A STUDY OF THE COPPER – TRIBUTYLAMINE

COMPLEXES, IN 2 – PROPANOL

By

DON ADAM CARLEY

Bachelor of Science

Bethany Nazarene College

Bethany, Oklahoma

1961

Submitted to the faculty of the Graduate School
of the Oklahoma State University
in partial fulfillment of the requirements
for the degree of
MASTER OF SCIENCE
May, 1964

A STUDY OF THE COPPER - TRIBUTYLAMINE

COMPLEXES IN 2-PROPANOL

Thesis Approved:

Paul Arthur
Thesis Adviser

Tom E. Moore

J. M. Boggs
Dean of the Graduate School

ii

ACKNOWLEDGMENT

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

In an investigation of the possibility of determining various additives in petroleum products by direct amperometric titration in nonaqueous solutions, Moran (34) found that high molecular weight amines appeared to form a complex with cupric chloride dihydrate in 2-propanol, with a metal-to-amine ratio of about 1:1.5. In a continuation of this work, Crowe (16), looking for steric hindrance effects, studied the same salt with ammonia, methylamine, ethylamine, and n-butylamine in the same solvent, likewise by amperometric titrations, and found an apparent ratio of metal-to-amine that varied from 1:2.21 to 1:1.54.

The investigation reported here was undertaken as one phase of a broad program to study the nature of the complexes formed with copper (II) salts reacting with amines in nonaqueous solutions and to determine the extent to which water (present in the $CuCl_2 \cdot 2H_2O$, and in traces in the 2-propanol) and the solvent itself compete with amines for co-ordination positions. The amine used (tertiary n-butylamine) was chosen for its possible increased steric hindrance and for its low volatility—a factor expected to be useful in some of the experimental techniques employed.

Three approaches were employed in this work; i.e., (1) the use of thermogravimetric techniques in an effort to determine the role of the solvent and of water in precipitated complexes, (2) analysis of the

1

precipitates for copper, chloride, and amines, to obtain a material-balance picture of the complexes, and (3) a correlation of data obtained by the above methods with results obtained by amperometric titrations.

A very important part of this research was the development of procedures, using the above tools, for studying similar complexes of other amines.

Thermogravimetric Analysis

In thermogravimetric analysis the data is usually recorded in graphic form. This may be a plot of weight versus temperature or of weight, at a fixed temperature, versus time. In the former case a definite heating rate usually is used; consequently, the resulting curve incorporates elements of both, and owing to this fact, the rate of increase of temperature is important.

Typical of the data obtained during a thermovravimetric analysis is the weight change versus temperature plot for $CuSO_4 \cdot 5H_2O$ in nitrogen atmosphere given by Wendlandt (44).

Applications too numerous to mention here have been made of the thermogravimetric balance. The variety of these, however, is suggested by the work of Chevenard and Wache (5) who used the balance to study the formation of the oxide film which gives certain unoxidizable alloys their resistance to chemical reaction; that of Doyle (17) who used the technique as a rapid method of assessing the thermal stability of polymers in inert atmosphere; of Duval (19) who applied the technique in studying the thermal stability of many precipitates of different elements to determine their usefulness, and the thermal conditions needed for their use, in gravimetric analyses for these elements; and of Wendlandt (45)

who used the technique to determine the steps in the thermal dissociation of the ethylenediamine, 1,2-propanediamine-, and 1,3-propanediamine-complexes of copper (II) sulfate.

Although the development of the thermobalance to its present state and a description of the particular thermobalance used in this investigation will be discussed in other sections of this paper, the nature of the instrument deserves some immediate mention. All well-designed thermobalances have three essential features which are as follows: (a) furnace or other heating device for subjecting the sample to known temperatures, either fixed or increased at a known rate; (b) a weight-change sensing device for following changes in weight of the sample; and (c) a recording device for making a record of the changes in weight. According to Gordon and Campbell (6), thermobalances may be divided into two groups -- namely, the null-type or the deflection-type.

