REACTIONS OF COPPER(II) SALTS WITH AMINES IN NONAQUEOUS SOLVENTS

By

WILLIAM MILLER HAYNES

Bachelor of Arts
Oklahoma State University
Stillwater, Oklahoma
1959

Submitted to the faculty of the Graduate College
the Oklahoma State University
in partial fulfillment of the requirements
for the degree of
DOCTOR OF PHILOSOPHY
May, 1966

REACTIONS OF COPPER(II) SALTS WITH AMINES IN NONAQUEOUS SOLVENTS

Thesis Approved:

Paul Arthur

Thesis Adviser

V. Brown Morsett

Louis P. Varga

Tom E Moore

Clarence M. Cunningham

JH Boggs

Dean of the Graduate College

ACKNOWLEDGMENT

I would like to express my gratitude to my wife, Nan, for her understanding and encouragement and to my adviser, Dr. Paul Arthur, for his guidance during the course of this investigation. Appreciation is also extended to Dr. T. E. Moore and Dr. L. P. Varga for their advice and assistance.

I would also like to acknowledge indebtedness to the Dow Chemical Company for financial assistance through a Research Fellowship and to the Department of Chemistry of Oklahoma State University for a teaching assistantship.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

BACKGROUND PRINCIPLES

Introduction

Investigations by Carley (9) and Warner (32) of complex ions formed from copper(II) salts and high molecular weight amines in 2-propanol solutions revealed unusual metal-to-amine ratios such as 1:1.765, and 1:1.61. This data indicated that copper combines with high molecular weight amines to form a mixture of complexes rather than a single complex. The amperometric technique employed to obtain the metal-to-amine ratios depended upon the supposition that a known metal amine complex would precipitate from solution. However, Carley found by analysis that the precipitate which was formed during an amperometric titration of copper(II) chloride dihydrate with tri-n-butyl amine contained little or no amine. This fact coupled with a thermogravimetric analysis of the precipitate led Carley to conclude that small amounts of water (which had previously been ignored) were probably influencing these results.

The investigation reported here was undertaken to study the nature of complexes formed with copper(II) salts and amines in 2-propanol solutions which are truly anhydrous. In order to achieve this, the first part of this research problem was devoted to devising a procedure for effectively removing water from solvents and solutions. This portion of the problem also involved the development of apparatus and techniques for handling and for analyzing the resulting extremely anhydrous solutions.

A second important area of this investigation was in the testing of existing methods and the development of new methods, by means of which the nature of copper amine complexes could be determined. Among the methods used were polarography, spectrophotometry, potentiometry and special chemical tests.

Spectrophotometry

Spectrophotometry has been used in a variety of ways for studying complex ions in solution. Among the more extensively employed spectral methods is that of continuous variations (more commonly called Job's (18) method).

The simplest case, in which a single complex MB_N is formed between metal M and ligand B, should suffice for illustration of Job's method. To determine the value of N, it is common procedure to start with solutions of M and B of equal concentration. These are mixed by adding X liters of B to (1-X) liters of M, where $X < 1$, so as to obtain a series of solutions with different ratios of M to B but for which the sum of the initial molar concentrations of M and B in each solution is a constant. This may be expressed:

$$C_M + C_B + C \qquad (1)$$

It is a simple matter to adjust each mixture by appropriate additions and dilution so that they are identical except for M, B, and MB_N concentration (e.g., in the case where volumes are not additive).

If equation (1) is divided through by the constant C and if $\frac{C_B}{C}$ is set equal to X, then the system is on a mole fraction basis:

$$\frac{C_m}{C} + \frac{C_B}{C} = \frac{C}{C} = 1 \tag{2}$$

where

$$\frac{C_B}{C} = X \text{ and } \frac{C_M}{C} = 1 - X$$

The solutions are then examined spectrophotometrically. Absorbances for each solution are measured at a wave length selected where MB_N absorbs but M or B do not. The absorbances are then plotted versus X. From the value of X at which the absorbance passes theough a maximum, and from the relationship $N = \frac{C_B}{C_M} = \frac{X}{1-X}$, the value of N is obtained. Figure 1 illustrates the type of curve obtained with this plot.

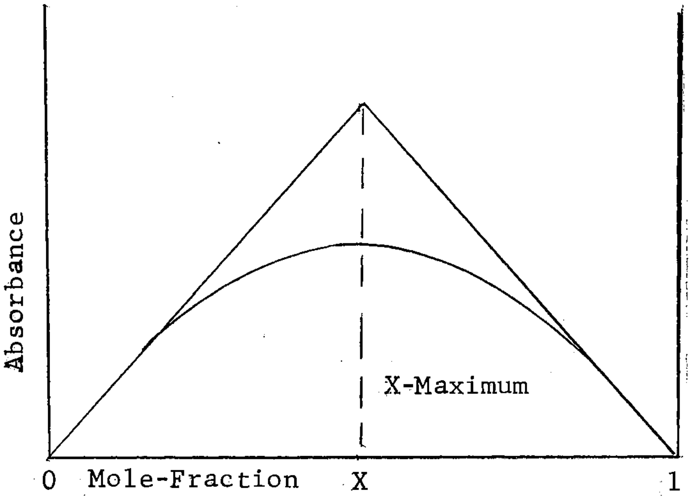


Figure 1. Typical Job's Spectral Plot.

Theoretical justification for this technique may be seen from the following discussion.

Let C'_M, C'_B, and C'_{MB_N} be the equilibrium concentrations of M, B, and MB_N, respectively. For any mixture the following equations apply:

$$C'_M = C(1-X)-C'_{MB_N} \tag{3}$$

$$C'_B = CM-NC'_{MB_N} \tag{4}$$

$$C'_M C'^{\,N}_B = KC'_{MB_N} \tag{5}$$

The condition for a maximum in the curve of absorbence (which is proportional to C'_{MB_N}) plotted against X is that $\frac{dC'_{MB_N}}{dX} = 0$. Differentiation of equations 3, 4, and 5 and combination of the three resulting differential equations with equations 1 through 4 gives:

$$N = \frac{X}{1-X} \tag{6}$$

Determination of the value of X for which the absorbance is a maximum allows the calculation of N by equation 6.

Vosburgh and Cooper (30) extended the theory of the method of continuous variations to include cases in which more than one compound is formed from a given pair of components and Katzin and Gerbert (20) derived equations for the general treatment of consecutive complexes by the continuous variations technique.

Woldbye (33) points out that many results reported in the literature must be considered unreliable because the investigators failed to take into full account two basic assumptions of Job's method.

The first assumption was that the law of mass action is valid in terms of concentration. Early investigators in many instances did not take into consideration variation of activity coefficients due to changes in ionic strength of the solutions. The omission of activity coefficients from the mass action expression causes serious difficulties in the calculation of valid complex formation constants. When an investigator wishes to get useful expressions of the law of mass action in terms of concentration, experiments are usually carried out in a salt medium of relatively high constant ionic strength. Under conditions of constant ionic strength and relatively low concentrations of metal ion, the activity coefficient variation due to changes in ligand and metal ion concentrations are minimized.

The second assumption is that the reactants form only one complex or, in the case of the extended method of Vosburgh and Cooper (30), that the complex under consideration be at a high degree of formation. The range of existence of the complex must be wide enough so that the central ion is present in the form of a particular complex at some appropriate value of the free ligand concentration. For example, in a solution in which $C_{Ni^{++}} = 0.5M$ and $C_{NH_3} = 3.0$ the nickel ion will be distributed approximately as follows: 50% $(Ni(NH_3)_5^{++}$, 25% $Ni(NH_3)_6^{++}$, 25% $Ni(NH_3)_4^{++}$. Very often, not more than 50% of the central ion concentration is present in the form of a particular complex and Woldbye points out that this readily explains why continuous variations in many cases has rendered imperfect results.

Another limitation of Job's method was given by Kolthoff and Elving (22) who pointed out that the precision of the identification of complexes MB_N suffers as N increases. For the range of mole fraction corresponding to N = 4, 5, and 6, an error of 2% in determining X (0.800, 0.833 and 0.857 for N = 4, 5 and 6) can result in a whole unit uncertainty in N.

Watkins and Jones (31) note that the objections raised by Woldbye illustrate the practical difficulties associated with the use of the method of continuous variation rather than a descrepancy in fundamantal principles. They further contend that if all the necessary chemical equilibria are considered, the method of relating the point of maximum concentration of the various species to other parameters (i.e., light absorption), should yield equations which are as valid theoretically as those methods which follow the complexation reaction in some other way. On this basis, they develop equations similar to those of Vosburgh and Cooper (30) which take into account the light absorption of complexes other than the major complex. By applying these equations to several systems for which the extinction coefficients and the stability constants are known, Watkins and Jones concluded that in the general case it is impossible to obtain detailed information on a system containing several successive complexes by use of this method alone. They further conclude that the method of continuous variation is not capable of furnishing all the information necessary for interpretation of the absorption curves, but must rely to some extent in data obtained using other methods.

One of the most general spectrophotometric methods for studying complexes is the one developed by Neuman and Hume (25). Their method is based on the fact that the absorbance of a mixture of successive complexes is a function of the extinction coefficients, E, stepwise formation constants, <u>k</u>, ligand concentration (X), and central metal concentration (M). Expressed as an equation:

$$A = E(M) + E_1k_1(M)(X) + E_2k_1k_2(M)(X)^2 + \cdots \qquad (7)$$

In the Hume and Neuman method, various functions of the extinction coefficients, complex constants, ligand concentration and experimentally determined absorbances are plotted to evaluate the unknown terms and coefficients of equation <u>7</u>. By using a large excess of metal ion and a small amount of ligand and then using large excess of ligand and small amount of metal ion, Hume and Neuman take advantage of the fact that, in the first case, the lowest complex is probably the predominating species and in the second case, the highest complex predominates. Consequently, their procedure consists of the evaluation of the various parameters in equation 7 while building up from the free metal ion toward the higher complexes and working down from the highest complex toward the lower ones.

Although their method has been successful in a number of cases (26), Hume and Neuman point out that systems containing more than three complexes at one time have proved to be unmanageable and that the method seems to be limited to the direct determination of four formation constants and, at each wave length, the extinction coefficients of the species involved.

Jones (19) mentions that since the molar extinction coefficients for the complexes are required for the Hume and Neuman method, their procedure suffers from the same drawbacks as the method of continuous variation because it is not always possible to evaluate the coefficients, expecially when the successive formation constants are close together.

Regardless of the spectral method employed, a study of unknown complex ion systems usually begins by analyzing, in both the ultraviolet and visible regions of the spectra, solutions containing a variety of metal and ligand concentration ratios. These spectral scans are most rapidly accomplished by using automatic recording spectrophotometers. Such studies are necessary because there is usually some regularity to the shift of the absorption spectrum as the absorbance becomes dependent on the different species. An examination of the spectral curves permits the investigator to select, for further study, wave length at which the various complexes absorb.

Polarography in the Study of Complexes

Polarography which is now a well-established technique in electroanalytical chemistry (10,19), is based on current-voltage curves obtained when an electroreducible or electrooxidizable substrate is electrolyzed in a cell containing two electrodes: a large, nonpolarizable reference electrode, and an indicating electrode which is small and polarizable. The most commonly employed reference electrode is the saturated calomel electrode (SCE) while the dropping mercury electrode (DME) is the most versatile indicator electrode. The DME has many desirable characteristics such as a continuously renewed surface, a large usable voltage range, and the ability to dissolve many of the reduction products (i.e., metals which form amalgams).

In certain instances, the dropping mercury electrode may be used to advantage to determine the stability constants of complexes. The measurement of the current that the potential causes to flow in the system is carried out with the simultaneous measurement of the applied potential. The limiting value of the current due to the electrode reaction and the characteristic half wave potential are of most direct value in the polarographic study of complexes. It is possible in some cases to use the polarograph to obtain successive stability constants or to use it to obtain overall constants for systems in which one or two complexes predominate. The reaction taking place at the dropping mercury electrode may involve the reduction of either the free metal ion (solvated) or the complex ion or both. The polarographic reduction wave of the solvated metal ion is usually shifted toward more negative potentials on addition of a complexing agent. (See Figure 2.)

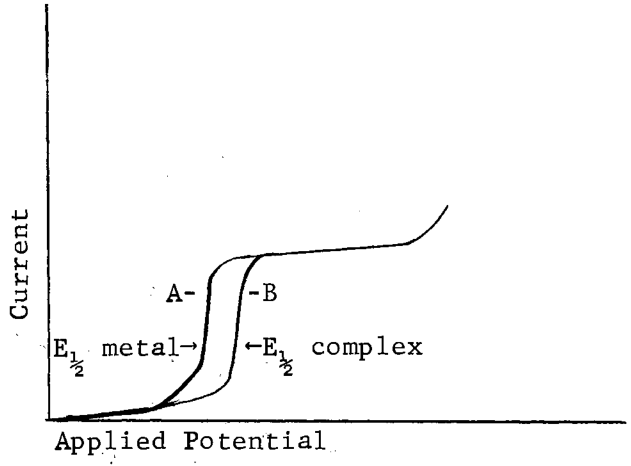


Figure 2. Polarogram of a Complex which has a Fast Rate of Dissociation.

If the metal complex is reducible but has a slow rate of dissociation, a wave due to any solvated metal ion present will appear at its usual voltage, followed at a more negative potential by the wave of the complex. This situation is illustrated by Figure 3.

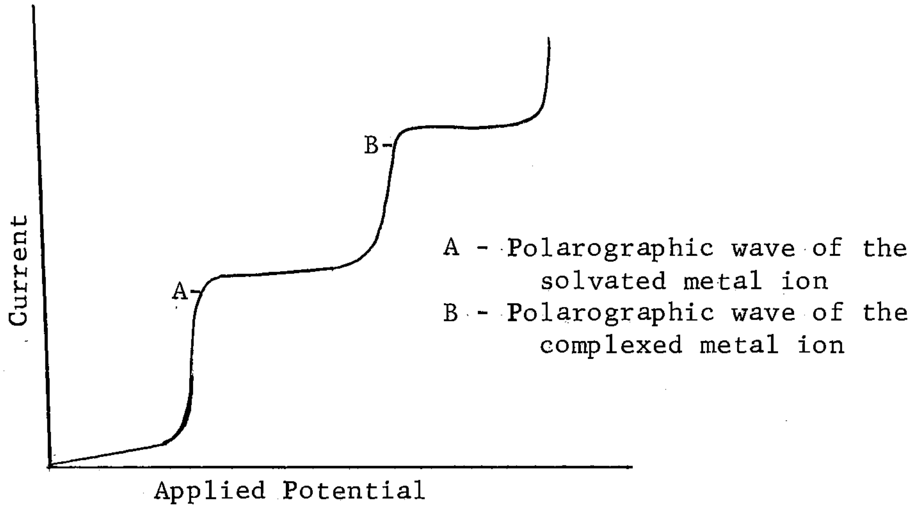


Figure 3. Polarogram of a Complex which has a Slow Rate of Dissociation

When several reducible complexes which have slow rates of dissociation are formed, a polarographic wave is produced for each. The rates of dissociation of complex species thus control to a great extent the shapes of the polarographic waves.

