slow precipitation reaction occurred which was evident only after standing some time. In this work, if a solution remained clear overnight, the complex was judged soluble. It is quite possible that less amine could have been used if more shaking and longer times were involved. However a fairly large excess amine concentration was desired so it would remain essentially constant during the titrations. Several trialkylamines were tried, tributylamine and triethylamine, but would not dissolve even 0.01M EGTA in 1M amine.

Since 2-propanol was the preferred solvent and nBA gave the easiest and best solubility of EGTA, these were chosen as the system for further study.

#### Experiments to Find a Carrier Electrolyte

It was known from previous work (31) that the lithium from the  $\text{LiNO}_3$

carrier electrolyte caused precipitates with the EDTA-type chelating agents. So next an effort was made to find a replacement carrier. It was hoped that one could be found that would give a conveniently large range and that would cause no interference in the titration system. Since both the solutions used in the titrations would have a fairly high amine concentration, the first thought was to use a salt of the amine as carrier. The  $\text{HNO}_3$  and  $\text{HCl}$  salts of n-butylamine, diethylamine and cyclohexylamine were tried. First the polarogram of a 0.1M salt solution was run. Then enough amine was added to make the solution approximately 0.2M in excess amine. None of the salts gave the simple carrier wave hoped for. Most had extra waves, some small, some larger indicating impurities. All of the amines were then distilled under nitrogen and the polarograms of a 0.2M amine solution run, using 0.1M  $\text{LiNO}_3$  as carrier. None of the amines alone gave a wave. Polarograms of the salts were run as before, taking care to keep the amine present in slight excess in the salt solutions.

The diethylammonium chloride (DEA-HCl) salt gave a smooth carrier wave with a range of -1.5V but gave a wave with the addition of excess DEA (Figure 15).

Diethylammonium nitrate (DEA- $\text{HNO}_3$ ) alone and with excess DEA showed a regular carrier, but the range was only -1.2V (Figure 16).

Cyclohexylammonium nitrate (CHA- $\text{HNO}_3$ ) had a range of -1.2V and a wave at -0.9V. With excess CHA, the wave was very nearly the same (Figure 17).

The cyclohexylammonium chloride (CHA-HCl) salt carrier wave was regular with a range of -1.7V but an extra wave appeared at -1.4V with the addition of excess CHA (Figure 18).

Normal butylammonium nitrate ( $n\text{BA-HNO}_3$ ) gave an even carrier wave without and with excess nBA but had a range of only -1.2V (Figure 19).

A range of -1.5V was given by n-butylammonium chloride ( $n\text{BA-HCl}$ ) but a large rising wave appeared with the addition of excess nBA (Figure 20).

It was decided that the amine salts could not be used. Those that did give a level carrier wave both alone and with the amine, did not give the range desired.

#### Metal Amine Solutions

The chelating agents of interest could be used only when made soluble by the use of an amine of relatively high concentration. Since the metals to be titrated could be complexed by the amine as well as the chelating agent, it was necessary to have the metal present as the amine complex from the start. It was known from earlier work (31) that for many metals, a small amount of amine will cause a precipitate and the addition of more amine will cause it to dissolve presumably as a soluble higher complex. Studies were thus undertaken to determine the amounts of amine necessary to keep the metals in solution as the complex. The amine was added dropwise to 100 ml of a 0.001M metal solution at room temperature. If it became cloudy, more amine was added slowly and with shaking until it became clear or until the amine concentration became too high for use. From the amount of amine added and the volumes, the approximate molarity could be calculated. If a metal was found to be soluble, a solution was made with the metal and amine known exactly. If it remained clear overnight, it was judged soluble. Lead(II), Cd(II) and Zn(II) were tried first. Both Zn and Cd were soluble to the extent

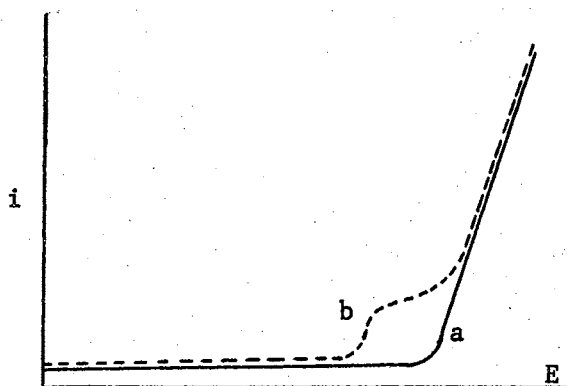


Figure 15.

Polarograms for (a) DEA-HCl and  
(b) DEA-HCl + excess DEA

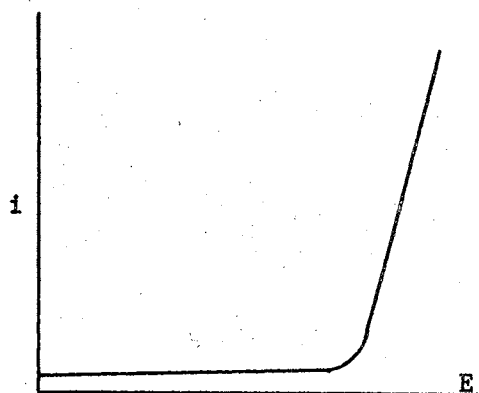


Figure 16.

Polarogram for DEA-HNO<sub>3</sub> or  
DEA-HNO<sub>3</sub> + excess DEA

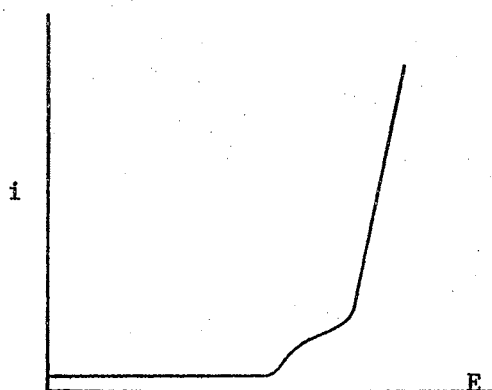


Figure 17.

Polarogram for CHA-HNO<sub>3</sub> or  
CHA-HNO<sub>3</sub> + excess CHA

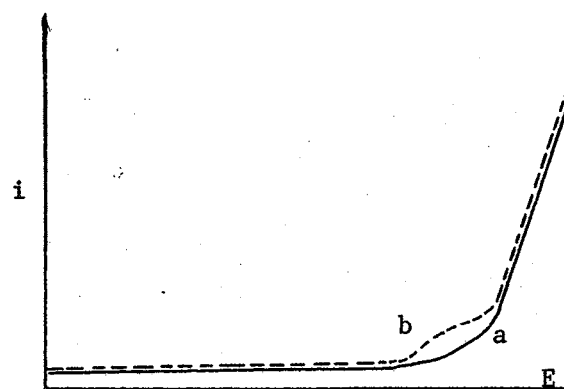


Figure 18.