The null-type thermobalance may be illustrated schematically by Figure 1. This type balance consists of a sensing element, which detects a deviation of the balance beam from its null position, and a device for supplying a restoring force of the proper direction and magnitude to return the balance to its null position. An example of this type thermobalance is one manufactured in Germany by Gebruder Netzsch and available in this country through C. A. Brinkmann and Co., Inc., Great Neck, Long Island, New York.
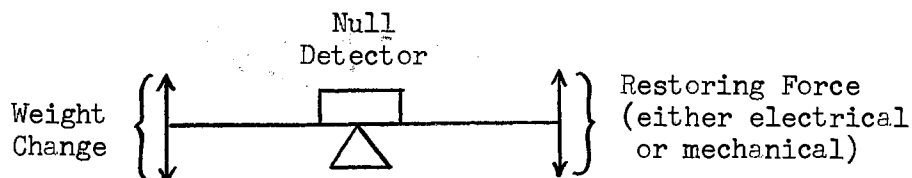
Figure 1. Null-Type Balance

The deviation of the balance beam from the null-point is due to the change in weight; therefore, the restoring force will be proportional to the change in weight. This restoring force is recorded either directly or through an electro-mechanical transducer, thus giving a record of the weight change.

Deflection-type thermobalances may be illustrated schematically by Figure 2. This type of balance involves the conversion of balance beam deflections about the fulcrum into photographically recorded traces, the recording of electrical signals generated by appropriate displacement-measuring transducers, or the production of electromechanically-drawn curves.

Beam   Cantilever

Spring
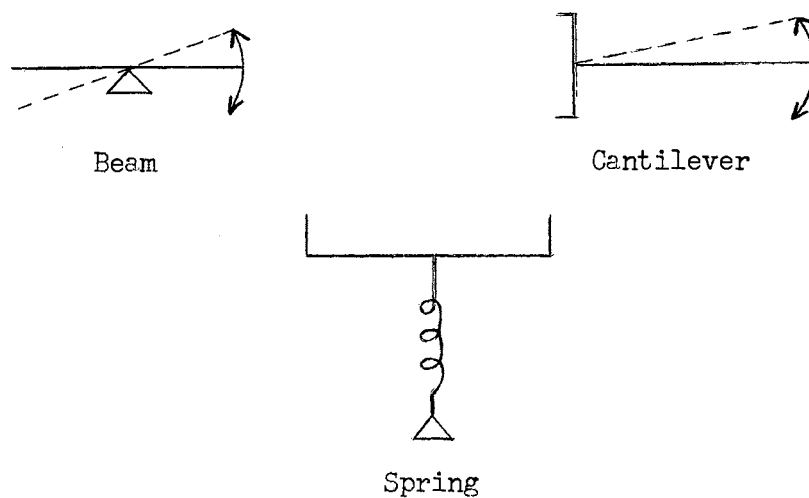
Figure 2. Deflection-Type Balances

An example of the beam-type deflection thermobalance is the Chevenard thermobalance described by Duval (19). In this balance a mirror, mounted on the end of the balance beam, reflects a pin-point source of light onto photosensitive paper mounted on a drum which is rotated at a constant rate. An example of the spring-type deflection thermobalance is the one constructed by Gordon and Campbell (25). In this balance a linear variable

differential transformer armature is suspended below precision metal springs and inside a stationary coil. The sample pan is mounted below the armature. As the sample changes weight the armature moves in the coil causing a change in the current which is demodulated and recorded. The third type of deflection thermobalance is the cantilever-type. This is the type of thermobalance used in this investigation and was pattern-ed after one constructed by Wendlandt (44). This thermobalance will be described in detail in another section of this paper.