Although many polarographic techniques have been developed for special types of complexes in special environments, the simplest case of a single complex formation should provide ample illustration of the usefulness of the polarograph for obtaining the ligand number of a complex. The polarographic half wave potential ($E\frac{1}{2}$) varies with the concentrations of the species present in a manner given by the Nernst equation. Thus, for the reduction:

$$\text{Oxidized} + \text{Ne} = \text{Reduced} \tag{8}$$

in which the oxidized form is reduced reversibly to a metal which forms an amalgam with the dropping mercury electrode, one writes the Nernst equation:

$$E = E^{o} + \frac{0.059}{N} \log \frac{[\text{oxidized}]}{[\text{reduced}]} \; . \tag{9}$$

When a complexing ligand is present, the reduction equation 9 is not the only chemical reaction taking place. The additional complexing reaction is written

$$\text{Ox} + \text{pA} = \text{OxAp} \tag{10}$$

where A is the ligand and p is the coordination number.

For this complex equilibrium, the stability constant $K_{\text{stab.}}$ is given by:

$$K_{\text{stab.}} = \frac{[\text{OxA}_p]}{[\text{Ox}][\text{A}]^p} \tag{11}$$

From this equation,

$$[Ox] = \frac{[O_xA_p]}{K[A]^p} \tag{12}$$

Substitution of this into equation 9 yields:

$$E = E^o + \frac{0.059}{N} \log \frac{[O_xA_p]}{K[A]^p[Red]} \tag{13}$$

The half wave potential $E_{\frac{1}{2}}$ is defined as the potential at which half of the oxidized form which reaches the DME is reduced. If the complex is fairly stable and the ligand concentration, A, is sufficiently large then at $E = E_{\frac{1}{2}}$, and Red = O_xA_p equation 13 becomes

$$E_{\frac{1}{2}} = E^o + \frac{0.059}{N} \log \frac{1}{K[A]^p} \tag{14}$$

or

$$E_{\frac{1}{2}} = E^o - \frac{0.059}{N} \log K - p\left(\frac{0.059}{N}\right) \log [A] \tag{15}$$

The ligand number, p, may be obtained from a plot of $E_{\frac{1}{2}}$ versus log A which should be a straight line of slope - 0.059 P/N where N is known from the charge on the ion. K may also be determined from a polarogram run on a solution for which [A] = 1.

Little more than stability constant data has resulted from the polarographic study of complex systems in the past. More recently work has turned to the elucidation of the overall kinetics of complex systems in addition to the calculation of stability constants for thes systems.

The above theory is considered applicable to polarographic studies in any solvent; however, polarographic studies of complexes in non-aqueous solvents are complicated by the extremely high resistance of the solutions. This high resistance in nonaqueous solutions can obliterate all polarographic waves which would normally be produced in aqueous systems. In 1961 Arthur (1) reported the development of a compensator which can be used with the conventional polarograph to obtain normal polarographic waves in nonaqueous solution. The polarographic cell used with this compensator contains two calomel electrodes and the usual DME. This instrument compensates for the iR drop encountered in these solvents, thus allowing regular polarograms of complexes to be obtained.

Potentiometry

Various potentiometric methods have been developed to study complex ions. Among these are Leden's method (23) and Bjerrum's method (5). Leden's method utilizes a reversible electrode to determine the concentration of free metal ion in solution. It has been used mostly with complexes of cadmium, mercury, lead, silver, tin, and more active metals which form reversible amalgam electrodes with mercury.

Bjerrum's method is probably the most widely used as well as the most successful of the potentiometric methods. In studying the complexation equilibria of metal amines, Bjerrum employed the glass electrode which is a reversible electrode for hydrated protons. By using a medium which contained a large amount of an ammonium salt, Bjerrum was able to generate the ammines by adding a strong base. For any solution:

$$[NH_3] = K_{NH_4^+} \frac{[NH_4^+]}{[H^+]} \tag{16}$$

where $K_{NH_4^+}$ is the acid dissociation constant of the NH_4^+ ion. From the pH, the total ammonia concentration can be determined, while the total ammonium ion concentration is fixed by experimental conditions.

Using pH measurements to obtain the free ammonia concentration, $\bar{N}$ the average ligand number may be calculated from the expression:

$$\bar{N} = \frac{C_{NH_3} + [H^+] - [NH_3]}{C_M} \tag{17}$$

where C_{NH_3} = analytical concentration of NH_3

C_M = analytical concentration of metal

or by the approximate equation:

$$\bar{N} \doteq \frac{C_{NH_3} - [NH_3]}{C_M} \tag{18}$$

For the various equilibria in which $M(NH_3)_X$ are formed, the successive stability constants can be determined using:

$$N = \frac{k_1 [NH_3] + 2k_1k_2 [NH_3]^2 + \cdots}{1 + k_1 [NH_3] + k_1k_2 [NH_3]^2 + \cdots} \tag{19}$$

where k_1, k_2, etc., are the successive stability constants. The glass electrode has not been employed to any appreciable extent in nonaqueous solutions. In nonaqueous solutions, the glass electrode begins to fail to measure hydrogen ion concentration after a few minutes exposure, primarily because of the dehydration of the glass surface (4). However, Carley (9) noticed that in 2-propanol the time for dehydration was about 20 minutes. This presents the possibility of measuring the ammonia concentrations before the glass electrode begins to fail.

CHAPTER II

HISTORICAL BACKGROUND

Complexes of Copper Salts and Amines in Nonaqueous Solutions

Although water has been by far the most commonly used solvent for the study of copper complexes, investigation of the literature reveals that a small number of research workers are studying such complexes in nonaqueous solvents. Much of the nonaqueous work done on copper complexes, however, has been limited to the precipitation of solid crystals from such solvents followed by the x-ray study of their composition and structure.

German and Jamsett (14) studied the precipitation of $Cu(NH_3)_2Cl_2$ from absolute ethanol by following the decrease in conductivity of the solution until precipitation was complete. They report that the same compound is precipitated from acetone and from isoamyl alcohol. In methanol, German and Jamsett's conductivity titration gives the composition of the complex salt as $Cu(NH_3)_3Cl_2$. The conductometric titration of cupric chloride with monoethanolamine in ethanol was reported by Pinkston and Briscoe (28). Their titration indicated that an unstable ion, $Cu(H_2NC_2H_4OH)^{++}$, is first formed, but on further addition of amine, the stable ion $Cu(H_2NC_2H_4OH)_3^{++}$ is produced. Pinkston and Briscoe also ran conductometric titrations in ethanol on cupric chloride using diethylamine and piperidine as ligands. Their results showed that the complex ions $Cu(C_2H_5)_2NH^{++}$ and $Cu_2(C_5H_{11}N)_3^{++++}$, respectively, exist during diethylamine and piperdine titrations.

Burkin (8), using anhydrous solvents such as chloroform, benzene, and light petroleum (BP 100-120°C), prepared amine complexes of cupric chloride, cupric bromide and cupric acetate. Burkin employed n-octyl-, n-dodecyl-, n-tetradecyl, n-hexadecyl-, and n-octodecyl amines as ligands. For all three copper salts, the ratio of ligand to copper in the crystalline precipitates formed was 2 amines to 1 Cu^{++}. He mentions having difficulty with water displacing the amine in the copper-amine salt crystals and described the resulting product as a basic salt of copper.

Using spectrophotometry and potentiometry (pH), Pflaum and Brandt (27) studied copper sulfate complexes formed with the following unsaturated ligands: pyridine, 2,2' bipyridine, 1,10-phenanthroline and 2,2',2"-terpyridine. These complexes were prepared in aqueous solutions and then extracted into the immiscible organic phases, benzene, chloroform, carbon tetrachloride, isoamyl alcohol, and toluene. Pflam and Brandt also studied the effects of 50 volume-percent mixtures of water with nonaqueous solvents on the complex formations.

Broome, Ralston and Thornton (7) applied the method of continuous variations as expanded by Vosburgh and Cooper (30) to cupric acetate-dodecylamine systems in an anhydrous 90% chloroform and 10% ethanol mixture. They report the failure of the method to yield conclusive results about the stability constants, attributing this to the rapid dissociation of the complex in this solvent system. However, their work did show evidence for the existence of a 2 amine to 1 copper species in this solvent.

Miki and Yamada (24) discuss the configurations of the complexes they prepared with bis(succinimidato)copper(II) and pyridine, α, β, and γ picolines, 2,4-, 3,5-, and 2,6-lutidines in such solvents as $CHCl_3$, CH_2Cl_2 and ethanol. The pyridine and picolene complexes were four coordinated and square planar in shape. The lutidine formed both five and six coordinated complexes of the octahedral type.

Hein and Ludwig (16) prepared crystals of a complex formed from anhydrous copper(II) perchlorate and dimethylaminoethanol in methanol solutions. The ratio of copper to amine was 1 to 3 for this complex. They also reported having trouble with hydrolysis of the complexes.

J. Bjerrum and Lamm (6) used the glass electrode and the spectrophotometer to measure stability constants for copper(II) nitrate with n-butyl and methyl amines in aqueous solutions. They extended this work to include a complex formed in pure n-butyl amine which they report as a pentamine complex. However, they were not able to treat their data quantitatively because of the slight stability of the pentamine complex. They further point out that in order to prevent the formation of basic precipitates of copper in the presence of water it is necessary to use high concentrations of amine (>7N) and n-butyl ammonium salt (1N).

CHAPTER III

REAGENTS

Ammonium Hydroxide. Fisher Scientific reagent grade was used without further purification.

n-Butyl amine. Matheson reagent grade was used after double distillation in a stream of nitrogen.

Cupric Chloride Dihydrate. Fisher Scientific reagent grade was used after dehydrating at 130°C.

5(p-Dimethylaminobenzylidene) rhodanine. Eastman Kodak Co., No. 2748 was used without further purification.

2,2'-Diquinolyl-(biquinoline). Eastman Kodak Co., No. 6183 was used without further purification.

Hydrogen peroxide. Baker and Adamson 30% stabilized solution was used without further purification.

Hydroxylamine hydrochloride. Baker and Adamson reagent grade was used without further purification.

Hydrochloric Acid. Fisher Scientific 0.100N standard volumetric solution and J. T. Baker reagent grade were used without further purification.

Karl Fischer Reagent. Baker and Adamson stabilized solution was used.

Lithium Chloride. Fisher Scientific reagent grade was used without further purification after drying at 110°C for 2 hours.

Mercury. Redistilled mercury was filtered on a gold filter and vacuum distilled in this laboratory.

Molecular Sieve 4A. Union Carbide Corporation was used after activating at 300°C under nitrogen purge for 2 hours.

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

Nitron reagent. Eastman Kodak Co. No. 1077 reagent was used after recrystallization from 2-propanol-water mixture.

Nitrogen. Linde laboratory grade nitrogen was used for purging equipment after drying with a Molecular Sieve column. For the polarographic analysis, Linde laboratory grade nitrogen was used after being passed through two towers of chromous sulfate - sulfuric acid - amalgamated zinc, (2) a column of glass wool, a column of silica gel drying agent, and two presaturator towers filled with 2-propanol and Molecular Sieve 4A.

Potassium Carbonate. J. T. Baker anhydrous grade was used without further purification.

Potassium Chloride. Fisher Scientific reagent grade was used without further purification.

Potassium Chromate. Fisher Scientific reagent grade was used without further purification.

Potassium Hydrogen Phthalate. Fisher Scientific reagent grade was used without further purification after drying for 2 hours.

Potassium Hydroxide. J. T. Baker reagent grade was used without further purification.

Potassium Iodide. Baker and Adams reagent grade was used without further purification.

Potassium Thiocyanate. Fisher Scientific reagent grade was used without further purification.

Potassium Thiosulfate. Fisher Scientific reagent grade was used without further purification.

2-Propanol. J. T. Baker reagent grade was used after being distilled first in the presence of potassium hydroxide and then in the presence of anhydrous potassium carbonate.

Sodium Hydroxide. Fisher Scientific reagent grade was used without further purification.

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

Tri-n-butylamine. Eastman Organic Chemicals white label grade was used after double distillation under nitrogen purge.

2,2,4-Trimethylpentane. Eastman Organic Chemicals practical grade was used without further purification.

Zinc Metal. Matheson, Coleman and Bell, powder form, was used without further purification.

CHAPTER IV

THE DETERMINATION OF WATER

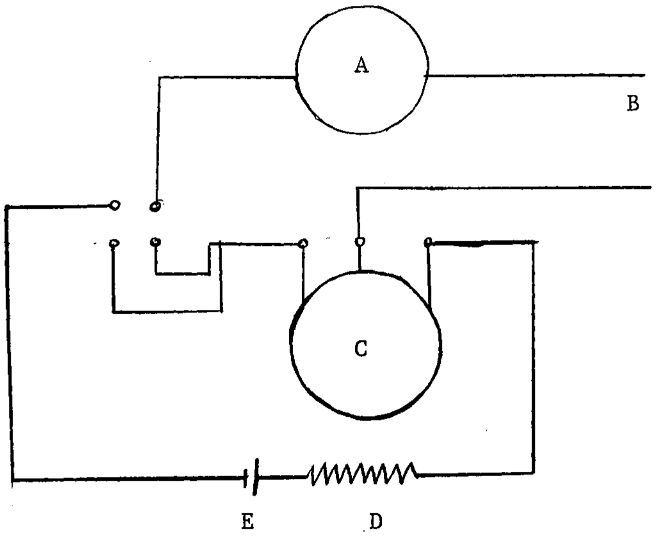
The determination of water was an important analytical operation in this research. The method employed was the Karl Fischer (K.F.) technique (12). In this technique, water is determined through its reaction with a solution made from iodine, sulfur dioxide, pyridine and a solvent such as methanol. The essential reactions may be illustrated as:

$$I_2 + SO_2 + H_2O + 3Py \rightarrow 2Py \cdot HI + Py \cdot SO_3$$

$$Py \cdot SO_3 + CH_3OH \rightarrow Py \cdot HSO_3 \cdot OCH_3$$

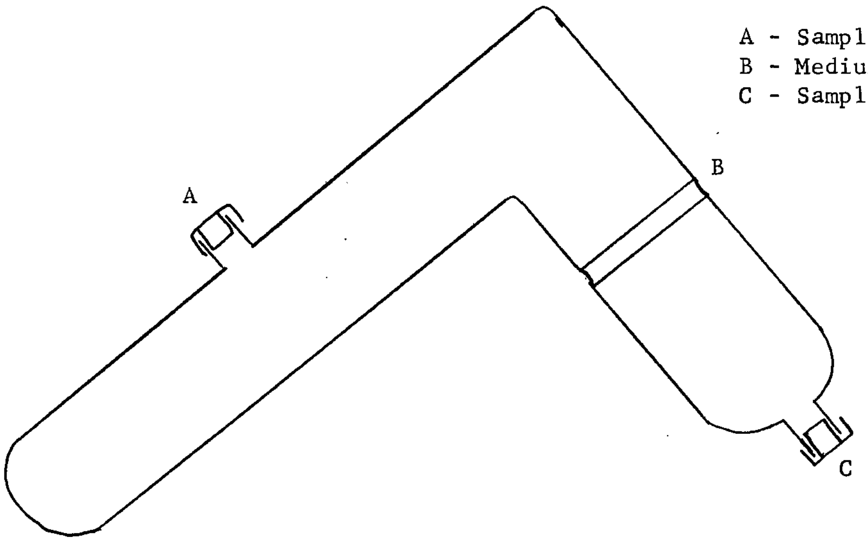
The end point of such a reaction can be determined visually; however, electrochemical methods, especially biamperometric titration, are more widely employed because they possess high sensitivity. A biamperometric titration circuit is shown in Figure 4.