Polarograms for (a) CHA-HCl and  
(b) CHA-HCl + excess CHA

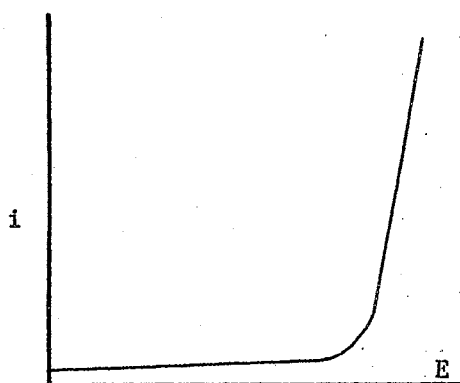


Figure 19.

Polarogram for nBA-HNO<sub>3</sub> or  
nBA-HNO<sub>3</sub> + excess nBA

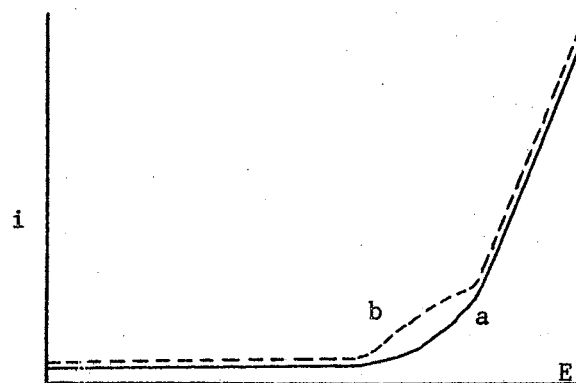


Figure 20.

Polarograms for (a) nBA-HCl and  
(b) nBA-HCl + excess nBA

of 0.001M in 2-propanol, but Pb was not. Zn, 0.001M was soluble in 0.15 M DEA but Cd was not soluble in even 0.5M DEA. Pb would not dissolve in up to 1M DEA. Millimolar Cd was soluble in 0.2MnBA and 0.001M Zn in 1M nBA. Lead would not go 0.001M in even 2MnBA.

#### Amperometric Titrations of Cadmium and Zinc With EGTA in 2-Propanol

An amperometric titration of Cd was tried to see how the system worked. Since nBA was the best for dissolving EGTA and would keep Cd in solution, it was used. The carrier was 0.03M LiNO<sub>3</sub>. It was hoped that keeping the LiNO<sub>3</sub> concentration low would minimize its interference. Fifty ml of approximately 0.001M Cd, 1M in nBA and 0.03M in LiNO<sub>3</sub> were used. The titrant was 0.100M EGTA, 1M in nBA. The Cd-nBA complex gave a fairly level wave with  $E_{1/2}$  of -0.48V. On the first addition of titrant the metal wave height decreased and a second wave appeared, presumably the Cd-EGTA complex wave. As titrant was added the solution became cloudy. When enough titrant had been added to reach and pass the endpoint, there was still a sizable Cd wave left (Figure 21). The Li was apparently precipitating the EGTA.

The titration was repeated using fifty ml of approximately 0.001M Zn in 1M nBA and 0.03M LiNO<sub>3</sub> in 2-propanol. The Zn-nBA complex had an  $E_{1/2}$  of -0.96V which did not leave much room for the wave to form before the carrier wave was reached. The addition of titrant did decrease the Zn wave height, but as before, the solution became cloudy and there was a Zn wave still present when the titration had been carried past the endpoint (Figure 22),

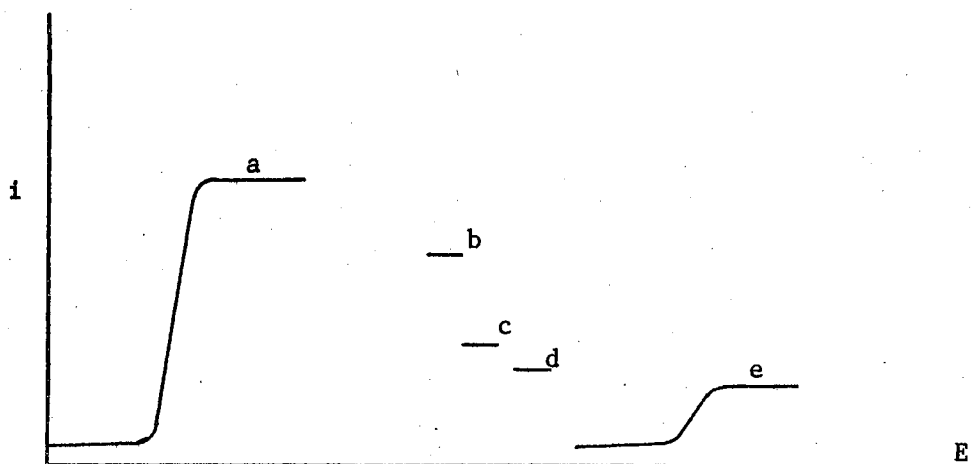


Figure 21.

Polarograms for the titration of 0.001M Cd(II) with EGTA using  $\text{LiNO}_3$  as carrier electrolyte (a) Cd-nBA complex wave, (b, c, d) wave heights for successive addition of titrant, (e) wave after addition of enough titrant to pass endpoint.

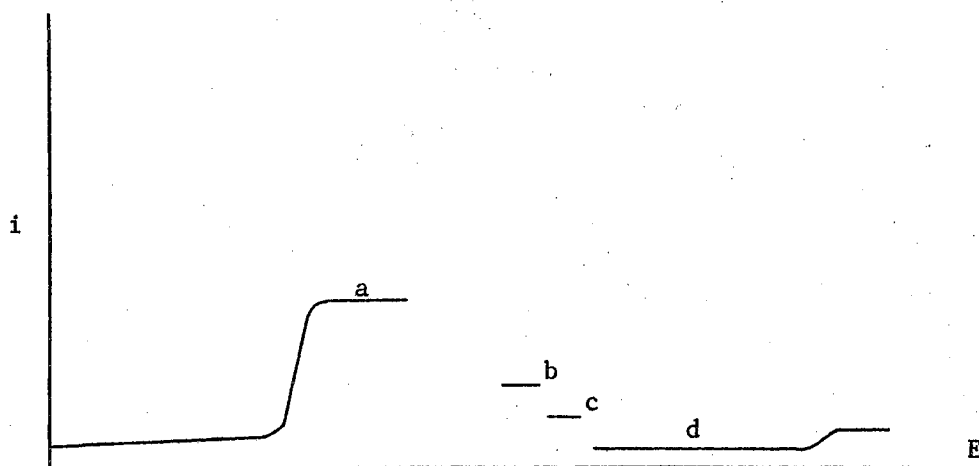


Figure 22.