Amperometric Titrations

Amperometric titrations are electrometric titrations based on the measurement of the diffusion current of the substance being titrated, of the reagent, or of both, during the titrations. The diffusion cur-rents plotted are the same as would be obtained if complete polarograms had been made of the solution after each addition of titrant. It is known from polarography that the diffusion current is proportional to the concentration of a reducible or oxidizable substance. Therefore, in amperometric titrations, the voltage applied across the indicator electrode and the reference electrode of a polarographic cell is kept at a suitable constant value and the current passing through the cell is measured and plotted against the volume of reagent added.

The voltage applied to the cell is selected from a voltage which would keep the currents on top of the polarographic wave of the diffus-ing substance. If a complete polarogram is made after each addition of reagent, a series of polarographic waves like the ones in Figure 3 are obtained; consequently, if the voltage is kept at a value equal to "a", the current would change, as shown, during the titration.
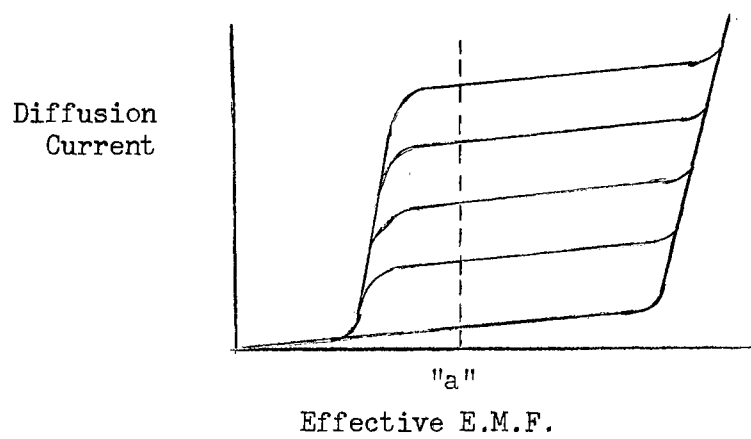
Figure 3. Illustration of Amperometric Titration

CHAPTER II

HISTORICAL

Complexes of Copper Salts and
Amines in Aqueous Solutions

Since Alfred Werner, in 1893, proposed the theory of auxiliary or secondary valence, many tools have been applied to the study of these "Werner complexes" and many new theories have been developed. The methods most often used to investigate these complexes were spectrophotometric, conductometric or potentiometric in nature. It was not until recently that the technique of thermogravimetric analysis was applied to the study of these complexes (45) though decomposition temperatures of cupric chloride ammines were studied in 1919 (21) and again in 1925 (6).

Most of the investigation of complexes of metal salts with amines and with ammonia have been in aqueous media. The properties of particular metal-ammonia complexes, such as $Ag(NH_3)_2^{++}$, $Zn(NH_3)_4^{++}$, and $Cu(NH_3)_4^{++}$ have been well established.

Cupric salt-ammonia complexes having coordination numbers from one to six have been reported in the literature. Ephraim and Bolle (20) conducted dissociation pressure studies on copper salts with ammonia and found evidence of coordination numbers of four, five and six with ammonia molecules. Ephraim (21) reported a complex, stable to 107° C., in which

7

the cupric ion appeared to coordinate with three and one-third moles

of ammonia. Rencker (40), studying the thermal decomposition of cupric

sulfate-ammonia complexes, reported diammine and monoammine compounds

or intermediates. Bhattacharya and Dey (5), while investigating mix-

tures of cupric sulfate and ammonium hydroxide solutions by conducto-

metric methods, found points of maximum conductivity corresponding to

two, four, five, and six moles of ammonia per mole of cupric sulfate.