The schematic in Figure 4 shows a battery, two resistors (one fixed and one variable), microammeter, and two platinum electrodes. When a small potential of 10→15 mv. is applied by means of the variable resistor to the platinum electrodes, they become polarized and no current flows in the galvanometer. An appreciable continuous flow of current is possible only if both electrodes are maintained in a depolarized state. For this condition to exist, the iodide produced in the reaction with water must be oxidized at the anode and iodine from an excess of Karl Fischer reagent must undergo reduction at the cathode.



A - 25 µA meter
B - leads to Platinum electrodes
C - 500-ohm variable resistor
D - 5000-ohm resistor
E - 1.5-volt battery
F - Double pole single throw switch

Figure 4. Biamperometric Circuit for Karl Fischer Titration Unit.



A - Sample injection port
B - Medium glass frit
C - Sample removal port

Figure 5. Copper Displacement Apparatus.

Thus, at the anode,

$$2I^- \rightarrow I_2 + 2e$$

while at the cathode

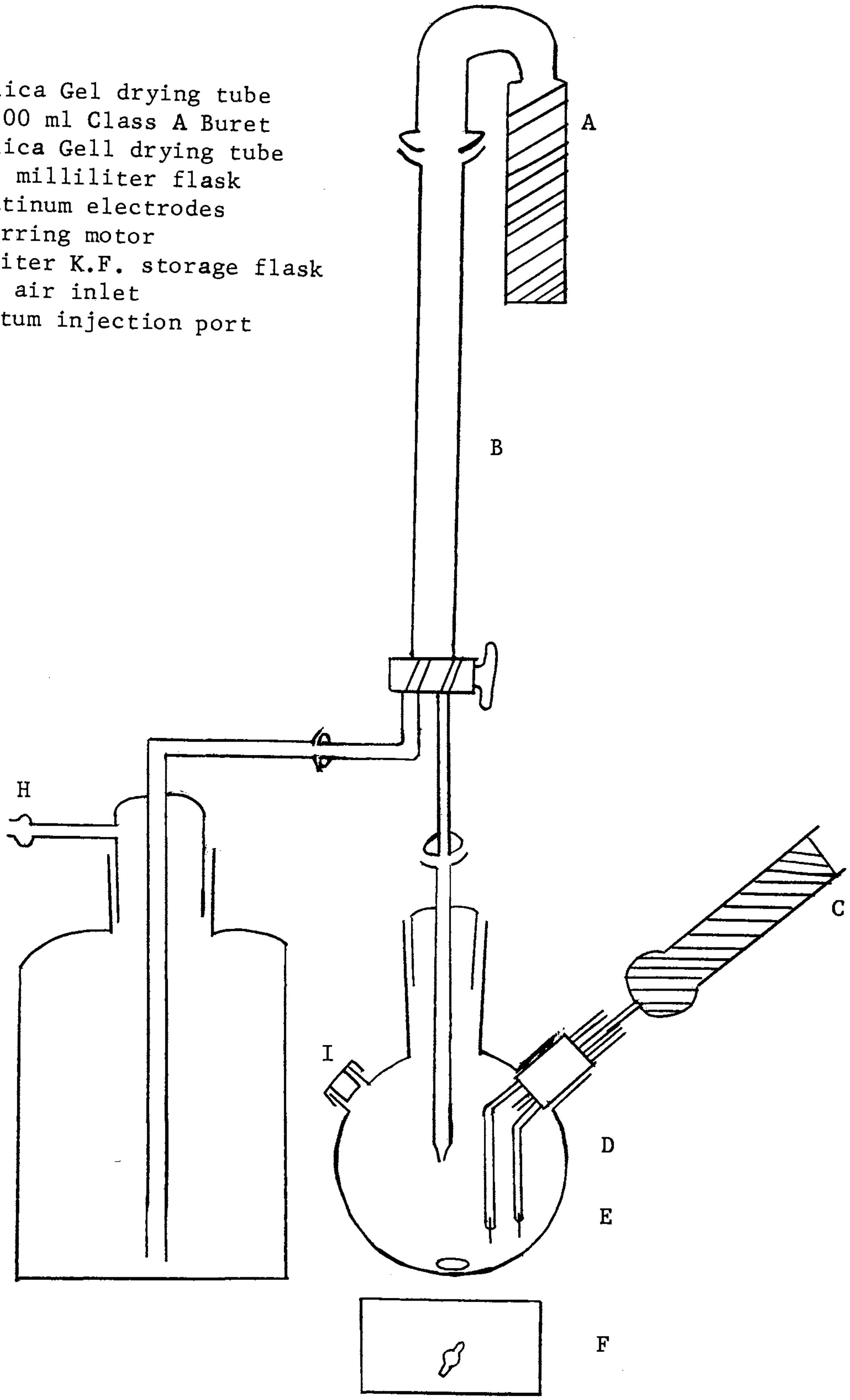
$$I_2 + 2e \rightarrow 2I^-$$

During an analysis, there is always sufficient iodide for the anode reaction; but no free iodine exists in solution unless an excess of Karl Fischer reagent is present. The first excess iodine from the Karl Fischer reagent depolarizes the cathode and a current begins to flow through the galvanometer, signaling the end point.

The Karl Fischer titration cell used in this research is shown in Figure 6.

Several modifications of the original Karl Fischer apparatus were needed in order to obtain the high sensitivity required by this work. The first Karl Fischer apparatus used in this research employed a 50.00 milliliter buret for the addition of K.F. reagent. At values above 0.01% water in 2-propanol, this was adequate. However, as the water content in the 2-propanol decreased, the amount of K.F. reagent needed for the titration likewise decreased to values below 1 milliliter. By changing to a 10 milliliter buret, it was made possible to measure to ±0.02 milliliter which was satisfactory for analyzing water contents to 0.001%.

Another modification of the original Karl Fischer unit was in the form of a change in the method of sample introduction. The original method of introduction into the titration vessel was through a ground glass joint. Considerable variation in repetitive runs and the fact that the lowest water analysis obtained was greater than 0.01%, indicated that moisture absorbed from the air was causing difficulty. This



A - Silica Gel drying tube
B - 10.00 ml Class A Buret
C - Silica Gell drying tube
D - 500 milliliter flask
E - Platinum electrodes
F - Stirring motor
G - 2 liter K.F. storage flask
H - Dry air inlet
I - Septum injection port

Figure 6. Karl Fischer Titration Unit.

problem was solved by using a rubber septum large enough to fit the ground glass joint so that samples could be introduced by hypodermic syringe without exposure to the air.

Handling extremely dry solvents and solutions constituted a difficult problem in this research. This problem was partly overcome by using the hypodermic syringe technique for transferring the solvents and solutions. The syringes were pretreated by spraying the plunger barrel with a teflon coating and then drying the entire syringe for one hour or more at 130°C. The syringes were then purged with dry nitrogen until cool to remove any remaining surface moisture. The syringes used were Yale, Luer-Lok type, which allowed the 19-gauge needles to be locked to the syringe.

In the early portion of this research, the samples were taken into the syringes by pressuring the sample storage vessel with predried air to force the liquid into the syringe. This minimized exposure to air moisture which would occur if the samples were taken by drawing the syringe plunger slowly out of the syringe to create a partial vacuum. After the syringe was filled, the needle was quickly sealed by inserting it into a silicone rubber cap. A later modification of this technique was made by placing a Luer-Lok stainless steel stopcock between the syringe and the needle. This stopcock allowed the sample to be sealed in the syringe, thus reducing the danger of spillage due to accidental bumping of the syringe plunger.

Before a technique was developed for drying to very low levels, a 10 milliliter syringe was used for sampling; after the solutions were dried to less than 0.01% water, a 30 milliliter syringe was necessary so that the sample contained enough water to permit a titration.

Standardization of the K.F. reagent was accomplished by adding sufficient K.F. reagent to the vessel to obtain a steady current of about 15-17 microamperes as read on the microammeter shown in Figure 4. Then 20 to 40 milligrams of pure distilled water were added to the vessel by means of a weighing dropper. Upon addition of the water sample, the current fell to zero on the meter. Karl Fischer reagent was then added until the current on the microammeter again read the same as the original value. The volume of K.F. reagent was read and the number of milligrams of water per milliliter of K.F. reagent was calculated.

A typical series of K.F. standardizations are given below:

$$\frac{24.6 \text{ mg of } H_2O}{19.82 \text{ ml of K.F.}} = 1.2411 \text{ mg/ml} \qquad \frac{40.6 \text{ mg } H_2O}{32.90 \text{ ml K.F.}} = 1.2340 \text{ mg/ml}$$

$$\frac{40.9 \text{ mg of } H_2O}{33.10 \text{ ml of K.F.}} = 1.2356 \text{ mg/ml} \qquad \frac{34.4 \text{ mg } H_2O}{27.81 \text{ ml K.F.}} = 1.2369 \text{ mg/ml}$$

Standard deviation = 0.0037 mg/ml

The analysis for the water content in the dried solvents was made by injecting 30 milliliters of the solvent into the K.F. vessel. The sample weight was obtained by weighing the syringe before and after addition. The current had been previously adjusted to 17 μA in the biamperometric circuit. After the sample addition, K.F. reagent was added until the current was again stabilized at 17 μA. As the end point was approached, more time was required for readings because the reaction between K.F. reagent and water is apparently slow at very low concentrations of water. The length of time required for the total titration was about 30-40 minutes.

After the titration, the percentage of water was calculated from the number of milliliters of K.F. reagent used, the sample weight, and the number of milligrams of water per milliliter of K.F. reagent as determined in the standardization.

A typical water analysis on 2-propanol which had been dried for 4 hours with the Molecular Sieve drier (see Chapter V) is given below:

$$\frac{0.25 \text{ ml of K.F.} \times 1.332 \text{ mg/ml } H_2O \times 10^{-3} \text{g/mg} \times 100}{23.8835 \text{ gram sample}} = 0.0014\%$$

The water content of anhydrous solvents containing copper(II) ion cannot be determined directly by the Karl Fischer technique. The cupric ion interferes with this analysis by reacting with the iodide (formed from the reaction of K.F. reagent and water) to form insoluble cuprous iodide and free iodine. Therefore, it was imperative to remove the cupric ion before analyzing such solutions. This was accomplished by using the copper displacement apparatus shown in Figure 5.

The displacement apparatus is preheated at 400°C for 2 hours and then stored in a 130°C oven until it was removed for use. The exit port labeled C in Figure 5 was attached to a dry nitrogen line while the apparatus was still hot so that the glass frit would be purged free of any moisture. About 1 gram of hot powdered zinc was then introduced into the displacement apparatus through the inlet port and both ports were sealed immediately with rubber septums. The apparatus was then allowed to cool. Although granular zinc was tried first, it proved to be too slow in displacing the copper from solution. After the apparatus cooled to room temperature, a 30 milliliter sample of the solution was injected into port A. The whole apparatus was shaken vigorously for 15 minutes, care being used not to allow the solution to come into contact with the glass frit. When the solution became colorless (indicating the copper was removed), the apparatus was tilted so the solution came into contact with the glass frit. A syringe filled with dry nitrogen was used to pressure the solution through the frit, thus filtering out the precipitated copper and the unused zinc metal. As soon as the solution passed through the frit, a sample was taken from the exit port (port C) with a 30 milliliter syringe. The resulting sample of 2-propanol was then analyzed for water in the regular manner.

During the course of this research it was noticed that the water analyses of copper solutions by this technique were consistently higher than those of the 2-propanol solvent. To check for the possibility that the higher water content might be from water being picked up by the solution from the zinc powder, a sample of 2-propanol was treated in the same manner as the copper solutions. By analysis, the 2-propanol contained 0.00032% water before it was introduced into the displacement apparatus. After treatment, the solvent was found to contain 0.0020% water. From this data, it was surmised that at least part of the water was due to absorption from the apparatus.

CHAPTER V

PREPARATION OF ANHYDROUS SOLVENTS AND SOLUTIONS

The need for extremely anhydrous 2-propanol solutions when working with copper-amine complexes became apparent during the early stages of this research. Previous workers (9,32) had dried the 2-propanol solvent by first treating with potassium hydroxide for 24 hours to remove aldehydes, distilling under nitrogen purge, treating the distillate with anhydrous potassium carbonate for 24 hours and finally distilling again under nitrogen pressure. No analysis for water was made by these workers on the resulting alcohol. Carley (9) mentions that the trace of water remaining after this treatment may have been a source of the trouble encountered during his study of copper-amine complexes.

Using the Karl Fischer unit described in Chapter IV, an analysis of several 2-propanol batches treated by the KOH and K_2CO_3 method showed that the water content varied from 0.57% to 0.1%.

When polarography and spectrophotometry are used for studying copper(II) complexes, the concentration range for the copper is usually 0.005M or less. A 2-propanol solution containing 0.1% water is approximately 0.05M with water which is about 10 times more concentrated than was normally used for the metal ion under investigation. These facts made it obvious that the water content of the solutions would have to be lowered so that water would not compete with the amines for ligand sites around the central metal ion. Carley's (9) work also revealed the fact that basic salts of copper were formed when amines are mixed with copper(II) salt solutions containing water.

To improve the drying technique, a method was devised using Molecular Sieve 4A (Linde Company Division of Union Carbide Corporation). Molecular Sieves (17) are synthetic zeolites which are prepared by dehydrating alkali metal aluminasilicates. When the water of hydration is removed, the crystal structure remains unchanged and therefore contains a network of empty cavities. Water is absorbed from solution presumably by fitting back into these empty pores.

A communication from Linde Company (29) stated that drying tests made on pure 2-propanol indicated that 2-propanol could be dried to less than 10 parts per million water by passing the solvent through a 4 foot bed of Molecular Sieve 4A and that 2-propanol was excluded from absorption on the Molecular Sieve 4A.

The equipment first used in this research for drying solvents was a 50 mm diameter glass column approximately two feet in length and closed at its bottom with a stopcock. A coarse sintered glass frit was built into the glass at the bottom of the column for support of the Molecular Sieve. The top of the column was fitted for a ground glass joint onto which was placed a tube for holding a drying agent. A piece of Whatman #1 filter paper was placed in the bottom of the column to prevent clogging of the frit by the dust from the surface of the Molecular Sieve. The one-sixteenth-inch pellets of Molecular Sieve were activated at 300°C and cooled in a vacuum desicator. The column was then packed loosely with the Molecular Sieve pellets, filled with 2-propanol, and closed with a tube containing Molecular Sieve.

This drying method proved to have several disadvantages. One of these was the fact that when copper(II) salt solutions came into contact with the zeolite column, the copper(II) ion underwent ion exchange with the sodium ion of the Molecular Sieve. One test showed that when a 0.1363M copper(II) chloride in 2-propanol solution was passed through the column, the copper concentration was reduced to 0.086M.

The range of water analysis on the 2-propanol solvent dried by this column was 0.05 to 0.01%. Also, the copper-amine solutions prepared with 2-propanol from the Molecular Sieve column continued to give basic precipitates of copper. The high water analysis, the precipitates, and the ion exchange prompted the development of a better drying system.

Figure 7 shows the apparatus which finally was developed. Two filter papers were placed on the coarse frit and the space above the coarse frit in Part A was filled with previously dehydrated Molecular Sieve 4A in one-sixteenth inch pellet form.