Polarograms for the titration of 0.001M Zn(II) with EGTA using  $\text{LiNO}_3$  as carrier electrolyte (a) Zn-nBA complex wave, (b, c) wave heights for successive additions of titrant, (d) wave after addition of enough titrant to pass endpoint.

Studies of Some Quaternary Ammonium Salts For Use as Carrier Electrolytes.

The results of the EGTA titrations using  $\text{LiNO}_3$  as carrier electrolyte, showed definitely that a substitute must be found. It was known that the quaternary ammonium salts form precipitates in 2-propanol with Zn, Cd, Pb and many other heavy metals. However, it was discovered that these precipitates do not form if enough amine is present. First tetramethylammonium chloride (TMAC) was tried. Amine was added to a mixture of 0.001M metal and 0.05M TMAC in 2-propanol at room temperature with shaking. From the amount of amine added and the volumes, the approximate molarity of amine needed could be determined. A solution remaining clear overnight was judged soluble.

It was determined that to make 0.001M Cd also 0.05M in TMAC, the solution had to be 0.5M in ethanolamine or 1M in nBA.

It required 0.12M ethanolamine or 0.14M nBA to keep 0.001M Zn and 0.05M TMAC in solution.

A solution that was 0.001M Pb, 1.5M EA and 0.05M TMAC was clear.

To be useful the carrier electrolyte not only had to be soluble in the system but had to be free from impurities that could give extraneous waves so polarograms were run.

A polarogram of 0.10M TMAC gave a range of about -1.8V but there was a small wave present. Addition of enough nBA to make the solution 1M in the amine caused no change in the wave (Figure 23). Since the purpose of the research was to develop a simple straightforward titration, extensive purifications were to be avoided so other salts were tried.

Tetramethylammonium nitrate was tried but it was not soluble even



to the extent of 0.05M. Tetramethylammonium bromide was not soluble enough for use either.

Ammonium nitrate 0.05M gave a nice level carrier wave but had a range of only about -1.3V (Figure 24).

Tetraethylammonium perchlorate was not soluble to the extent of 0.03M.

Tetraethylammonium bromide (TEAB) 0.02M gave a range of -2.1V but had a small wave (Figure 25). Recrystallization did not remove the wave.

A 0.02M solution of tetra-n-butylammonium bromide (TBAB) gave a range of -2.25V and an even base line. An anodic wave was present from 0 to -0.15V but would cause no problems in a titration (Figure 26). Addition of 1M nBA still gave only the carrier wave on the polarogram. Since TBAB was quite soluble, gave a conveniently large range and could be used without further purification, it was chosen as the carrier electrolyte to be used in all further amperometric titrations. See Table I for summary of results.

## Applications of EGTA to the Determination of Metals in Nonaqueous Solvents

### Amperometric Titration Studies With EGTA

To determine how well EGTA worked in metal determination, some titrations were performed. Fifty ml of approximately  $10^{-3}$  M Cd, 1M in nBA and 0.01M in TBAB were titrated with 0.100M EGTA, 1M in nBA (Figure 27). End points were determined graphically from plots of wave height versus milliliters of titrant added (Figure 29). A potential of -0.96V

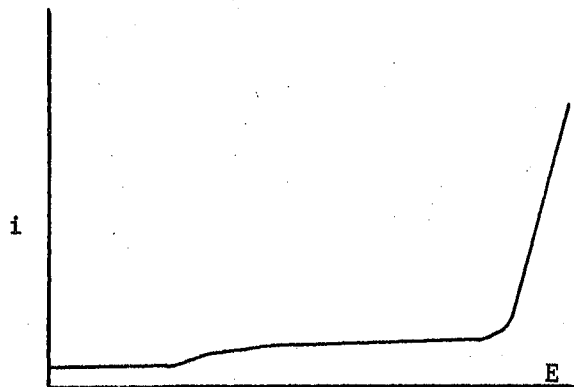


Figure 23.  
Polarogram for TMAC or  
TMAC + excess nBA

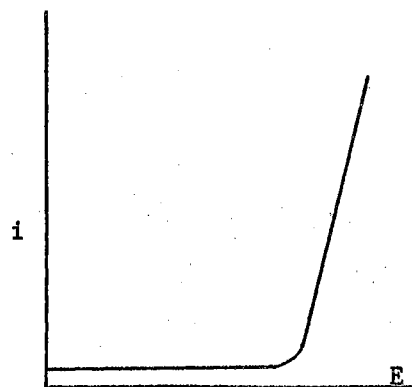


Figure 24.  
Polarogram for  $\text{NH}_4\text{NO}_3$

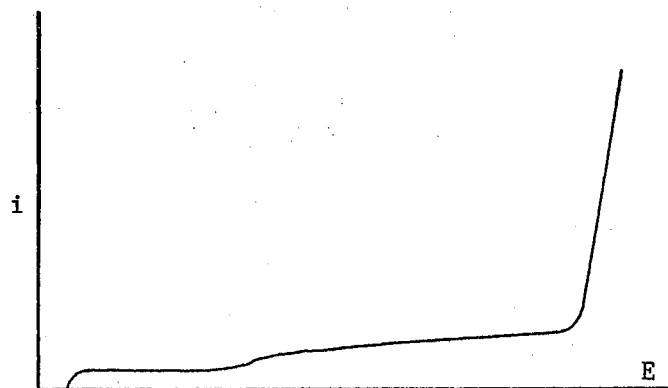


Figure 25.  
Polarogram for TEAB or TEAB + excess nBA

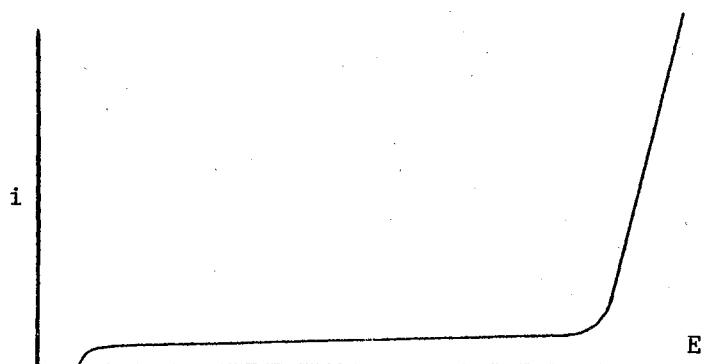


Figure 26.  
Polarogram for TBAB or TBAB + excess nBA

vs ASCE was selected as the potential at which to measure wave height for the Cd titration. No dilution corrections were needed at these concentrations since the 0.5 ml needed to reach the endpoint was negligible in the 50 ml. Some titrations were performed using 0.01M EBTA and amine concentrations of 0.2M and 0.5M. Here dilution corrections were made. Somewhat different potentials were used in plotting these titration curves since the Cd waves were not shifted to such a negative potential at the lower amine concentrations. However, the values for the metal concentrations under these varying amine concentrations were in very good agreement (Table II).