Urazov, et al. (42) in studying the thermal decomposition of $CuCl_2 \cdot$

$5NH_3 \cdot H_2O$, by using a pyrometer and examining the product after each

step by chemical analysis, found it to decompose in the following steps:

$$CuCl_2 \cdot 5NH_3 \cdot H_2O \xrightarrow{\ 65° \ } CuCl_2 \cdot 4NH_3 \cdot H_2O \xrightarrow{\ 100° \ }$$

$$CuCl_2 \cdot 2NH_3 \cdot H_2O \xrightarrow{\ 143° \ } CuCl_2 \cdot 2NH_3 \xrightarrow{\ 290° \ }$$

$$CuCl + NH_4Cl$$
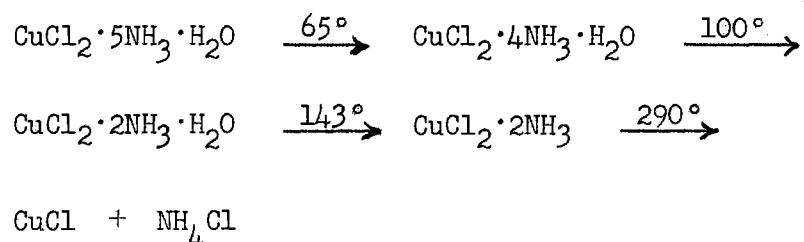
It is seen that cupric ion with ammonia has been reported in the litera-

ture to have coordination numbers from one to six.

Cupric ion complexes with organic amine molecules have also been

reported in the literature. Knobloch (30), employing a potentiometric

method, reported complexes of cupric ion with methylamine, dimethylamine,

and pyridine. These complexes had the general formula $Cu(Amine)_4^{++}$ in

which the cupric ion had a coordination number of four. A complex be-

tween cupric ion and two pyridine molecules was reported by Bruehlman

and Verhoek (10). Ethylenediamine and isobutylenediamine form with cu-

pric chloride, dimeric complexes. Propylenediamine forms a complex

with cupric chloride with a ratio of two moles of diamine for each mole

of cupric chloride (35). It is readily apparent from the above mentioned

diamine complexes that cupric salts exhibit a coordination valency of 4

for cupric ion in the most stable chelate complexes. However, benzidine unites with cupric chloride in 1:1 molar ratio (33).

Using the method of continuous variation, Haendler (27) found that the cupric ion forms complexes with one and two moles of diethylenetriamine. The diethylenetriamine molecule occupies 3 coordination positions. Another tridentate ligand is 2-(2-aminoethylamino) ethanol. It is reported to form complexes with the cupric ion also in molar ratios of 1:1 and 1:2 (28).

In a polarographic study of the copper (II) complexes of monoethanolamine, diethanolamine, and triethanolamine, Sturrock (41) reported the following complexes:

(1) Monoethanolamine (MEA):

$Cu(MEA)_2(OH^-)_2$ and $Cu(MEA)_2(OH^-)$

(2) Diethanolamine (DEA):

$Cu(DEA)(OH^-)_3$; $Cu(DEA)(OH^-)_2$; and $Cu(DEA)(OH^-)$

(3) Triethanolamine (TEA):

$Cu(TEA)(OH^-)_3$; $Cu(TEA)_2(OH^-)_2$; and $Cu(TEA)(OH^-)$
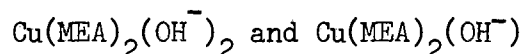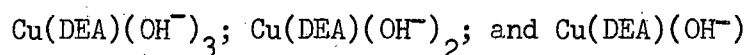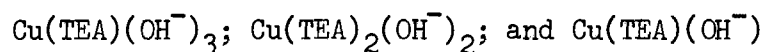
In aqueous solutions cupric salts most often exhibit coordination numbers of 4 and 6.

Complexes of Copper Salts and
Amines in Mixed Solvents

An ion solvation study by Pominov (38) in alcohol-water solutions showed that both water and alcohol molecules may be in the solvation envelope. An ethanol solution of cupric chloride with some water added was investigated by absorption spectra. Results indicated two molecules of water were present in the mixed alcohol-water envelope of cupric ions

in 0.0784 mole of cupric chloride per liter of ethanol. Pominov also showed that the degree of hydration of cupric chloride depends on the concentration of cupric chloride in aqueous-ethanol solutions.

Vainshtein and Antipova-Karataeva (43), investigating the solvation of ions in water, methanol, and ethanol, reported cupric chloride dihydrate to be solvated in the form of a tetragonal bypyramid.