The reflux condenser shown in Part A was attached to a cold water faucet. The moisture trap (Part B) was filled with Molecular Sieve 4A and fitted to the top of the reflux condenser.

The 2-liter flask (Part C) was fitted with a sampling tube equipped with a 2-mm stopcock having a Teflon plug. The end of the sampling tube was sealed with a rubber septum so samples could be removed for analysis by means of a hypodermic syringe. The flask was filled about three-fourths full of the solution to be dehydrated. Silicone stopcock grease, applied around the upper part of each ground glass joint, was used to seal these parts of the apparatus. In the first experiments using the apparatus, the solution was heated by means of a heating mantle.

The principle employed in this apparatus is similar to that of the Soxhlet extractor except that the water in the solutions being dehydrated

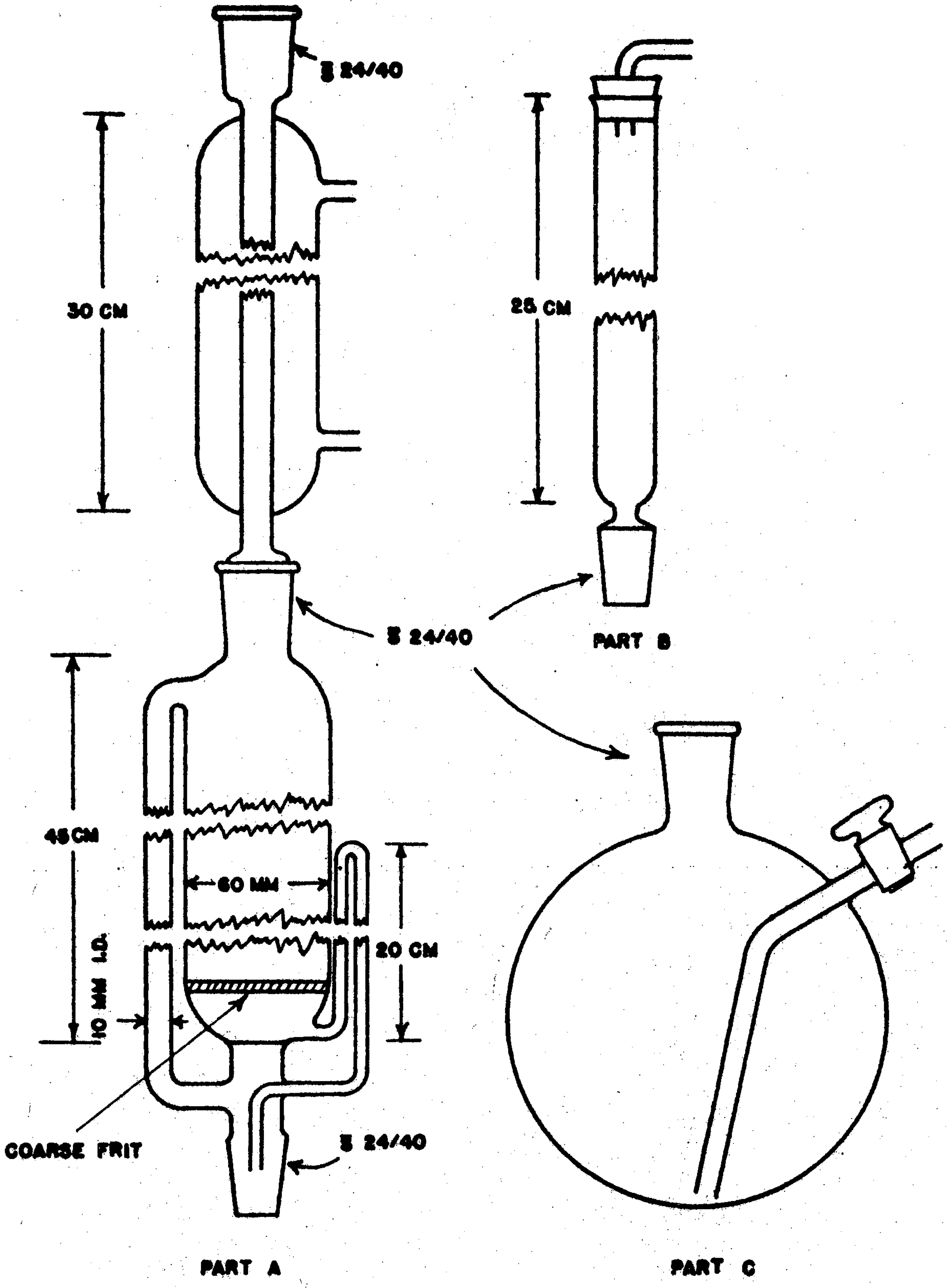


Figure 7. Molecular Sieve Drying Apparatus.

vaporizes with the solvent, rising from the boiling solution to the condenser. There the mixed vapors condense and the resulting liquid phase passes down through the bed of molecular Sieve where the water is removed, the dried solvent returning to the boiling flask.

The extractor method has two advantages over the drying column. The first is that the copper(II) salt does not leave the boiling flask; therefore, the ion exchange process is minimized. A small ion exchange probably does occur with the Molecular Sieve dust which is carried over from the extraction.

The second advantage is that the solvent is passed over the Molecular Sieve bed many times during the treatment. This cycling process increases the efficiency of the drying process greatly.

The initial tests of this apparatus were made on 0.1M nickel perchlorate in 1-butanol which contained 0.813% water. This solution was selected because nickel ion does not interfere with the Karl Fischer titration. About 3 hours treatment in the dehydrator reduced the water level to 0.0019%. The drying was allowed to continue, but soon it was noticed that above the liquid level on the walls of the flask small spurts of flame occurred and black products were formed. Apparently, the nickel perchlorate was reacting vigorously with the very anhydrous 1-butanol on the hot, dry walls of the flask. There was reason to believe that if the concentration of perchlorate in the main solution had been sufficiently high the mixture might have exploded.

To minimize such occurrences and reduce its inherent hazards, the procedure was modified by replacing the heating mantle with a water bath automatically held at 45°C. So the solution would boil at this temperature, a vacuum line was connected to the top of Part B of

Figure 7. The vacuum line was connected, through a second moisture trap filled with indicating-type gel, to a water aspirator. To prevent loss of vapor (which would otherwise be large at the low pressures employed) the condenser was cooled with water from an ice bath.

One further testing with this apparatus (but with boiling at atmospheric pressure), it was found that pure 2-propanol solvent containing no salt could be dried from an original 0.28% water content to 0.0014% in about 4 hours reflux time. At reduced pressure and 45°C, a 0.005M copper(II) perchlorate hexahydrate solution in 2-propanol was dried from approximately 0.35% water content to 0.0021% after 10 hours treatment. Owing to the trapping of part of the 2-propanol in the extractor (Part A of Figure 7), the copper(II) perchlorate was concentrated to 0.0067M.

Some difficulty was encountered with the Molecular Sieve dust being suspended in the solvents and solutions. Because this dust absorbs light, spectral studies were made after the dust had settled. Erratic drop times indicated that the suspended dust also influenced polarographic measurements. Consequently, efforts were made to eliminate the dust from the solutions. One of these efforts was to try to filter the dust out by placing filter papers on top of the coarse glass frit shown in Part A. Several combinations of filter paper using different porosities, were tested for flow rates. The best combination seemed to be that using one coarse filter paper on top of two finer filter papers (Whatman 42). This reduced the amount of dust somewhat but did not completely eliminate it. Larger numbers of filter papers would not allow the solution to pass through fast enough, thus causing flooding of the extractor column.

Another attempt to reduce the amount of dust was made by putting a smaller solvent return tube on the extractor unit (Part A of Figure 7). With the longer tube, the amount of solvent builds up in the Molecular Sieve bed until the liquid level reaches the top of the return tube, then the liquid siphons back into the flask in a rapid surge. It was reasoned that perhaps if the tube was shorter, this surge could be eliminated, thus reducing the amount of dust picked up by the solvent. Experimentally, however, it proved to be difficult to decide if the amount of dust picked up was reduced significantly.

The method finally selected and which seemed to remove the largest quantity of suspended dust was one employing the filter paper combination coupled with a preflushing of the entire system with 2-propanol solvent. The preflush consisted of packing the extractor column with fresh Molecular Sieve 4A and then pouring one and one-half liters of 2- propanol through the top of the extractor. This allowed the Molecular Sieve to be washed while the 2-propanol passed over the bed and into the main flask (Part C, Figure 7). The entire extractor was then assembled and run as in a normal drying process. After thirty minutes to one hour, the flask containing the 2-propanol and surface dust was removed and was replaced with a similar flask containing the solution which was to be dried. This preflushing procedure was made possible because the amount of Molecular Sieve in the bed was well in excess of that needed to dry any 2-propanol solution used in this research. The 2-propanol used for flushing was saved and most of it, after the dust had settled, was decanted off and used in later flushing operations.

The small amount of dust that remained in solutions after this treatment was allowed to settle before the solutions were used.

It was found that extremely anhydrous solutions could not be transferred and stored in other vessels without picking up some moisture. Therefore, several drying units were built so that the solutions could be stored in the unit after drying. This proved to be the most satisfactory storage method because if a small amount of water exposure did take place, the extraction procedure could easily be started up again.

The absorption of water by Molecular Sieve is reported to be an irreversible process at temperatures below 250°C. However, it was possible to regenerate the Molecular Sieve by heating it to about 300°C. This was done by first evaporating the 2-propanol off of the surface of the Molecular Sieve at room temperature, in a hood. Then preheated nitrogen was passed through a heated (300°C) column of the 2-propanol-free Molecular Sieve, the nitrogen gas carrying off the water as it was expelled from the zeolite crystals. After 2 hours of heating at 300°C, the Molecular Sieve was removed and placed in a vacuum desicator to cool.

CHAPTER VI

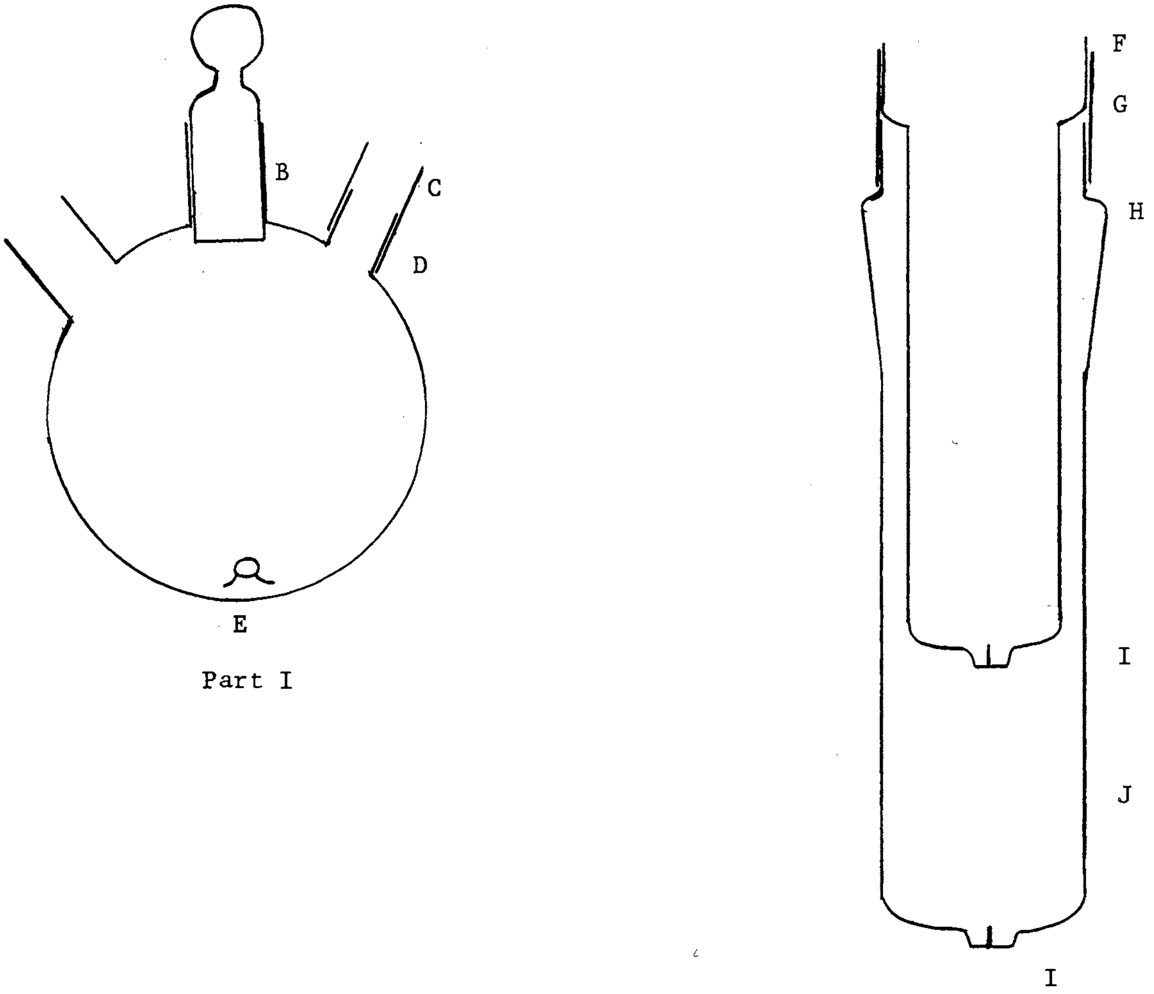
POTENTIOMETRIC MEASUREMENTS

The potentiometric measurements made in this research employed a pH meter. The apparatus used at the start of this research was the same as that described by Carley (9). This consisted of a Beckman Zeromatic pH meter which could be read in 0.1 pH increments, a Beckman Type E-2, 0-14 pH glass electrode, and a Beckman fiber junction calomel electrode which was fitted by Carley with a fiber junction sleeve filled with a 0.1M solution of lithium chloride. This sleeve was employed to prevent potassium chloride which is quite insoluble in 2-propanol, from precipitating out in the fiber junction of the calomel electrode when the electrode is used with 2-propanol.

Titrations of solutions of amines were made using a 200 ml. tall form beaker fitted with a septum injection port. The titrant (0.1N HCl) was added by means of a motor-driven, 10 cc. calibrated hypodermic syringe. The apparent pH during the titration was followed by feeding the output of the Beckman pH meter to a Sargent Model SR recorder.

After it was learned that water caused interference with the study of copper-amine complexes, a special apparatus was constructed to measure the pH changes of various copper-amine mixtures under anhydrous conditions. The apparatus is shown in Figure 8.

Measurements on the pH of individual copper-amine solutions were made as follows:



Part I

Part II

Figure 8. pH-Measuring Apparatus.