The potential at which the wave heights were measured was selected so that it would be on a level portion of the metal amine wave for all steps in the titrations. The average wave height was used in calculating the  $i_d$  for use in plotting the titration curves (See Figure 31).

To check the accuracy of the titrations, standard EDTA was used. To ten ml of the Cd stock in 2-propanol was added TBAB to make 0.01M. Fifty ml of water was added and the solution was diluted to 100 ml with 2-propanol. This gave a  $10^{-3}$ M Cd solution, 0.01M in TBAB and 50:50 in water and isopropanol. Fifty ml of this solution was titrated with 0.001M EDTA in  $H_2O$  (Figures 28 & 30) (Table III).

Attempts were made to perform similar studies using zinc. However, efforts to standardize the Zn solution under these conditions were unsuccessful. The Zn wave did not appear until about -1.2V (Figure 32) and when EDTA was added, the complex wave formed on top of the Zn wave (Figure 33). Addition of more EDTA caused an increase in wave height. No simple Zn wave could be seen so no titration curve could be plotted. Apparently the EDTA-Zn complex was not very stable under these condi-

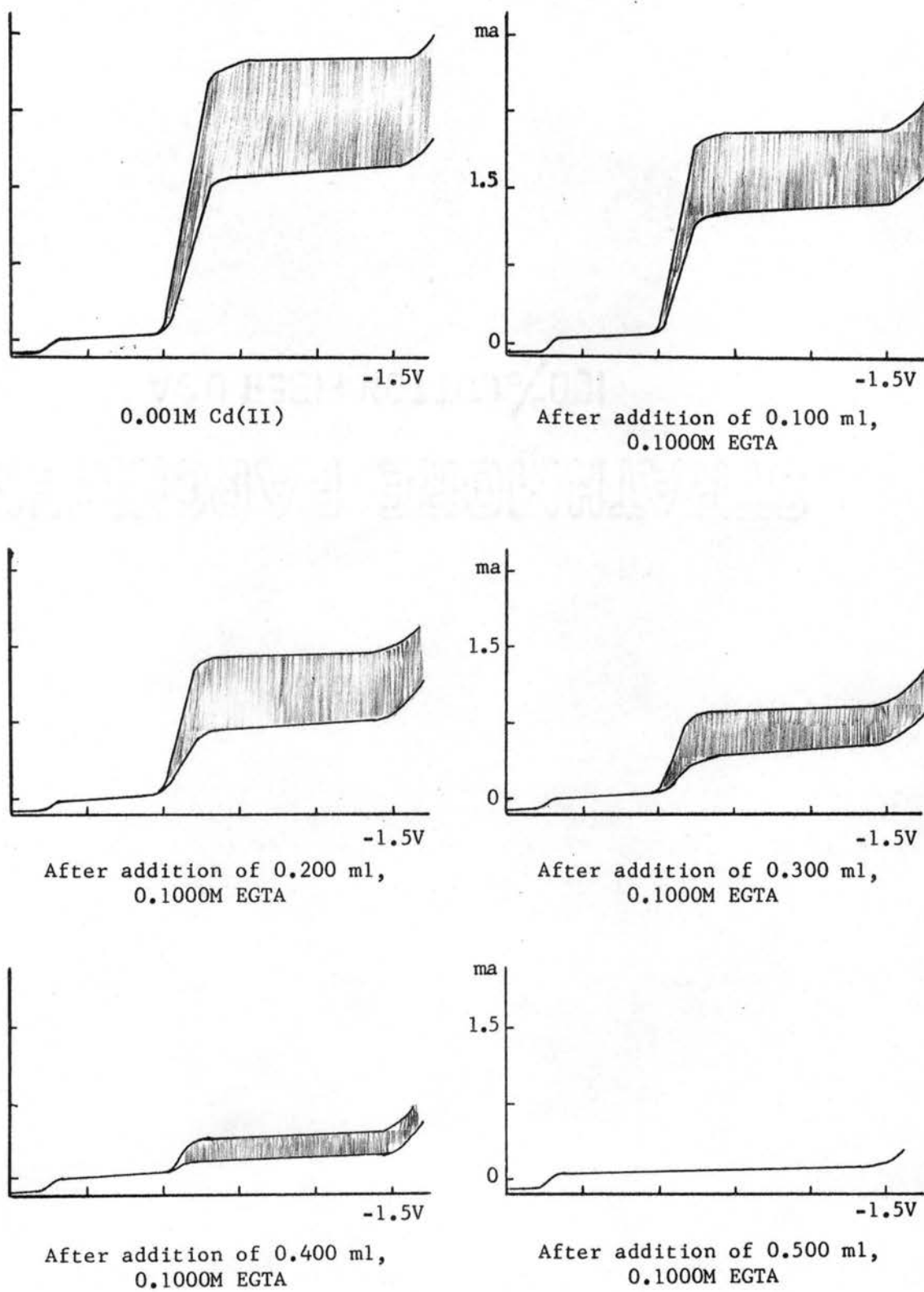


Figure 27. Polarograms for Steps in the Amperometric Titration of 0.001M Cd With 0.100M EGTA.