Aumeras and Tamisier (1) studied complexes between copper salts and the nitrogen bases, pyridine, nicotine, quinoline, allylamine, and ammonia. They found the stability of the complex to decrease with the degree of substitution and with increases in molecular weight of the amine.

Korshunov and Malyugina (32), in a polarographic investigation of complexes of copper with pyridine, in a water-pyridine solution, found evidence for the formation of $Cu(C_5H_5N)_6^{++}$ complex.

Complexes of Copper Salts and Amines
in Non-aqueous Solvents

In comparison to the amount of work done in aqueous solutions, the work done in anhydrous solvents is meager. However, enough work has been published to indicate certain coordination numbers that are exhibited by cupric chloride in a limited number of anhydrous solvents.

In anhydrous alcoholic solutions cupric chloride has been reported as exhibiting coordination numbers ranging from 1:1 to 1:5 copper-to-amine ratios. German and Jamsett (22) studied the reaction between metal salts and ammonia in methanol and ethanol by conductometric titrations. Their results showed the existence of a complex with 1:2 and 1:3 copper-to-amine ratios in methanol and a 1:2 copper-to-amine

ratio in a complex which precipitated from ethanol solution. Pinkston
and Briscoe (37), also using conductometric titrations, studied the
complexes formed between cupric chloride and monoethanolamine, diethy-
lamine, and piperidine in ethanol solution. The copper-to-amine ratios
were found to be as follows:

    (1) Monoethanolamine gave 1:1 and 1:3;

    (2) Diethylamine gave 1:1;

    (3) Piperidine gave 1:1.5.

Metal chloride complexes with ethylethanolamine and ethyldiethanolamine
in methanol were studies by Brintzinger and Hesse (7). Each of the
amines combined with cupric chloride mole for mole in forming complexes.
Using alcoholic media, Parasad and Sharma (36) reacted cupric chloride
with a number of primary, secondary and tertiary amines. Cupric chlo-
ride apparently coordinated with 2 moles each of aniline, p-toluidine,
and o-toluidine. The secondary amines likewise coordinated 2 moles of
amine to each mole of cupric chloride, but the tertiary amine appeared
to coordinate mole for mole with cupric chloride. The formation of the
compound $CuCl_2 \cdot 5NH_3 \cdot 2C_2H_5OH$ by the NH_3 treatment of a saturated solu-
tion of cupric chloride and lithium chloride in ethanol, was reported
by Brusset and Burgard (11).

Anhydrous methyl acetate and ethyl acetate were used as solvents
by German and Jamsett (23) in studying the formation of ammines with
cupric chloride and other salts. In methyl acetate the complex $CuCl_2 \cdot 3NH_3$
precipitated from solution. The same compound was formed in ethyl
acetate.

High molecular weight amines have also been used in studying copper-

amine complex formation. Broome, Ralston, and Thornton (8), using the anhydrous solvents ether and chloroform prepared complexes from cupric chloride and three different amines by six different methods. The amines used were dodecylamine, octadecylamine, and dioctylamine. They could prepare no complex with a higher metal-to-amine ratio than 1:2. Later, in a spectrophotometric study (9) of dodecylamine-cupric acetate system, in absolute methanol and chloroform, they could find no evidence of metal-to-amine ratios other than 1:2. Burkin (12) also studied the formation of cupric chloride-amine complexes in nonaqueous solvents, using higher molecular weight amines, by elemental analysis of the precipitated complex. He found the amines combined with cupric chloride in a ratio of 2 moles of amine to 1 mole of cupric chloride. The amines used were as follows: (1) n-octylamine; (2) dodecylamine; (3) tetradecylamine; (4) hexadecylamine and (5) octadecylamine. When benzene was used as a solvent, ethylamine formed a complex with a 1:4 metal-to-amine ratio.