A - Female 24/40 ground glass joint
B - Female 24/40 ground glass joint ant stopper
C - Rubber Sleeve
D - Straight glass tube
E - Septum covered injection port
F - Inner glass calomel electrode shield containing aqueous o.1N lithium chloride
G - Rubber Sleeve
H - Male 24/40 ground glass joint
I - 50,000 ohm asbestos fiber junctions
J - Outer glass electrode shield containing 0.1M lithium perchlorate in anhydrous 2-propanol (<0.01% water)

1. The flask and electrode shields were predried at 130°C.
2. The outer glass shield (J of Figure 8) was placed in the ground glass joint (A of Figure 8) and a ground glass stopper was placed in B of figure 8 while the flask was still hot.
3. The apparatus was then purged through the injection port with nitrogen which had been dried by passing it through a four-pound Molecular Sieve bed.
4. When the apparatus was about cool to touch, the glass electrode was placed in the straight glass tube (D of Figure 8) through the rubber sleeve, C, of Figure 8.
5. The nitrogen purge line was removed, and a septum was placed over the injection port.
6. The inner electrode shield (F of Figure 8) was placed into the outer electrode shield (J of Figure 8) and sealed with a rubber sleeve (G of Figure 8).
7. A solution of 0.1N lithium perchlorate in anhydrous 2-propanol was injected into the outer electrode shield through the rubber sleeve by means of a hypodermic syringe. Enough lithium perchlorate solution was added to cover the fiber junction of the inner electrode.
8. Aqueous 0.1N lithium chloride was then added to the inner electrode shield.
9. The Beckman calomel electrode was inserted into the inner electrode shield.
10. The electrodes (calomel and glass) were then connected to the pH meter.
11. The solution to be measured was injected into the flask

through the septum on the injection port and the pH was taken.

When it became necessary to titrate copper solutions with amine solutions, the same procedure (steps 1-10) was followed as for single samples except that the copper solution was injected into the flask and then the amine solution was injected by means of a motor driven hypodermic syringe. The pH was recorded automatically.

As the research problem progressed, it was found that the Beckman Zeromatic was not sensitive enough; therefore, pH measurements were made on copper-amine solutions with a Heath Recording pH meter which could be read to the nearest 0.001 pH unit.

CHAPTER VII

EXPERIMENTATION AND DISCUSSION

Previous investigators (9,32) have studied the complexation reaction of copper(II) chloride dihydrate and tri-n-butylamine. From their work, it was learned that precipitates were formed which contained little or no amine and approximately half the stoichiometric amount of chloride needed for the copper(II) ion. It was postulated by one of these workers (9) that these precipitates were basic salts formed by the removal of protons from the hydrated copper(II) ions by the basic amine.

Copper(II) chloride dihydrate and tri-n-butylamine were also employed at the outset of this research, the difference being that the copper(II) chloride dihydrate was first dried at 130°C until the brown, anhydrous copper(II) chloride remained. Initial 2-propanol solutions of copper(II) chloride in excess tri-n-butylamine were placed over Molecular Sieve. These non-quantitative mixtures yielded brown to yellow solutions and no precipitates.

The Molecular Sieve column described in Chapter V was used to lower the water content of the 2-propanol which was used to prepare the solutions given in Table 1. A series of solutions was prepared by weighing out the appropriate weight of anhydrous copper(II) chloride, tri-n-butylamine, and lithium chloride and placing them predried volumetric flasks, then diluting each mixture with 2-propanol to the concentration listed in the table. The spectra of these solutions were taken with a Beckman DK-1 spectrophotometer using 1 cm quartz cells

TABLE I

COPPER(II) CHLORIDE-TRI-n-BUTYLAMINE MIXTURES 0.1M WITH LITHIUM CHLORIDE

	Concentrations and Ratios			Absorbance at Spectral Peaks			
Flask	$CuCl_2$	Amine/Cu	Amine	750 mμ	850 mμ	900 mμ	950 mμ
A	$3\text{x}10^{-3}$M	0	0	0.280	0.385	0.380	0.375
B	$3\text{x}10^{-3}$M	0.20	$6\text{x}10^{-4}$M	0.330	0.575	0.550	0.525
C	$3\text{x}10^{-3}$M	0.40	$1.2\text{x}10^{-3}$M	0.475	0.730	0.710	0.685
D	$3\text{x}10^{-3}$M	0.80	$2.4\text{x}10^{-3}$M	0.260	0.320	0.320	0.325
E	$3\text{x}10^{-3}$M	1.2	$3.6\text{x}10^{-3}$M	0.360	0.390	0.405	0.420
F	$3\text{x}10^{-3}$M	2.0	$6\text{x}10^{-3}$M	0.230	0.190	0.165	0.142
G	$3\text{x}10^{-3}$M	4.0	$1.2\text{x}10^{-2}$M	0.210	0.160	0.140	0.120

It should be noted that the solutions in Table I gave no indication of precipitate formation.

From Table I it can be seen that the solution of $3 \text{ X } 10^{-3}$M copper(II) chloride (flask A) had a broad peak at about 900 mμ. When tri-n-butylamine was added, the absorbance increased in the region of 900 mμ until the amine-to-copper radio reached about 1:1, then decreased and continued to decrease with increase in amine concentration. The peak at 750 mμ showed a similar trend.

Spectral shifts observed were interpreted as being due to various complexes being formed as the amine concentration increased. These shifts in wave length indicated that at least two, and possibly three, complexes were being formed.

Copper(II) chloride-tri-n-butylamine solutions which were prepared without lithium chloride continued to give precipitates. Table II gives the results obtained from a series of copper(II) chloride-tri-n-butylamine solutions without lithium chloride..

TABLE II

COPPER(II) CHLORIDE* WITH TRI-n-BUTYLAMINE IN 2-PROPANOL SOLUTION

(after six weeks storate)

Flask	Amine/Cu	Color of Soln.	Amine Conc.	Amount of Precipitate	Apparent pH
I	1.1	lt. green	6.5x10^{-3}M	most	5.85
II	2.1	progressively darker	13X10^{-3}M	progressively less	6.25
III	3.2		19.4x10^{-3}M		6.55
IV	3.9		23x10^{-3}M		6.85
V	4.2		26x10^{-3}M		6.93
VI	5.2	dark brown	32x10^{-3}M	trace	6.95

*Concentration of Cu(II) chloride in all cases was 6 x 10^{-3}M.

These solutions were prepared by weighing out copper(II) chloride and tri-n-butylamine into predried 50 ml volumetric flasks and diluting with 2-propanol. The flasks were closed with ground glass stoppers and the top of each flask was wrapped with plastic foil to prevent leakage. The flasks were stored in the dark for six weeks. At the end of that time, the colors of the solutions were noted to be about the same as when the solutions were prepared (see Table II). The amount of precipitate decreased from the flask containing the lowest amine concentration (flask I) to practically no precipitate in the flask with the highest amine concentration (flask VI). The pH was noted to increase as the amine concentration increased.

Since the precipitates were not formed when lithium chloride was present and did form in its absence, an explanation of the results given in Tables I and II might be that when lithium chloride is present in large concentrations (0.1M) compared to the copper concentration ($3x10^{-3}M$), the copper(II) ion is probably present as a chlorocomplex and not as the simple solvated or hydrated ion. Thus the amine has more difficulty in the formation of basic copper precipitates because most of the copper(II) ion is not in the form of a hydrated cationic acid. However, when lithium chloride is absent, the trace amounts of water present in these solutions are probably bound, in greater quantity to copper ions, this allowing the amine to remove a proton from such ions and form the basic precipitate. When excess amine is present, it is probable that the basic precipitates go back into solution through the formation of soluble amine complexes by mass action. This explanation for the lack of precipitates in the presence of lithium chloride seems plausible in view of the fact that Broome, Ralston and Thorton (7) report a complex ion of the formula $Cu(dodecylamine)_2Cl_4^{=}$ which forms yellow ethanol solutions.

Because of the ability of the chloride ion to complex with the copper(II) ion, the copper salt used for the remainder of this research was copper(II) perchlorate. The perchlorate ion was reported by Friedman and Plane (13) to have little or no association with the copper(II) ion in acetone and in ethanol solutions. Therefore, the perchlorate ion was not expected to compete appreciably with the amine for the coordination sites of copper(II) ion in 2-propanol solutions.

Copper(II) perchlorate was not available in the anhydrous form;

therefore, the development of the dehydrating apparatus described earlier proved to be extremely useful in this work.

This apparatus was used to dry the copper(II) perchlorate solutions, the tri-n-butyl solutions, and the 2-propanol solvent. Because the solutions tend to become concentrated in the dehydration apparatus, it was necessary to analyze the copper and amine solutions after drying and before using them.

Copper Analysis

The method used for the analysis of copper solutions was similar to the one given by Ayres (3). The analysis procedure for copper was as follows:

1. An aliquot of copper solution to be analyzed was placed in a 250 ml flask and about five times its volume of water was added.
2. 2.0 grams of potassium acid phthalate were added to buffer the solution to a pH of 3.5.
3. 3.0 grams of potassium iodide were then added to react with the copper(II) ion releasing free iodine.
4. The freed iodine in the solution was titrated with 0.1N standard sodium thiosulfate until the solution became straw yellow.
5. 2 grams of potassium thiocynate were added to precipitate copper(I) thiocyanate and help drive the copper(II)-iodide reaction to completion.
6. 5 drops of starch indicator were added and the titration was continued until the solution changed from blue to colorless.

From the normality of the sodium thiosulfate, the copper(II) ion concentration was calculated.

Amine Analysis

The analysis of the amine solutions was the same as the one given in Chapter VI on potentiometric measurements.

The results of preliminary tests on the drying efficiency of the drying apparatus are given in Chapter V.

A 0.025M copper(II) perchlorate solution in 2-propanol was prepared and dried with the drying apparatus for 12 hours. The copper content was analyzed to be 0.0389M and the Karl Fischer water analysis of the solution showed that 0.023% water remained. Thus, the copper(II) ion to water mole ratio was 0.0389M to 0.0097M, or approximately 4 to 1.

A 0.025M solution of tri-n-butylamine-2-propanol solution was prepared and dried in a second extractor column. The amine concentration after drying was found to be 0.0290M. The water content of this amine solution was 0.0013%.

Qualitative mixtures of the 0.0389M copper(II) perchlorate solution and 0.0290M tri-n-butylamine were made by injecting the components through a septum into a 100 ml volumetric flask. A mixture of 30 ml of copper solution and 30 ml of amine solution yielded a dark emerald green solution. The final concentration of copper and amine in this mixture was 0.0194M and 0.0145M, respectively. This made the ratio of copper to amine slightly more than 1 copper to 1 amine. A spectrum of this solution revealed a peak shift from 790 mμ for the pure copper(II) perchlorate solution to 725 mμ for the copper(II) perchlorate-tri-n-butylamine mixture.

When the amine concentration was increased, dark green precipitates were formed. Because of the emerald green solutions and the spectral shift, it was felt that a complex was being formed at lower amine concentrations, but, when the amine concentration was increased, the water on the copper ion was causing a basic precipitate to form.

However, in order to make sure that the dark green precipitate was not an amine complex of copper, a sample of precipitate was analyzed for copper, amine, and perchlorate.

The method of analysis selected for perchlorate ion was one using nitron reagent as described by Kodoma (21). The analysis consists of precipitating the perchlorate ion as the nitron acid perchlorate from an acid solution and weighing the precipitate. The analysis of the dark green copper-amine precipitate proceeded as follows:

1. The precipitate was vacuum filtered through a sintered glass funnel, the precipitate being protected from air moisture during filtration by placing a 1-hole stopper in the top of the funnel and attaching through this a Molecular Sieve drying tube. By means of this arrangement, a vacuum could be used to draw air through the Molecular Sieve bed into the funnel and, at the same time, suck the precipitate dry.
2. After the filtration was complete, the precipitate was washed 3 times with 10-ml portions of ligroin.
3. The washed precipitate was dissolved in 10-15 drops of 3N sulfuric acid and diluted to 100 ml in a volumetric flask.
4. The resulting 100-ml solution was divided into two 50-ml portions.
5. To one of the 50-ml aliquots was added 12 ml of nitron reagent

(prepared by adding 10 grams of nitron to 100 ml of 5% acetic acid).

6. The nitron precipitation reaction mixture was cooled to ice temperature for 2 hours.
7. The precipitate from the reaction was filtered through a preweighed filter crucible, washed 3 times with 10 ml of ice water, then placed in an oven at 100°C.
8. The crucible was cooled and weighed. The compound weighed was $C_{20}H_{16}N_4HClO_4$. The weight of perchlorate was calculated from the weight of the precipitate and a gravimetric factor.
9. The second 50-ml aliquot was made basic with a 1:1 mixture of concentrated ammonium hydroxide and water and extracted with five 5-ml portions of isooctane as described by Carley (9).
10. The isooctane extract was titrated with 0.01N standard hydrochloric acid. The amount of amine in the precipitate was calculated from this titration.
11. The aqueous phase remaining from the amine extraction was analyzed for copper by means of the iodometric titration described earlier.

The results of the analysis gave a copper molarity of 0.0155, an amine molarity of 0.0084, and a perchlorate molarity of 0.00013. This would be a copper-to-amine-to-perchlorate ratio of 1 to 0.54 to 0.08.

The amine concentration was probably high due to some of the ammonium hydroxide being inadvertently carried over into the titration with hydrochloric acid. This suspicion was supported by the fact that infra-red analysis of a KBr pellet of the supposed copper-amine precipitate failed to show any tri-n-butylamine present in the precipitate.

When the nitron reagent was added to 50 ml aliquot of the dissolved copper-amine precipitate, very little nitron perchlorate precipitate formed. When a portion of the 2-propanol filtrate was tested, however, a large nitron perchlorate percipitate formed. These results confirmed the other results which had indicated that perchlorate was not a significant part of the dark green copper-amine precipitate.

Because of the low amount of perchlorate present in the copper-amine precipitate, it was suspected that perhaps some hydroxide ion was present in the 2-propanol, either from carry-over from the KOH and K_2CO_3 pretreatment or from the Molecular Sieve (which is somewhat basic). A check of the pH of the alcohol after the KOH and K_2CO_3 pretreatment showed that the pH was about 10; consequently, the pretreatment was changed to a straight distillation without using KOH and K_2CO_3.

The tri-n-butylamine was also checked for purity by gas chromatography. The amine employed in this research was double-distilled before use. A 1 microliter sample of freshly distilled tri-n-butylamine was injected onto a 10 ft., 1/4 inch, 20% by weight Ucon Polar, Chromasorb W column at $180^{\circ}C$. The carrier gas was helium, and the flow rate of the helium was 90 ml/min. The chromatographic analysis revealed that the tri-n-butylamine contained some di-n-butylamine and a larger amount of n-butylamine.

A sample of freshly distilled n-butylamine was also chromatographed under the same conditions. The chromatographic analysis of the n-butylamine showed that it contained only n-butylamine. For the remainder of this research, therefore, n-butylamine was employed as the complexing agent.

n-Butylamine Complexes

A solution of 0.1M n-butylamine in 2-propanol was prepared and dried in the extractor for 22 hours. The analysis of the amine concentration showed it to be 0.0964M. The water content by Karl Fischer analysis was measured as being 0.0004%.

A 0.01M solution of copper(II) perchlorate was prepared and dried for 22 hours. The copper concentration was 0.0118M after drying, while its apparent water content was 0.0155%.

Four qualitative mixtures of these two solutions were made by injecting them through a septum into a predried 5-cm quartz cell. The spectra of these mixtures was run versus the same 2-propanol used for dilution, a Beckman DK1 spectrophotometer being employed. The mixtures prepared were as described in Table III, 1 ml of the copper salt being used in each case.

TABLE III

COPPER(II) PERCHLORATE-n-BUTYLAMINE MIXTURES

Mixture	Final Copper conc.	Volume of Amine used	Diluted Amine conc.	Amine/Cu
A	0.00078M	14 ml	0.09M	115
B	0.00078M	10 ml	0.064M	82
C	0.00078M	5 ml	0.032M	41
D	0.00078M	1 ml	0.0064M	8.2

The final volume was adjusted to 15 ml by adding sufficient 2-propanol (0.001% water content).