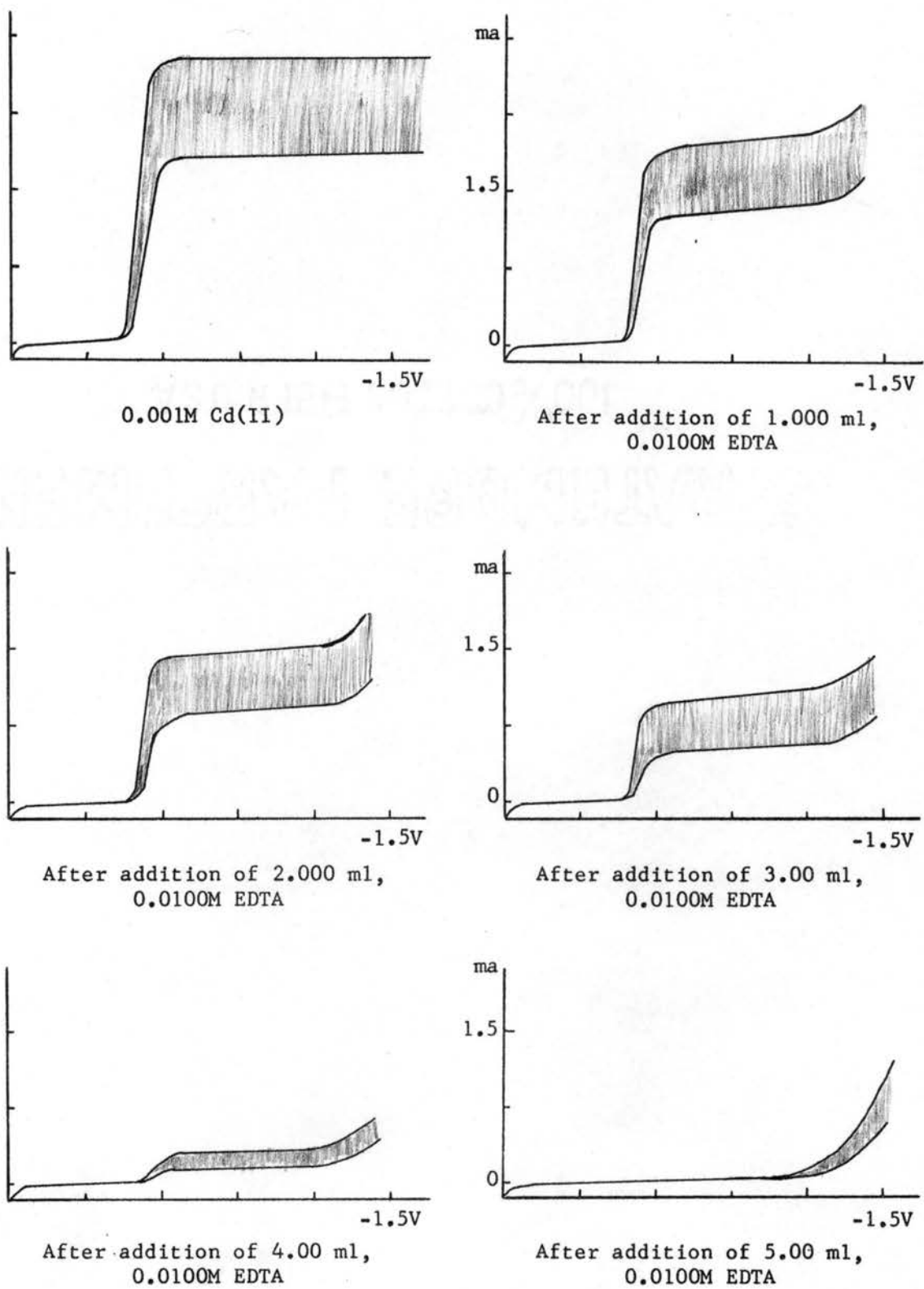


Figure 28. Polarograms for Steps in the Amperometric Titration of 0.001M Cd With 0.0100M EDTA.