Caglioti, et al. (13) prepared several solid complexes between cupric chloride and diamines. The diamines used were $H_2N(CH_2)_nNH_2$, with n = 2, 3, 4, 5, 6, 8, and 10, and $H_2NCH_2C_6H_4NH_2$. Alcoholic solutions of cupric chloride and the diamines were mixed and precipitation usually occurred immediately. Three types of complexes were obtained:

(1) $CuCl_2 \cdot \frac{1}{2}$Amine;

(2) $CuCl_2 \cdot$ Amine;

(3) $CuCl_2 \cdot 2$Amine.

If two coordination positions were occupied by each diamine, the cupric ion thus exhibited coordination numbers of 1, 2, and 4.

Thermogravimetric Analysis

It is impossible to determine the origin of thermogravimetric analysis, for the idea of following the change in weight of a sample as a function of the temperature and time is very old. However, Honda (29) in 1915 coined the word "thermobalance" to describe the apparatus he constructed to study the pyrolysis of manganese and calcium sulfates and of calcium carbonate and the conversion of chromium(VI) oxide to chromium(III) oxide. The Honda thermobalance consisted of a balance with a quartz beam one arm of which had a porcelain dish suspended from it by way of a porcelain rod. The dish carrying the sample was suspended in an electrically heated furnace. A fine steel spring was attached to the other arm of the balance beam and anchored to the bottom of a Dewar flask containing an oil, the oil acting as a damper. Scale readings were made manually through an eye-piece in the side of the Dewar flask.

Many samples were studied by other Japanese investigators subsequent to Honda's invention of the thermobalance, but the next development in the evolution of the thermobalance to its present state was made by Guichard (26). The Guichard thermobalance consisted of a beam with the sample holder attached to one arm extending into the furnace and with a rod attached to the other arm extending into an oil bath. The balance was maintained at its zero point by adding oil to the bath from a buret. The addition of a certain amount of oil corresponded to a certain weight loss in the sample. Guichard's chief contribution was that of making the elevation of the furnace temperature a linear function of time. The original furnace was heated by a gas burner fed via

a constant level device consisting of a valve with an attached float. This gas burner furnace was later replaced by an electric furnace.

Rigollet (19), in 1934, inverted the electric furnace, thus making the sample opening at the bottom. This minimized disturbing convection currents and allowed working in atmospheres of gases whose specific gravities are less than unity at temperatures above 100°C.

The first apparatus for making a continuous record of the sample weight change was made by Dubois (18). His thermobalance consisted of a beam one arm of which held the sample crucible in the furnace. The furnace was inverted like the one used by Rigollet. The other arm of the balance was counterpoised. The continuous record was made by means of a mirror mounted at a 45° angle and fixed to the beam at its fulcrum. A pin-point source of light was focused on the mirror which in turn reflected the light through a series of mirrors to be finally focused on a photographic paper or plate.

In 1936 some experiments were conducted at the Acieries d'Imphy which proved that the knife-edge and agate plate of a normal balance could no longer be recommended when there is continuous contact between them instead of the intermittent contact involved in the ordinary methods of weighing. This problem was overcome by the development of the Chevenard thermobalance.

P. Chevenard and R. Wache (15) in 1944 developed a thermobalance of the deflection type consisting of a wire-suspended balance beam with a mirror attached to one end of the beam. A pin-point source of light was focused on this mirror which, in turn, was reflected onto a photo-sensitive paper mounted on a drum being turned at a constant rate. As the weight of the sample changed, the beam fluctuated, thus moving the

spot of light on the photo-sensitive paper and giving a record of weight change versus time.

An electric furnace controlled by a rheostat was used with the Chevenard thermobalance. The rheostat was motor-driven, thus enabling the investigator to program the rate of heating. By varying the motor speed, the heating rate could be varied from 7°C. per minute to 2.7°C. per minute. The furnace was also equipped with a thermostat. By stopping the drive motor on the rheostat, the furnace could be maintained at a fixed temperature for a period of hours with only a few tenths of a degree fluctuation. The furnace could also be operated on a temperature cycle; -- that is, the furnace would heat at a predetermined rate, reach a maximum temperature, hold it for a predetermined period of time, and cool at a predetermined rate.