The letters designating the mixtures listed in Table III corresponds to the letters on the spectra given in Figure 9. The very high amine to copper ratios employed were used, first to force the formation of the highest complex so it could be studied and, second, to avoid the precipitates which formed in such quantities at lower ratios as to give too much interference in spectral studies.

The spectra of mixtures A and B gave an expected shift in the absorption peak from 790 mμ for copper(II) perchlorate in 2-propanol to about 590 mμ for the n-butylamine complex, which is a considerably larger shift than that for the tri-n-butylamine complex.

Mixtures C and D formed precipitates, with mixture D forming the largest amount of the two. It was believed that the precipitate formation accounted for the radical general increase in absorbance of D and as compared to C, the effect being presumably due to the absorption of light by the precipitate.

The precipitates were probably formed from the residual water in the solution and from water picked up in handling.

An experiment was devised to eliminate the water absorbed during handling by mixing the copper(II) perchlorate hexahydrate, n-butylamine, and 2-propanol before drying, then dehydrating the mixture to try to form the complex without the basic precipitates. A 500 ml solution containing 0.005M copper(II) perchlorate hexahydrate, 0.02M n-butylamine, and 0.05M lithium perchlorate in 2-propanol was prepared. The lithium perchlorate was added as a carrier electrolyte in the event that polarograms of the mixture were needed. Initial mixing of these reagents gave a greenish brown solution with no precipitate formation. The solution was dried for 24 hours in the Molecular Sieve extractor. After 3-4 hours, it was noticed that a dark brown precipitate had formed. When a

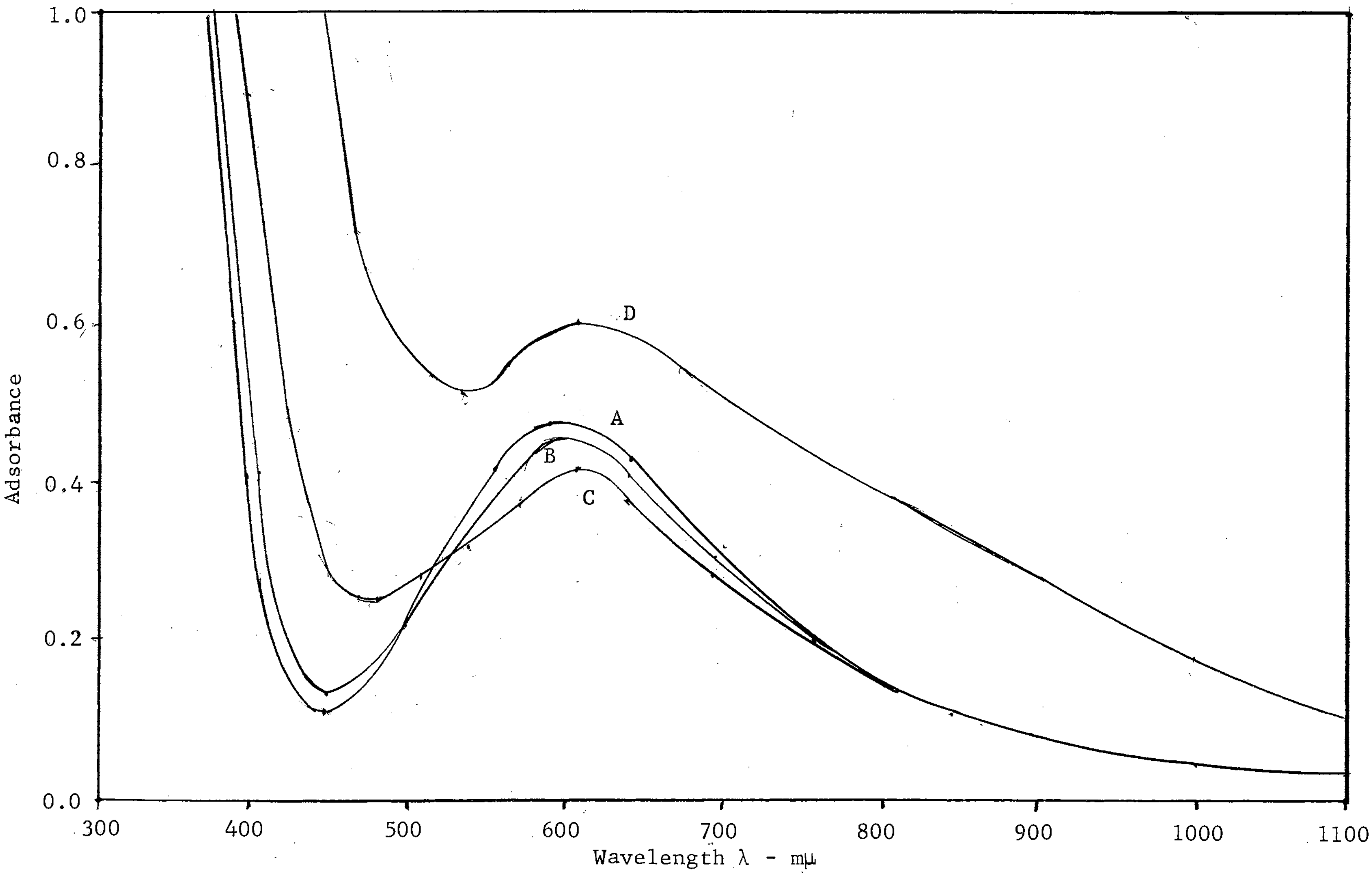


Figure 9. Spectra of Mixtures A to D Given in Table 3.

sample taken for water analysis was injected into the copper displacement apparatus and shaken, no apparent displacement of the copper took place, the brown precipitate remaining even after 12 hours of shaking with the zinc powder.

A water analysis after 12 hours of shaking, gave the water content to be 0.01%--a result which probably was high due to the exposure during the unusual length of time used in shaking the apparatus.

After 3 days of continuous drying, the brown precipitate still remained in the solution. A sample of the precipitate was obtained by filtration and examined. It appeared to be copper oxide. The brown precipitate was insoluble in water but dissolved readily in 6N hydrochloric acid. The hydrochloric acid solution was neutralized with excess concentrated NH_4OH and the solution turned blue. This was taken as an indication of the copper(II) ion. It was postulated that the brown precipitate was copper oxide possibly formed from a reaction such as:

$$2\,\mathrm{Cu(OH)ClO_4} \xrightarrow{\text{dehydration}} \mathrm{CuO} + \mathrm{Cu(ClO_4)_2} + \mathrm{H_2O}$$

the water being mostly removed by the Molecular Sieve. Because of the formation of CuO, the direct method of dehydrating the complex mixtures was not pursued further.

The formation of precipitates by mixtures C and D of Table III having indicated that the water content was still too high, to lower the water content of the copper(II) perchlorate solution, a 0.005M solution was dried continuously for 10 days with the extractor using the vacuum technique given in Chapter V. At the end of 10 days, the water content had been lowered to 0.0026% and a copper analysis gave a molarity of 0.00582M for the copper(II) perchlorate in this solution.

A n-butylamine solution was dried for 24 hours and was found to contain 0.00057% water and 0.0989M n-butylamine after drying.

A 2-propanol solution was also dried for 24 hours and analyzed for water. The Karl Fischer analysis gave 0.00064% water content for this solution. Each of the above solutions was also 0.05M in lithium perchlorate so that polarographic analyses could be made on the resulting solutions.

Because of the inaccuracy of the delivery from syringes, the solutions given in Table IV were prepared by injecting each component into a 50 ml volumetric flask through a septum and then weighing the flask to obtain the sample weight. From measured densities, the volume delivered was calculated. By knowing the volume of each component and the total volume, it was possible to calculate the molarity of copper(II) perchlorate and n-butylamine in the final solutions. The volumetric flasks used for this series were pretreated by baking at 300°C for 12 hours, cooling in a vacuum desicator over Molecular Sieve, and purging with dry nitrogen before being sealed with a rubber septum.

Table IV lists the molarities, the amine to copper ratios, the pH's and the colors of the resulting solutions. The Roman numeral of the solution corresponds to the numbers on the curves of Figure 10.

Figure 10 shows the spectra of the first five solutions in Table IV. The spectra of samples VII and VIII (the ones with large amounts of precipitate) were made after several hours of settling time; but since, some precipitate still remained suspended in the solutions, the spectra were not included in Figure 10. The spectra were run on a Beckman DK1, using 1-cm quartz cells equipped with a rubber septum on top. Samples were removed from the 50-ml volumetric flask by forcing

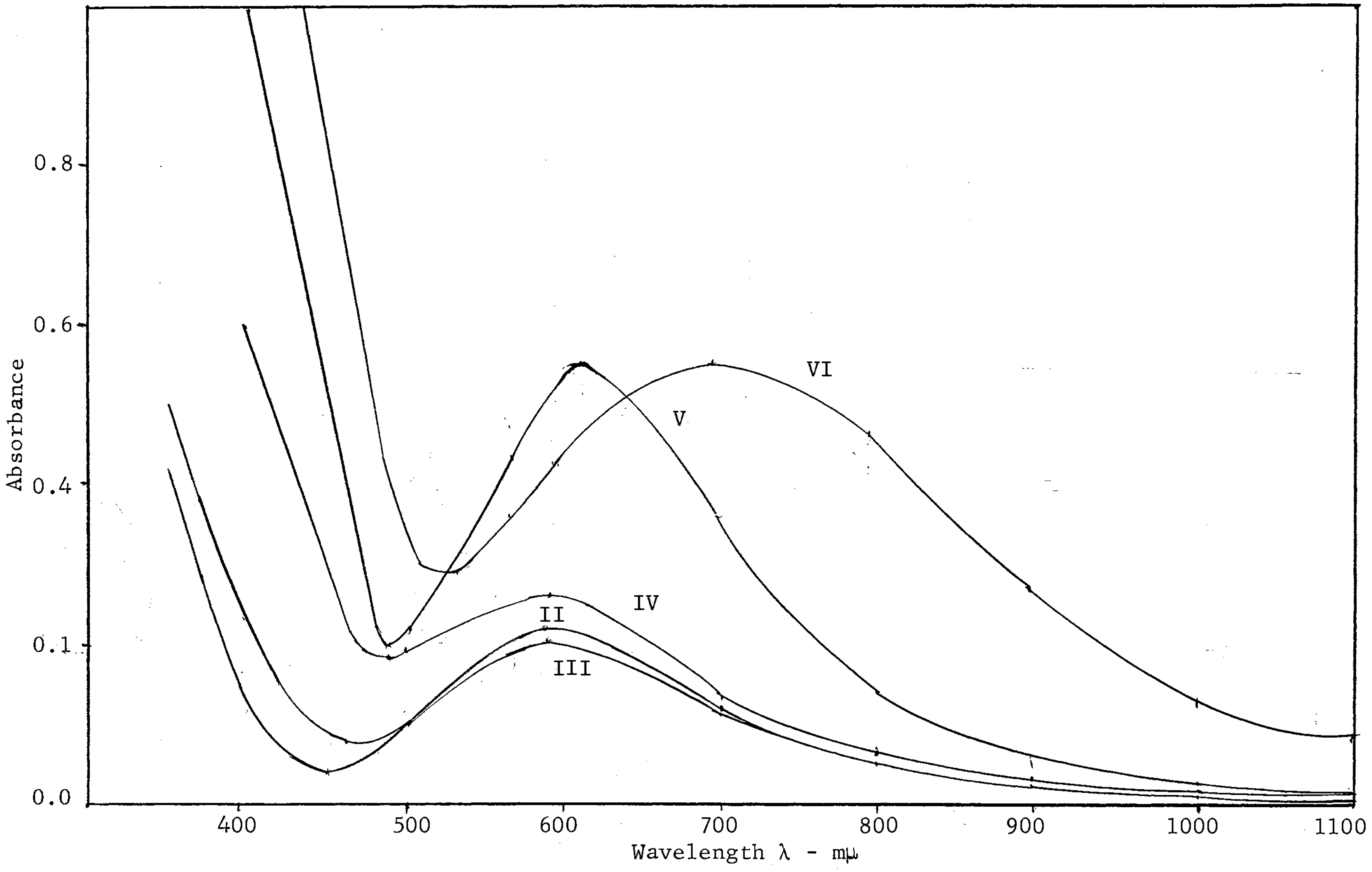


Figure 10. Spectra of Solutions Given in Table 4.

TABLE IV

SOLUTIONS PREPARED FROM 0.00582M COPPER(II) PERCHLORATE, 0.0989M n-BUTYLAMINE AND 2-PROPANOL

(All Solutions Contain 0.05M Lithium Perchlorate Carrier)

Solution	Molarity after mixing		Amine to copper ratio	pH	Color
	$Cu(ClO_4)_2$	n-Butylamine			
II	0.00184M	0.0675M	36.6/1	10.425	Blue
III	0.00180M	0.0490M	27.2/1	9.781	Blue
IV	0.00178M	0.0299M	16.7/1	9.772	Blue-slight turbidity
V	0.00174M	0.0103M	5.9/1	10.518	Blue green-turbid
VII	0.00179M	0.00199M	1.1/1	2.430	Light green solution and precipitate
VIII	0.00175M	0.00399M	2.28/1	8.340	Light green solution and precipitate
IX	0.00177M	none	none	2.001	Light green solution

the liquid into a syringe with predried nitrogen introduced through a syringe needle. The liquid was then injected into the 1-cm quartz cells through the septum top on the cell.

Solution IX of 0.00177M copper(II) perchlorate gave the characteristic peak of copper(II) ion at 795 mμ (not shown in Figure 10). Solution VI was analyzed spectrally after 8 hours settling time. The spectra of solution VI shows the beginning of the shift from the 795 mμ peak, thus indicating a complex formation. As the amine to copper ratio was increased (that is, going from solution VI to solution II), the spectra continued to shift to lower wave length until the spectra reached about 590 mμ. The spectrum of solution II is quite similar to that obtained for mixture A of Table III.

The method of preparation caused the time involved for each spectral analysis to be rather lengthy. The samples were saved after each analysis. A startling change in color was noticed after a few hours. The color of the samples began as a dark blue, but after about 1 hour, the color had faded to light blue. The color of these solutions continued to fade until after 24 to 36 hours the solutions became yellow. Upon further aging, the color became distinctively orange. It was first suspected that this radical color change was due to either water being absorbed by the solutions or to the slow formation of a new complex.

The most striking spectral change was found in solution IV. This is shown in Figure 11. This shows that the original complex peak at 590 mμ has almost disappeared, while a large peak at 500 mμ has appeared.