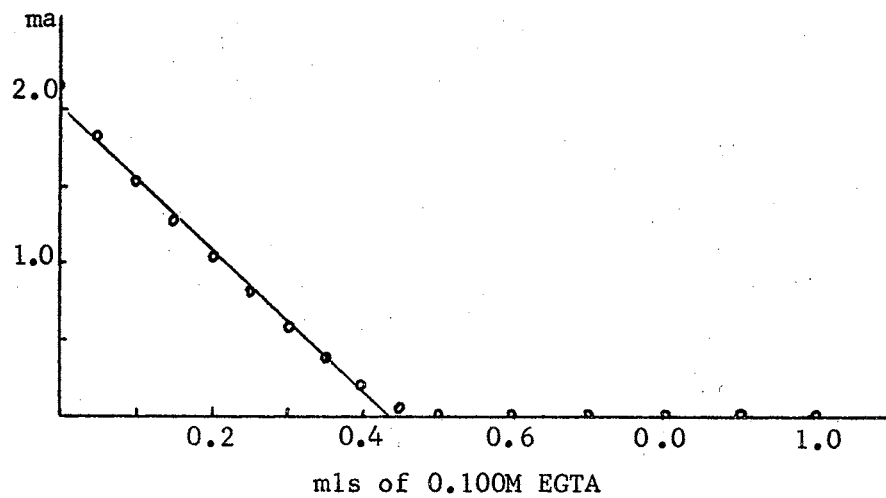


Figure 29. Amperometric Titration of Cd(II) With EGTA

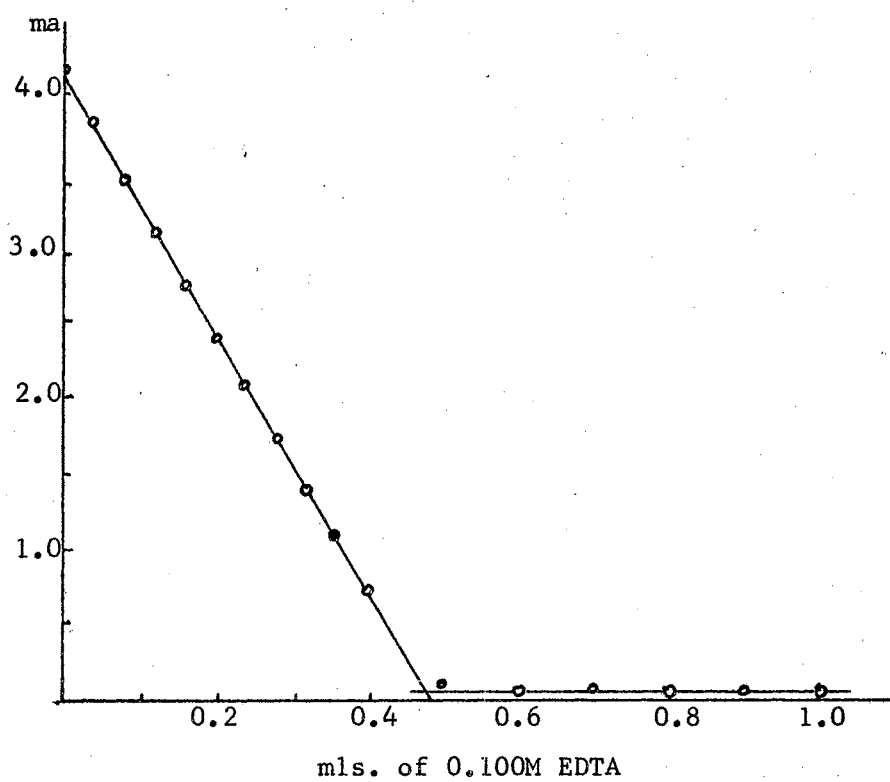


Figure 30. Amperometric Titration of Cd(II) With EDTA

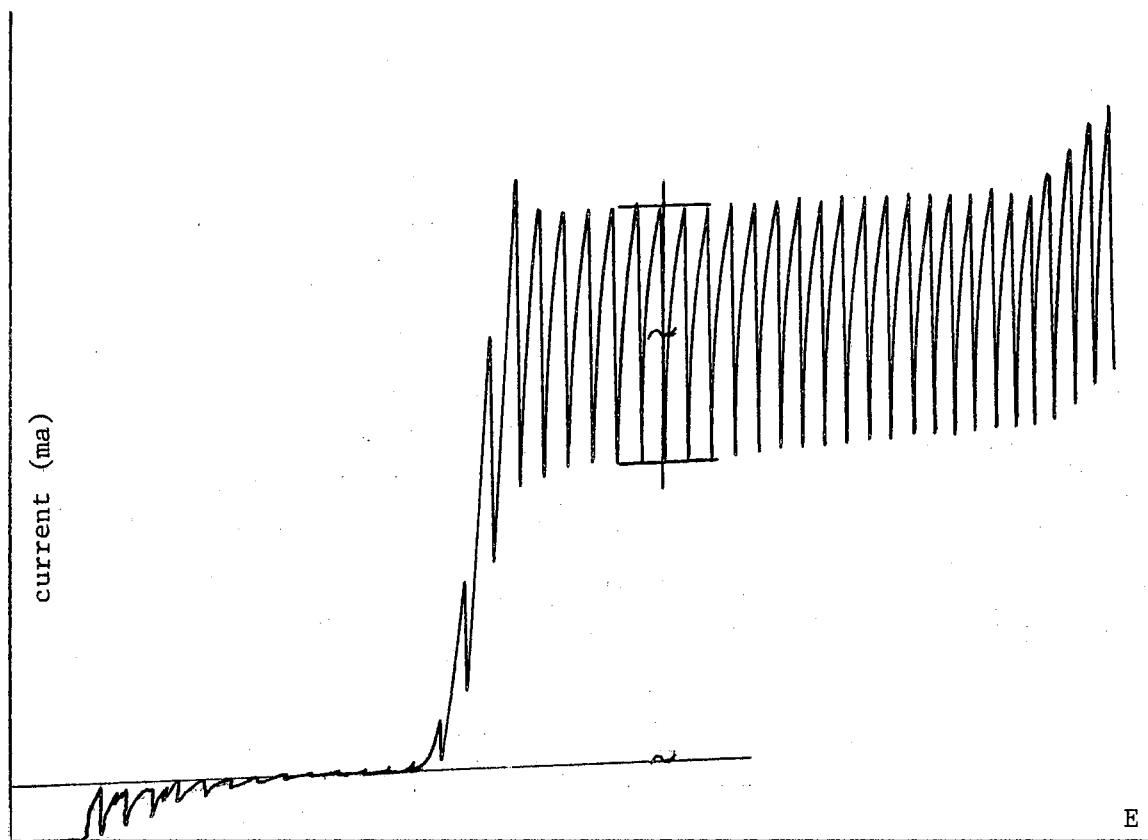


Figure 31. A Typical Polarogram Showing the Measurement of Wave Height

tions since a more stable complex is characterized by a larger difference in the  $E_{\frac{1}{2}}$  of the metal and the  $E_{\frac{1}{2}}$  of the metal-complex. This also could have been caused by the carrier. In acetonitrile the influence of anions has been noted (30). Zinc nitrate in tetraethylammonium perchlorate gives a reversible wave at  $-0.70V$  while zinc chloride in tetraethylammonium bromide gives an irreversible wave at almost  $-2.0V$  and in the presence of tetraethylammonium iodide, the horizontal portion of the diffusion current cannot be measured. In any case the titration was not successful.

### Indicator Studies

Since amperometric titrations are a bit tedious, it was hoped that a suitable indicator could be found. First pyrocatechol violet was tried. It was dark red in 2-propanol and blue in an amine solution. When 0.01M Mg in isopropanol was added to a solution of the indicator, the solution gradually became orange. Addition of 0.01M Mg to a nBA-pyrocatechol violet solution caused no change from the blue but gradually the solution became murky and on standing a colorless solution and an apparently blue precipitate was observed.

Next Eriochrome Black T (EBT) was tried. A solution of this indicator in 2-propanol was red and with 1M nBA was clear blue. Addition of 0.01M Mg to the amine solution produced a red-violet color. Next a titration was tried. Cadmium was made 0.01M and 1M in nBA. EGTA was made 0.05M and 1M in nBA all in 2-propanol. EBT was made 0.2% in 2-propanol. Twenty ml of the Cd solution was used and 10 drops of the indicator gave a red-violet color. After about 0.5 ml of titrant had been added, a turbidity was noticed but disappeared after about 1 ml had been added.



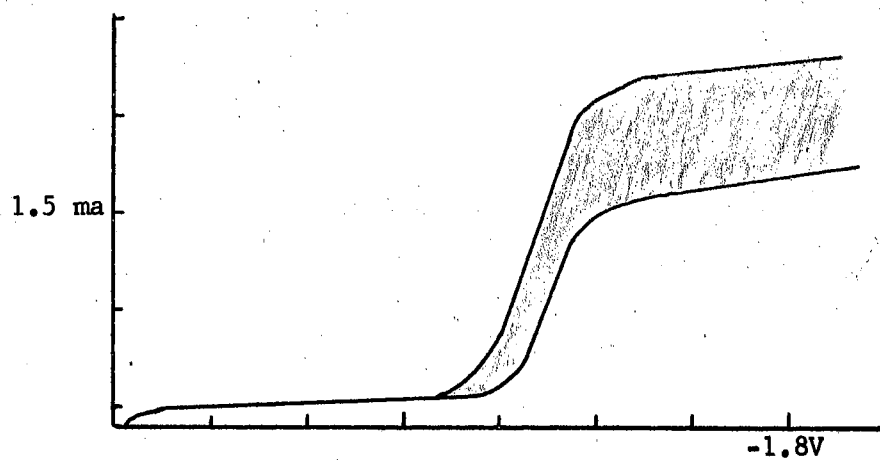


Figure 32.

Polarogram of 0.001M Zn(II) in  
50:50 H<sub>2</sub>O:2-propanol.

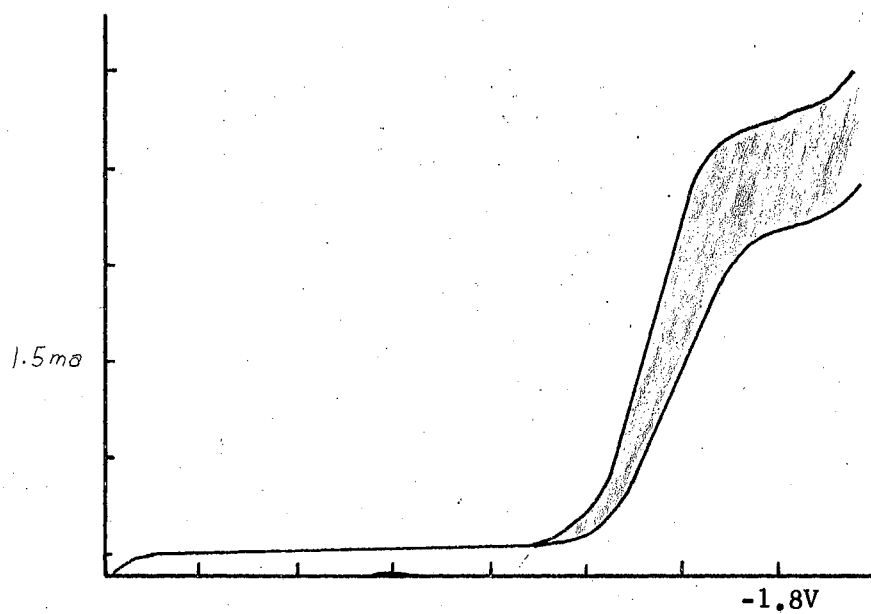


Figure 33.

Polarogram for 0.001M Zn in 50:50 H<sub>2</sub>O:2-propanol  
after first addition of 0.0100M EDTA.

The endpoint was sharp but tended to fade. However, by allowing the solution to stand a few moments when near the endpoint, the titration could be completed with no fading and a sharp color change. Trials with Ca and Zn showed that they too gave a color change with EBT that could be used.

#### Studies With Calcium and Magnesium

Neither Ca(II) nor Mg(II) can be determined amperometrically in 2-propanol so it was hoped that they could be determined using an indicator. First conditions had to be found where the metals would remain in solution with an amine. The amine was added to the 0.01M metal solution slowly, at room temperature and with shaking until the solution became clear or until the amine concentration was too high for use. From the amount of amine added and the volumes of the solutions, the molarity was calculated. As before, if the solutions remained clear overnight, the complex was judged soluble.

Magnesium, 0.01M would not stay in 1M nBA, up to 1.4M DEA or 0.15 to 1.5M ethylenediamine. Calcium, 0.01M would not stay in 0.04M to 2M nBA but would dissolve in 0.5M DEA, or 0.3M ethylenediamine. Since EGTA was known to be soluble in 0.5M DEA, this was chosen as the system in which to determine Ca.

#### Titration Studies Using Eriochrome Black T as Indicator

The titrations with EGTA were performed by taking a sample of the metal stock solution (in 2-propanol), adding enough of the appropriate amine and 2-propanol so the sample was approximately 0.01M in the metal and 1M in the amine, and titrating with 0.1000M EGTA in 2-propanol and

1M in the same amine.

For cadmium, 10 ml stock, 0.96 ml nBA, and 10 drops EBT were titrated with 0.1000M EGTA, 1M in nBA. See results Table IV.

No amine could be found that would keep Mg in solution and also EGTA, so no titrations of this type could be done for magnesium.

The calcium solutions were prepared by taking 10 ml of Ca stock, 5 ml DEA and diluting this to 100 ml with 2-propanol. Twenty-five ml aliquots were then titrated with 0.1000M EGTA, 0.5M in DEA and indicated by 10 drops EBT. For results see Table VI.

In the case of zinc, 5 ml Zn stock, 0.96 ml nBA plus 10 drops EBT were titrated with 0.1000M EGTA, 1M in nBA. There was no endpoint. Apparently the EGTA was not a strong enough chelating agent to take the Zn from the Zn-nBA complex. In hopes that perhaps another amine would work, the same titration was tried using DEA as the complexing amine and 0.1000M EGTA, 1M in DEA as titrant. However, there was no endpoint in this case either.

All the metal solutions were standardized using an aqueous solution of EDTA as titrant and having the metal solutions mostly aqueous. The only 2-propanol present was from the stock solutions and the indicator which was made up in the alcohol.

For cadmium, a solution of 2 ml Cd stock, 5 ml buffer, 10 ml water and 10 drops EBT was titrated with 0.0100M EDTA. The buffer used was one of pH 10, made by mixing 6.8g  $\text{NH}_4\text{Cl}$ , 57 ml concentrated  $\text{NH}_4\text{OH}$  and diluting to 100 ml with water. See results Table V.

Zinc was standardized by taking 2 ml Zn stock, 5 ml buffer, 25 ml water, 10 drops EBT and titrating with 0.1000M EDTA. Results are shown in Table VIII.

For magnesium, 2 ml stock, 25 ml water, 5 ml buffer and 10 drops EBT were titrated with 0.1000M EDTA. See Table IX.

Calcium stock was standardized by taking 2 ml Ca stock, 25 ml water, 5 ml buffer and 10 drops EBT and titrating with 0.1000M EDTA. Results are shown in Table VII.

For all titrations the color change was from clear violet to clear blue. In some cases a slight turbidity was noticed at the start of the titration, but in all cases disappeared long before the endpoint. Also there was some tendency for the endpoint to fade. However, if after the first color change, the solution was allowed to stand a few minutes, the second change was usually permanent.

TABLE I  
DATA ON SALTS TRIED AS CARRIER ELECTROLYTES

Salt	Concentration	Range	Remarks
DEA-HCl	0.1 M	-1.5 V	wave with excess DEA
DEA-HNO <sub>3</sub>	0.1	-1.2	short range
CHA-HNO <sub>3</sub>	0.1	-1.2	short range, extra wave
CHA-HCl	0.1	-1.7	wave with excess CHA
nBA-HNO <sub>3</sub>	0.1	-1.2	short range
nBA-HCl	0.1	-1.5	wave with excess nBA
TMAC	0.1	-1.8	small wave
TMAN	<< 0.05	—	not soluble enough
TMAB	<< 0.05	—	not soluble enough
NH <sub>4</sub> NO <sub>3</sub>	0.05	-1.3	short range
TEAP	<< 0.03	—	not soluble enough
TEAB	0.02	-2.1	small wave
TBAB	0.02	-2.25	long range, no extra waves, quite soluble

DEA - diethylamine	CHA - cyclohexylamine
nBA - normal butylamine	TMAC - tetramethylammonium chloride
TMAN - tetramethylammonium nitrate	TMAB - tetramethylammonium bromide
TEAP - tetraethylammonium perchlorate	TEAB - tetraethylammonium bromide
TBAB - tetra-n-butylammonium bromide	

TABLE II

## RESULTS OF Cd(II)-EGTA AMPEROMETRIC TITRATIONS IN 2-PROPANOL

Sample (50ml)	EGTA ml	M	Cd Concentration (calculated)	Deviations
1	4.45	0.0100	$0.890 \times 10^{-3}\text{M}$	$+0.005 \times 10^{-3}$
2	4.47	0.0100	$0.894 \times 10^{-3}\text{M}$	$+0.009 \times 10^{-3}$
3	0.443	0.1000	$0.886 \times 10^{-3}\text{M}$	$+0.001 \times 10^{-3}$
4	0.440	0.1000	$0.880 \times 10^{-3}\text{M}$	$-0.005 \times 10^{-3}$
5	0.437	0.1000	$0.874 \times 10^{-3}\text{M}$	$-0.011 \times 10^{-3}$
Average			$0.885 \times 10^{-3}\text{M}$	$\pm 0.006 \times 10^{-3}$ (7 pts/1000)