In order to see if these changes could be reversed by water, 3 ml of 2-propanol containing 0.01% water was added to the orange solution II of Table IV with the result that the solution changed from orange to

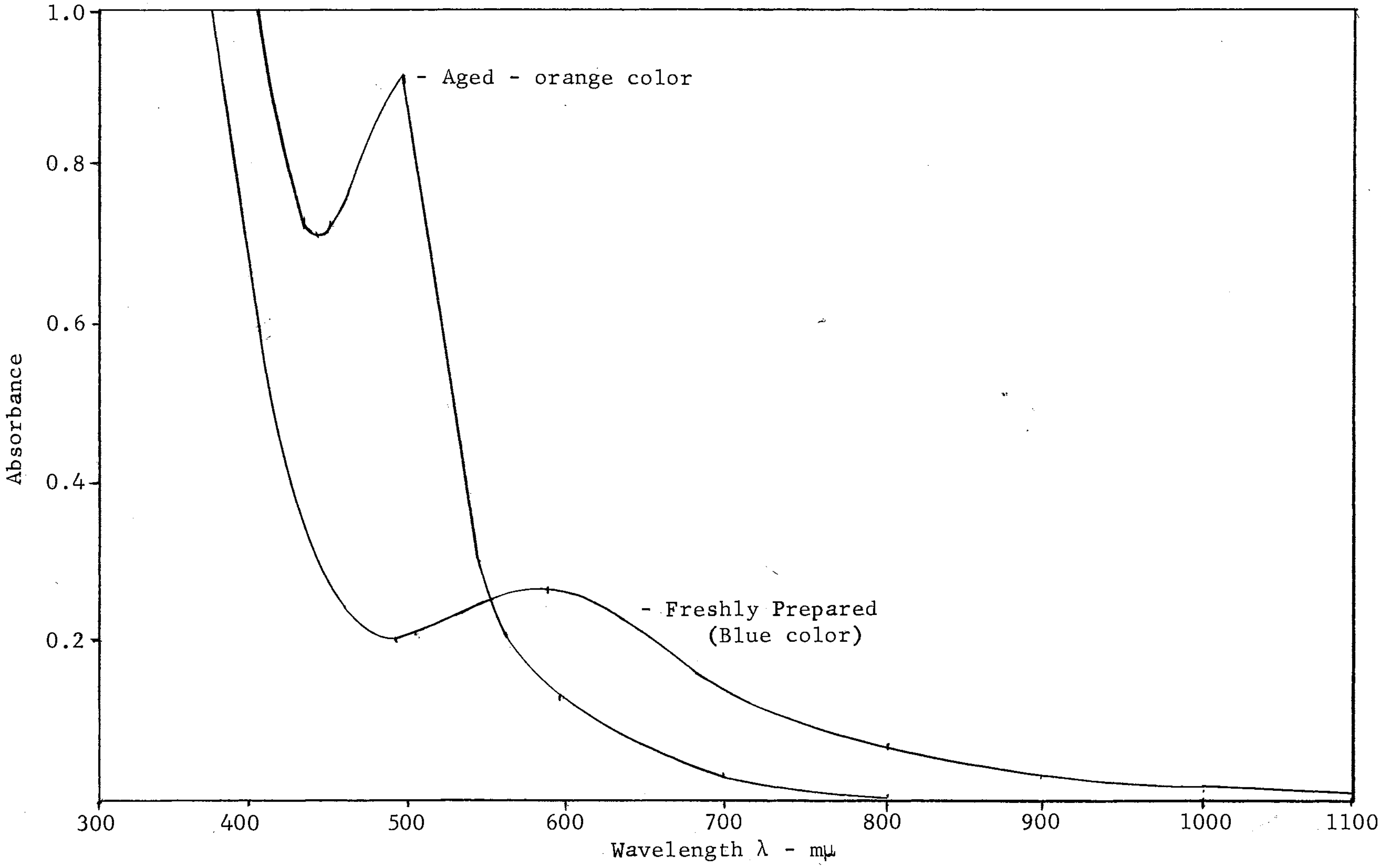


Figure 11. Spectra of Solution IV from Table IV Before and After Aging.

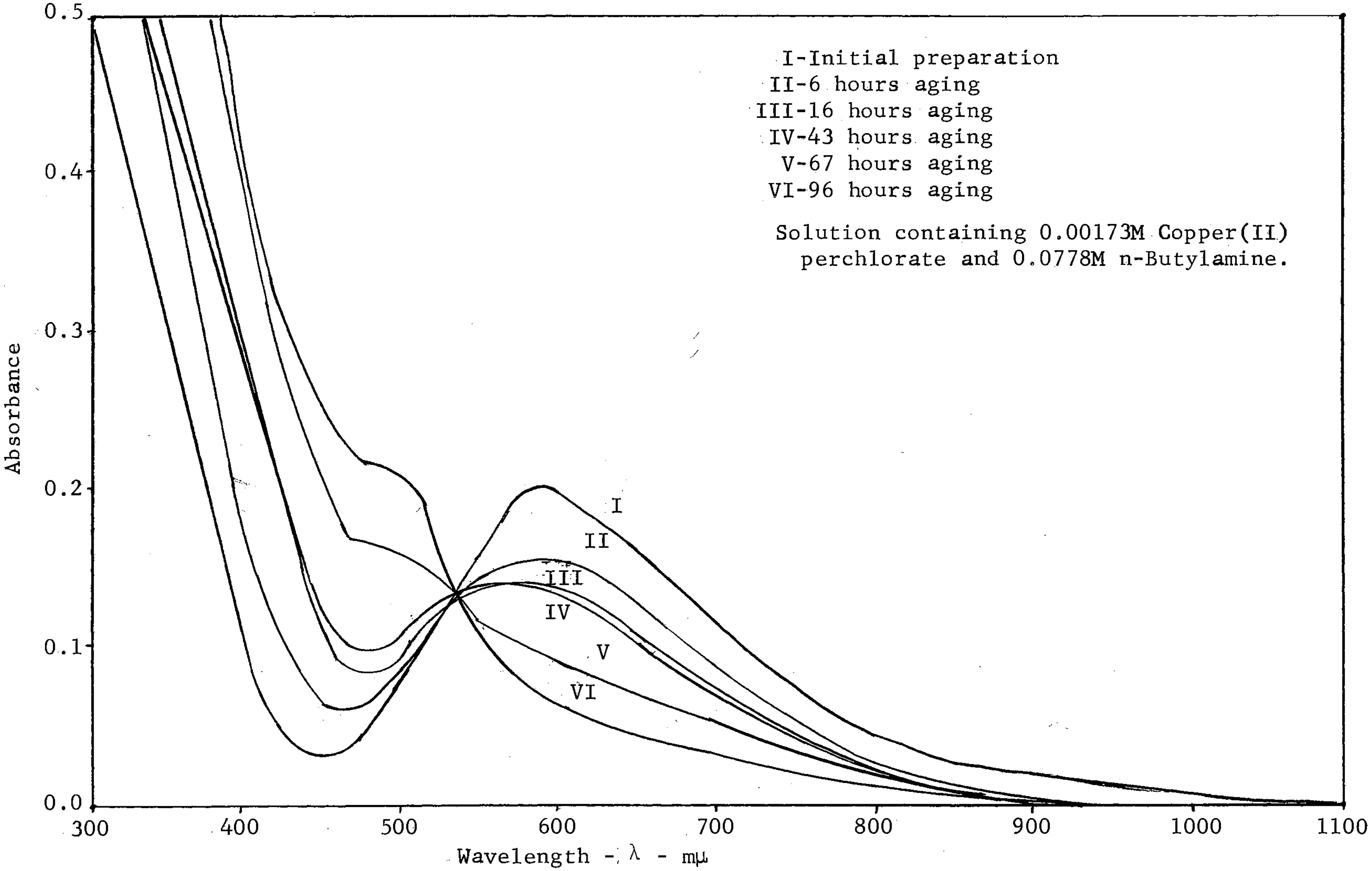
light yellow. This was taken as an indication that water would not, completely, at least, reverse the process.

The remarkable spectral changes given by Figure 11 prompted a time study of the spectral changes of one of these complexes. A solution containing 0.00173M copper(II) perchlorate and 0.0778M n-butylamine was prepared by the technique of weighing the components into a 50-ml volumetric flask. Within 20 minutes after preparation, a spectral curve of this solution was made. Curve I (Figure 12) represents the spectrum at the beginning and shows the same type of peak (at 590 mμ) as was obtained on previous samples. After six hours, considerable change had taken place in the solution. The color changed in this series from blue to orange in the same way as the series of Table IV. Curve (VI) made after 96 hours shows the same peak (500 mμ) as that given in Figure 11.

Two qualitative tests were now made, the first to see if water would inhibit the phenomenon shown in Figure 12, and the second to see if oxygen was the cause of the changes.

The water test was performed by preparing, in a dry box, a solution of approximately the same concentration range as the solution used in the time study. This solution was divided into two parts. One part was sealed and handled in the same manner as the solutions in Table IV. The second part was placed in a flask which was left open to the atmospheric moisture and oxygen of the air. The flask which was sealed changed to an orange within 2 days. The solution which was exposed to moisture and air changed from dark blue to light blue and remained light blue.

The test for the effect of oxygen was also made by preparing



Solution containing 0.00173M Copper(II) perchlorate and 0.0778M n-Butylamine.

Figure 12. Study of the Spectral Changes with Time.

approximately the same concentration solution as the one used for the time study. This solution was then degassed for one and one-half hours with dry deoxygenated nitrogen to remove the oxygen. This solution changed to orange in 24 to 36 hours.

These two tests indicated that water and/or oxygen did inhibit the changes taking place in the copper-amine solutions and it was concluded at the time that oxygen did not have any influence. The conclusion with respect to oxygen was later proven false.

The ultraviolet spectra of the solutions in Table IV were made using a 1-cm quartz cell with a 9-mm quartz spacer. The ultraviolet spectra obtained were erratic and not reproducible. This was probably due to the fact that the cell arrangement could not be sealed from atmospheric moisture and oxygen. In one case, where an orange solution (the solution from the water test above) was used, the solution had changed from orange to light blue-green before it had been removed from the dry box for U.V. analysis.

The pH of solutions III through IX are given in Table IV. The pH of these solutions was measured using the apparatus shown in Figure 8 as described in Chapter VI. There was a sharp change in the pH between the amine to copper ratios of 1.1 to 1 and 2.28 to 1.

The two pH titrations were made by injecting 30.12 ml of 0.00582M copper(II) perchlorate solution into the titration vessel and titrating with 0.0989M n-butylamine. The pH curves obtained with the Heath pH meter showed a typical titration break corresponding to an amine to copper ratio of 2.16 to 1 for one titration and 2.23 to 1 for the other.

It was felt that the difference in the two results might have been due to water pickup from the glass electrode (since the latter, of necessity, is first equilibrated with water) and that this water was coordinated with the copper(II) ion causing it to act as a cationic acid. To minimize such water absorption, a water-repellent silicone was used to coat the inside of the titration vessel and the surface of the glass electrode. The silicone compound, Desicote (obtained from Beckman Instruments, Inc.) was used for this purpose. Gilbert (15) reports that Desicote is a substituted chlorosilane which undergoes a hydrolytic reaction with the absorbed molecular film of water on the glass. This hydrolytic reaction leaves a film of polymerized substituted siloxane which provides water repellency.

After the vessel and glass electrode were treated with Desicote, the vessel was dried in an oven at 130°C and the glass electrode was dried in the air. Another titration was made using 30 ml of 0.00582M copper(II) perchlorate and 0.0989M n-butylamine. This titration gave very similar results to those obtained with untreated apparatus in that a break occurred in the curve at an amine to copper ratio of about 2 to 1.

A polarogram was made on the orange solution produced in the test made for the effect of water as mentioned above. This polarogram was made by injecting the solution into a 3-electrode polarographic cell and degassing the nitrogen for 30 minutes. The nitrogen was first deoxygenated by the method given by Arthur (2), then was passed through a silica gel column and finally through a Molecular Sieve bed which was filled with dry 2-propanol to remove the last traces of water and saturate the gas with solvent. The indicating electrode was a 6-second drop time dropping mercury electrode. The reference electrodes were of the saturated calomel acetone type.

The polarogram of the orange solution is shown in Figure 13. It can be seen from this figure that at least 5 components are present in the orange solution.

To analyze polarographically the changes in the complex solutions, a 100-ml solution was prepared containing 0.00582M copper(II) perchlorate, 0.069M n-butylamine, and 0.05M lithium perchlorate. This solution was divided into two parts. The first part was analyzed polarographically within 45 minutes after preparation. The second solution was deoxygenated with nitrogen and stored for about 2 days until it turned orange.

The polarograms of the two parts are shown in Figure 14. The polarogram made on the freshly prepared solution (curve A) shows the usual copper(II) ion waves, the first wave, beginning at - 0.3V being the reduction of cupric ion to cuprous ion and the second wave being from the reduction of cuprous ion to copper metal. In the normal cupric ion reduction, the height of the $Cu^{+2} \rightarrow Cu^{+1}$ wave (measured from the residual current to the top of the first wave) should be approximately half the height of the second wave (measured from the top of the first wave to the top of the second wave). This was the case for curve A except that the second wave was slightly (4 mm) higher than would be expected. A second and third polarogram of this initial solution showed that the height of the first wave was decreasing continuously while that of the second was increasing. These repetitive polarograms of the solution used for curve A revealed that the changes in the solution were occurring rather rapidly.

Curve B, the polarogram of the aged solution gave a completely different picture from that of curve A. The most striking feature of

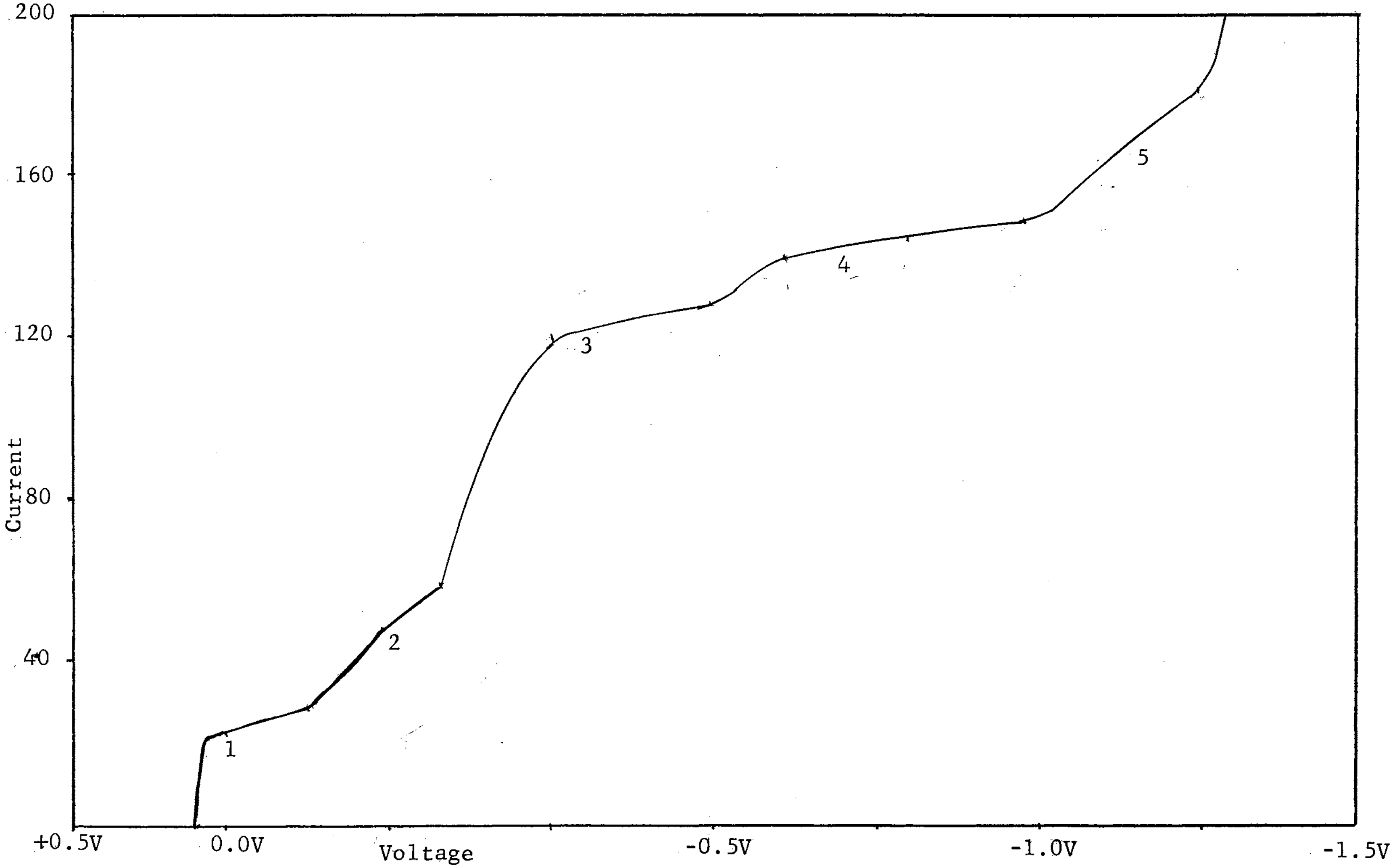


Figure 13. Polarogram of Orange Solution of 2:1 n-Butylamine/Copper(II) Perchlorate.