TABLE III

RESULTS OF Cd(II)-EDTA AMPEROMETRIC TITRATIONS  
STANDARDIZATION IN 50:50 WATER:2-PROPANOL

Sample (50ml)	EDTA ml	M	Cd Concentration (calculated)	Deviations
1	4.63	0.0100	$0.926 \times 10^{-3}\text{M}$	$\pm 0.001 \times 10^{-3}$
2	4.60	0.0100	$0.920 \times 10^{-3}\text{M}$	$-0.005 \times 10^{-3}$
3	4.65	0.0100	$0.930 \times 10^{-3}\text{M}$	$+0.005 \times 10^{-3}$
Average			$0.925 \times 10^{-3}\text{M}$	$\pm 0.004 \times 10^{-3}$ (4 pts/1000)

TABLE IV  
RESULTS OF Cd(II)-EGTA INDICATOR TITRATIONS IN 2-PROPANOL

Sample (10ml)	EGTA ml	M	Cd Concentration (calculated)	Deviations
1	1.003	0.1000	0.0100M	-0.0001
2	1.008	0.1000	0.0101M	0
3	1.012	0.1000	0.0101M	0
4	1.015	0.1000	0.0102M	+0.0001
5	1.012	0.1000	0.0101M	0
6	1.007	0.1000	0.0101M	0
Average			0.0101M	$\pm 0.00003$ (3 pts/1000)

TABLE V  
RESULTS OF Cd(II)-EDTA INDICATOR TITRATIONS  
STANDARDIZATION IN WATER

Sample (2ml)	EDTA ml	M	Cd Concentration (calculated)	Deviations
1	2.021	0.0100	0.0101M	+0.0001
2	2.010	0.0100	0.0100M	0
3	2.020	0.0100	0.0101M	0
4	1.993	0.0100	0.0100M	+0.0001
5	1.998	0.0100	0.0100M	0
Average			0.0100M	$\pm 0.0004$ (4 pts/1000)

TABLE VI  
RESULTS OF Ca(II)-EGTA INDICATOR TITRATIONS IN 2-PROPANOL

Sample (2.5ml)	EGTA ml	M	Ca Concentration (calculated)	Deviations
1	2.341	0.1000	0.0936M	+0.0003
2	2.330	0.1000	0.0932M	-0.0001
3	2.325	0.1000	0.0930M	-0.0003
4	2.325	0.1000	0.0930M	-0.0003
5	2.330	0.1000	0.0932M	-0.0001
6	2.341	0.1000	0.0936M	+0.0003
Average			0.0933M	$\pm 0.0002$ (2 pts/1000)

TABLE VII  
RESULTS OF Ca(II)-EDTA INDICATOR TITRATIONS  
STANDARDIZATION IN WATER

Sample (2ml)	EDTA ml	M	Ca Concentration (calculated)	Deviations
1	1.827	0.1000	0.0914M	-0.0002
2	1.835	0.1000	0.0918M	+0.0002
3	1.824	0.1000	0.0912M	-0.0004
4	1.826	0.1000	0.0913M	-0.0003
5	1.840	0.1000	0.0920M	+0.0004
6	1.831	0.1000	0.0919M	+0.0003
Average			0.0916M	$\pm 0.0003$ (3 pts/1000)



TABLE VIII

RESULTS OF Zn(II)-EDTA INDICATOR TITRATIONS  
STANDARDIZATION IN WATER

Sample (2ml)	EDTA ml	M	Zn Concentration (calculated)	Deviations
1	2.010	0.1000	0.1005M	-0.0004
2	2.040	0.1000	0.1020M	+0.0011
3	2.005	0.1000	0.1002M	-0.0007
4	2.024	0.1000	0.1012M	+0.0003
5	2.014	0.1000	0.1007M	-0.0002
Average			0.1009M	$\pm 0.0005$ (5 pts/1000)

TABLE IX

RESULTS OF Mg(II)-EDTA INDICATOR TITRATIONS  
STANDARDIZATION IN WATER

Sample (2ml)	EDTA ml	M	Mg Concentration (calculated)	Deviations
1	2.040	0.1000	0.1020M	+0.0015
2	2.010	0.1000	0.1005M	0
3	2.010	0.1000	0.1005M	0
4	2.000	0.1000	0.1000M	-0.0005
5	2.005	0.1000	0.1002M	-0.0003
Average			0.1005M	$\pm 0.0004$ (4 pts/1000)

## CHAPTER VII

### SUMMARY AND CONCLUSIONS

This research was intended to continue the development of a direct method of metal titration in nonaqueous solvents. Previous work had shown that metal-amine complexes in 2-propanol could be successfully titrated with a chelating agent kept in solution with amine. Problems had been encountered with the carrier electrolyte used in the amperometric titrations and new chelating agents needed to be found and their behavior studied.

Brief qualitative experiments with diphenylthiocarbazone showed that it would not work as a chelating agent in basic media.

Triethylenetetraamine proved unsuccessful as a titrant. Polarographic studies showed that two complexes were forming and no conditions were found in which quantitative titrations could be performed.

Studies with EGTA showed it to be soluble in 2-propanol made basic with nBA or DEA. Cd(II) and Zn(II) were soluble as nBA complexes and Ca(II) as a DEA complex. Pb(II) could not be made soluble as a nBA or DEA complex in 2-propanol.

Numerous amine salts were tried as carrier electrolytes since the  $\text{LiNO}_3$  interfered with the amperometric titrations in basic media. None of them worked.

Some quaternary ammonium salts were then tried. Tetra-n-butylammonium bromide was found to work well. It was readily soluble in 2-

propanol, gave the longest range of those tried and could be used without further purification.

A number of samples of Cd(II), in 2-propanol made basic with nBA were titrated amperometrically with EGTA in 2-propanol and nBA. TBAB was used as carrier electrolyte. These titrations were checked by titration of the metal ion in 50% water - 50% 2-propanol with aqueous EDTA. The titrations agreed within 4.3%. There was no independent means of checking the purity of the EGTA but the precision indicates the results were reproducible.

Similar titrations were attempted with Zn(II) but it was found that the Zn could not be standardized under comparable conditions so no studies were done with it.

Studies with indicators showed that Eriochrome Black T could be used to indicate the presence of Cd(II), Ca(II) and Zn(II) in 2-propanol made basic with amine. Titrations of Ca and Cd with EGTA using EBT to indicate the endpoint were successful with good precision. For Zn there was no endpoint. Titrations of the metals with aqueous EDTA was used for standardization.

Future studies should include the investigation of other chelating agents and metals with the hope of developing methods for determining mixtures of metals.

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