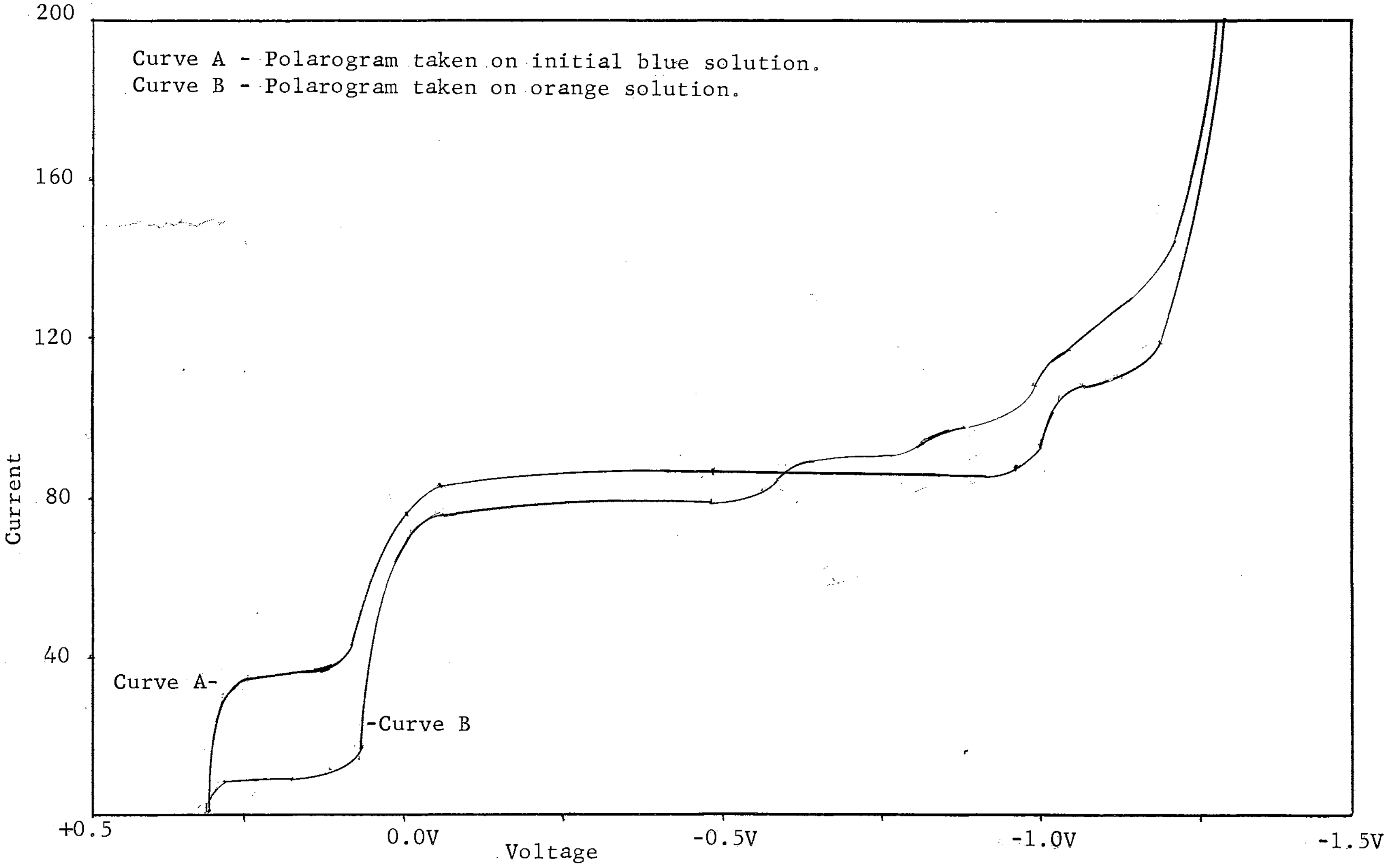


Figure 14. Polarogram of a Solution Containing 0.00582M Copper(II) Perchlorate, 0.069M n-Butylamine, and 0.05M Lithium Perchlorate.

this polarogram was that the cupric to cuprous ion wave was much smaller than would be expected, while the wave that was interpreted to be the cuprous to copper metal wave increased more than expected. This indicated that upon aging the amount of cupric ion had been lowered greatly while the cuprous ion concentration had increased greatly.

This polarogram provided the first true indication of what was happening to the copper-amine solutions when they began to change colors. It was reasoned that if the cupric ion was being reduced to cuprous ion in these solutions, a chemical test of the aged solutions could prove the presence of the cuprous ion.

The first qualitative test for the cuprous ion was made by adding hydrochloric acid to portions of the orange solutions (II and III from Table IV) and then adding concentrated ammonium hydroxide to make the solution basic; then 30% hydrogen peroxide was added to oxidize any cuprous ion to the cupric state. In the presence of ammonium hydroxide, cuprous ammines would be colorless, but cupric ions should be present in the blue tetraammine state. Solutions II and III changed from bluish green to blue but the change took about 10 minutes; consequently, the results did not constitute a reliable test for copper(I).

A second test using an organic reagent, dimethylaminobenzylidenerhodanine, was made on solutions IV and V. The rhodanine reagent forms a red precipitate with cuprous ion and this (11) is considered a specific test. The test on solutions IV and V gave no red precipitate. A test of this reagent with cuprous chloride also gave no red precipitate, which indicated that the reagent had deteriorated.

A third test for cuprous ion was with 2,2'-diquinolyl which gives a purple color with cuprous ion. According to Feigl (11), this reagent is specific for the cuprous ion and undergoes no reaction with the cupric ion. Feigl further states that the test is very sensitive in that it can detect 1 part per million of cuprous ion. The 2,2'-diquinolyl reagent dissolved in 2-propanol, was pretested using cupric chloride. When a few crystals of cupric chloride were added, the solution turned green. Then a few crystals of hydroxylamine hydrochloride were added to reduce the cupric chloride to cuprous chloride. The solution turned bright purple immediately.

Portions of solutions II, III, IV and V were then tested with the diquinolyl reagent. In each case, the solution immediately turned purple. This was a very positive test for cuprous ion.

When a portion of solution V was first treated with hydrogen peroxide and then the diquinolyl reagent, no purple color appeared. This was an indication that the cuprous ion was oxidized by the peroxide so that no cuprous ion remained for the diquinolyl test.

When the orange solution which was used for the oxygen test was opened to the atmosphere, the solution began to turn light blue immediately. This was interpreted as an indication that the oxygen of the air was oxidizing the cuprous ion to the cupric ion.

Since precipitates had formed in the case of solutions VI, VII, and VIII of Table IV, an analysis for n-butylamine was made on a precipitate formed at an amine to copper ratio of 2 to 1. This was about the same ratio as solution VIII of Table IV. The amine analysis was performed by dissolving the precipitate in a few drops of sulfuric acid and then making the solution basic with concentrated potassium hydroxide solution. This strong base displaced the n-butylamine which was then distilled into a hydrochloric acid solution of known concentration. The excess hydrochloric acid was back titrated with standard sodium hydroxide. This analysis revealed that little or no amine was attached to the precipitate. A similar analysis of the filtrate (from the filtration of the precipitate) showed that the amine was still in solution.

CHAPTER VIII

SUMMARY AND CONCLUSIONS

The object of this research was to develop methods for obtaining and studying complexes formed with copper(II) salts and amines in anhydrous 2-propanol. This, to some extent, was accomplished and evidence indicated that the methods would have worked except for the rapid reduction of the copper(II).

The spectral changes, the polarographic behavior, and the redissolving of the basic salt precipitates when large excess of amine were added, all made it obvious that complexes were forming. However, the rapid changes which followed indicated that other reactions were also occurring and made it extremely difficult to study the complexes properly. This other reaction proved to be an oxidation-reduction reaction involving the freshly formed complex.

Owing to the discovery that the copper of the copper-amine complexes undergoes rapid reduction in 2-propanol solutions of low water content, no attempt was made to study the complex formation constants. The nature of the oxidation-reduction reaction was not investigated; although, it probably involves the oxidation of the 2-propanol solvent or of the amine ligand (more probably the latter).

The formation of cuprous ion by means of this oxidation reduction explained many of the unusual results obtained in this research. It explained such results as the spectral changes with time, the decrease in the cupric ion wave with the corresponding increase in the cuprous ion wave in the polarograms, and the tests involving the removal of oxygen. It also answered the question of why the ultra-violet spectra were not reproducible.

The drying procedure and the water analysis were, for the most part, successful. The formation of copper oxide when the copper-amine solutions were dehydrated directly, however, made it necessary to mix the solutions independently, this causing undesirable exposure to moisture.

The polarographic and spectral methods used for this study were successful in that they revealed not only the reduction of the copper-amine complexes, but also the fact that complexes actually did form. The spectral and polarographic changes which occurred when the complexes first formed indicated that these methods could be used on other complex ion systems which are not easily reduced under anhydrous conditions. These changes indicated also that if these techniques could be speeded up sufficiently, even the copper-amine systems might yield useful information.

The potentiometric measurements and the analysis of precipitates seemed to show that there were at least two water molecules attached to the copper(II) ions involved in the pH titrations. There is a distinct possibility that this water was absorbed from the apparatus (possibly largely from the glass electrode) and was not present on the copper(II) ion before the solutions were mixed. The pH measurements were at best inconclusive so far as being able to measure the amine concentration directly was concerned. This should, however, be investigated farther.

This research opened up the possibility of future research using the techniques developed during this study on other metal amine complexes which do not undergo oxidation-reductions in anhydrous 2-propanol. It also pointed out the fact that when ligands which are moderately strong Bronsted bases are used with heavy metals, the possibility of acid-base reactions occurring must be considered even when only minute amounts of water are present.

SELECTED BIBLIOGRAPHY

1. Arthur, P., Anal. Chem. 33, 765 (1961).
2. Arthur, P., Anal. Chem. 36, 701 (1964).
3. Ayres, G. H., Quantitative Chemical Analysis, Harper and Brothers New York, 1958, pp. 666-70.
4. Bates, R. G., Electrometric pH Determinations, Chapter 2, 4, Wiley and Sons (1954).
5. Bjerrum, J., "Metal Ammine Formation in Aqueous Solution," P. Hasse and Son, Copenhagen (1941, 1957).
6. Bjerrum, J., and Lamm, C. G., Acta Chem. Scand. 4, 997-1004 (1950).
7. Broome, F. K., Ralston, A. W. and Thornton, M. H., J. Am. Chem. Soc. 68, 67-9 (1946).
8. Burkin, A. R., J. Cham. Soc. 122-7 (1950).
9. Carley, D. A., "A Study of the Copper-Tributylamine Complexes in 2-propanol," M.S. Thesis, Oklahoma State University, 1964.
10. Crow, D. R., and Westwood, J. V., Quart. Rev. 19, 57 (1965).
11. Feigl, F., Spot Tests in Inorganic Analysis, Elssvier Publishing Co., 91-93 (1958).
12. Fischer, K., Angew Chem. 48, 394 (1935).
13. Freidman, N. J., and Plane, R. A., J. Inorg. Chem. 2, No. 1, pp. 11-14 (1963).
14. German, W. L., and Jamsett, R. A., J. Chem. Soc. 1337-41 (1939).
15. Gilbert, P. J., Jr., Science, 114, 637-40 (1951).
16. Hein, F., and Ludwig, W., Z. Anorg. Allgem. Chem. 338 (1965).
17. Hersh, C. K., Molecular Sieves, Reinhold Publishing Co., Chapman and Hall, pp. 2-3 (1964).
18. Job, P., Ann. Chim. (10) 9, 113 (1928).

19. Jones, M. M., Elementary Coordination Chemistry, Prentice-Hall, Inc. (1964).

20. Katzin, L. I., and Gebert, E. L., J. Am. Chem. Soc. 72, 5455 (1950).

21. Kodama, K., Methods of Quantitative Inorganic Analysis, Interscience Publishers, John Wiley and Sons, New York, 1963.

22. Kolthoff, I. M., and Elving, P. J., Treatise on Analytical Chemistry, Interscience Publishers, Vol. 4, Part 1, 2980-83 (1959).

23. Leden, I., Zeit, Phys. Chem. 188, 160 (1941).

24. Miki, S., and Yamada, S., Bull. Chem. Soc. Japan 37, 1044 (1960) (English).

25. Neuman, L., and Hume, D. N., J. Am. Chem. Soc. 79, 4571 (1957).

26. Neuman, L., and Hume, D. N., J. Am. Chem. Soc. 4576-81 (1957).

27. Pflaum, R. I., and Brandt, W. W., J. Am. Chem. Soc., 76, 6215 (1954).

28. Pinksten, J. R., and Briscoe, H. I., J. Phys. Chem. 46, 469-73 (1942).

29. Private Communication, Collins, J. J., Superviser, Linde Division Union Carbide, March 19, 1964.

30. Vosburgh, W. C., and Copper, G. R., J. Am. Chem. Soc., 63, 437 (1941).

31. Watkins, K. O., and Jones, M. M., J. Inorg. Nucl. Chem. 24, 1607-16 (1962).

32. Warner, C. E., "A Study of Cupric Amine Complex Ions Formed in 2-Propanol," M.S. Thesis (1966).

33. Woldbye, F., Acta. Chem. Scand. 9, 299 (1955).

VITA

William Miller Haynes

Candidate for the Degree of

Doctor of Philosophy

Thesis: REACTIONS OF COPPER(II) SALTS WITH AMINES IN NONAQUEOUS SOLVENTS

Major Field: Chemistry

Biographical:

Personal Data: Born in Bartlesville, Oklahoma, July 26, 1936, the son of G. Miller and Ruth A. Haynes

Education: Attended public school in Bartlesville, Oklahoma; graduated from Bartlesville High School in 1954; received the Bachelor of Arts degree from Oklahoma State University, with a major in chemistry in May 1959; completed the requirements for the Doctor of Philosophy degree in May, 1966.

Professional Experience: Worked as spectrochemist for Phillips Chemical Company from July 1960 to August 1962; is a member of American Chemical Society, Oklahoma Academy of Science and Phi Lambda Upsilon, Honorary Chemical Society.