The light source-mirror-photosensitive paper recording system was later replaced by a pen recording system. The pen was linked mechanically to the balance beam. In 1956 Gordon and Campbell (24) converted the photographically recording Chevenard thermobalance by electronic means to graphic recording. This was done by suspending the core of a linearly variable differential transformer from the mirror-end of the balance beam by a thread so it hangs freely within the transformer coil. The electrical signal from the transformer was rectified and fed into a potentiometric strip-chart recorder.

While Chevenard developed his balance for the study of dry corrosion of metals, Duval (19) used it to study the pyrolysis curves of 967 precipitates proposed for inorganic gravimetric analysis. Although until around 1950 relatively little work had been done in thermogravimetric analysis, the fact that in 1950 the Chevenard thermobalance

became commercially available gave great impetus to the heretofore inadequately used technique of thermogravimetric analysis.

Between 1950 (when the Chevenard balance was made commercially available) and 1961, a large number of thermobalances were described in the literature. Most of these balances were converted analytical balances which used as weight change sensing devices a magnet and solenoid, a photocell and light beam arrangement, a linear-voltage differential transformer, or the mirror and light beam with photographic recorder.

Then in 1961, Wendlandt (44), seeking a thermobalance which could be used in vacuum or in a controlled atmosphere yet have a large load capacity, constructed a thermobalance using a strain gauge as the weight sensing device. This was approached by Williams (4) who in 1957 constructed a thermobalance using a length of strain gauge wire as the weight sensing device. However, Williams' instrument could not be operated under controlled atmosphere conditions.

The thermobalance used in this investigation, which was patterned after that constructed by Wendlandt (44), will be described in detail in another section of this paper.

Thermogravimetric Analysis of Complexes

Though as was mentioned earlier in this historical review the thermal decompositions of some metal-amine complexes have been studied, the only extensive thermogravimetric analysis of a copper-amine complex was conducted by Wendlandt (45). Wendlandt studied the thermal decomposition of mono-, bis-, and tris- (ethylenediamine)-, the bis-(1,2-propanediamine)-, the bis-(1,3-propanediamine)- complexes of copper(II) sulfate

and found that these complexes dissociate as follows:

(1) Mono-(ethylenediamine)-complex (en-complex):

$$Cu(en)(H_2O)_2SO_4 \xrightarrow{130°} Cu(en)SO_4 + 2H_2O$$

$$Cu(en)SO_4 \xrightarrow{300°} CuO + \text{Decomposition Products}$$

(2) Bis-(ethylenediamine)-complex:

$$Cu(en)_2SO_4 \xrightarrow{280°} CuSO_4 + en + \text{Decomposition Products}$$

$$CuSO_4 \xrightarrow{390°} CuO + SO_3$$

(3) Tris-(ethylenediamine)-complex:

$$Cu(en)_3SO_4 \xrightarrow{275°} Cu(en)_2SO_4 + en$$

$$Cu(en)_2SO_4 \xrightarrow{290°} Cu(en)SO_4 + en$$

$$Cu(en)SO_4 \xrightarrow{300°} CuO + en + \text{Decomposition Products}$$
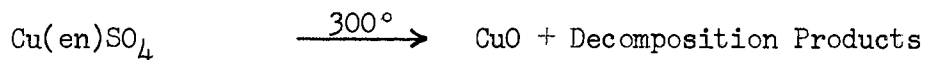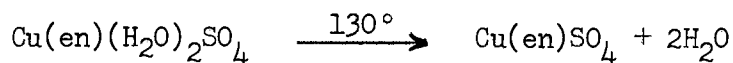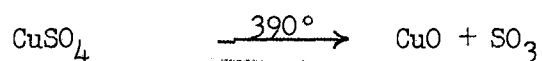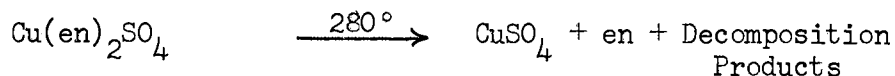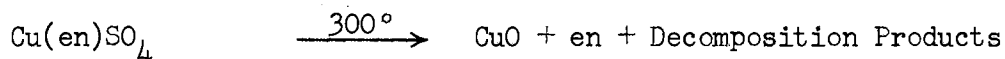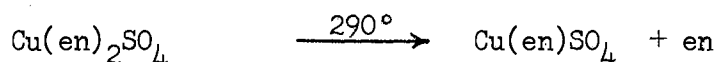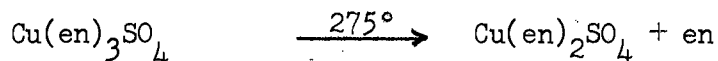
(4) Bis-(1,2-propanediamine)-complex (pn-complex):

$$Cu(pn)_2SO_4 \xrightarrow{250°} CuSO_4 + pn + \text{Decomposition Products}$$

$$CuSO_4 \xrightarrow{390°} CuO + SO_3$$
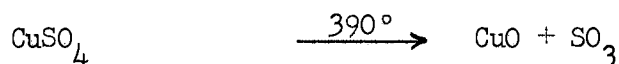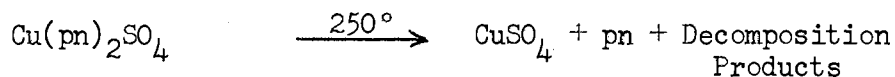
(5) Bis-(1,3-propanediamine)-complex (tm-complex):

$$Cu(tm)_2SO_4 \xrightarrow{200°} CuSO_4 + tm + \text{Decomposition Products}$$

$$CuSO_4 \xrightarrow{390°} CuO + SO_3$$
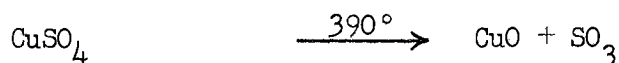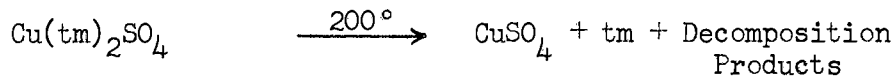
In comparing the bis-(amine)- complexes, the order of decreasing thermal stability was:

$$Cu(en)_2SO_4 > Cu(pn)_2SO_4 > Cu(tm)_2SO_4.$$
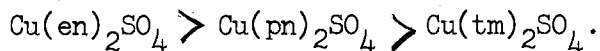
CHAPTER III

APPARATUS

The thermobalance used in this investigation, Figure 4, was built around strain gauge transducer Model No. GIOB-0.15-350 purchased from Statham Instruments, Inc., 12401 W. Olympic Blvd., Los Angeles 64, California. This is the same transducer which Wendlandt (44) used in his thermobalance. The 9-volt excitation voltage for the strain gauge was provided by two 6-volt lead storage batteries connected in series across a voltage-divider.

In Figure 4, the strain gauge, A, was provided with a 20 cm. stainless steel extension arm, B, to increase its sensitivity. A brass rod counterpoise, C, fitted with brass nuts, was used to counterbalance the extension arm, suspension wires, and sample pan.

The sample pan and suspension wires were all platinum metal. The sample pan, D, was constructed from 0.0035 inch thick platinum foil and was 15 mm in diameter. The platinum suspension consisted of three sections. The first section, E, of platinum wire was 12.5 cm. in length and 0.4 mm in diameter. The second section, F, was 17.5 cm. in length and 0.5 mm in diameter. The third section, G, was 25 cm. long and 0.8 mm in diameter.

The suspension wires were enclosed in a Pyrex tube provided with a water-jacket condenser, H, and a jacket for admitting the nitrogen gas, I. The furnace chamber, J, was constructed of Vycor tubing 25 mm
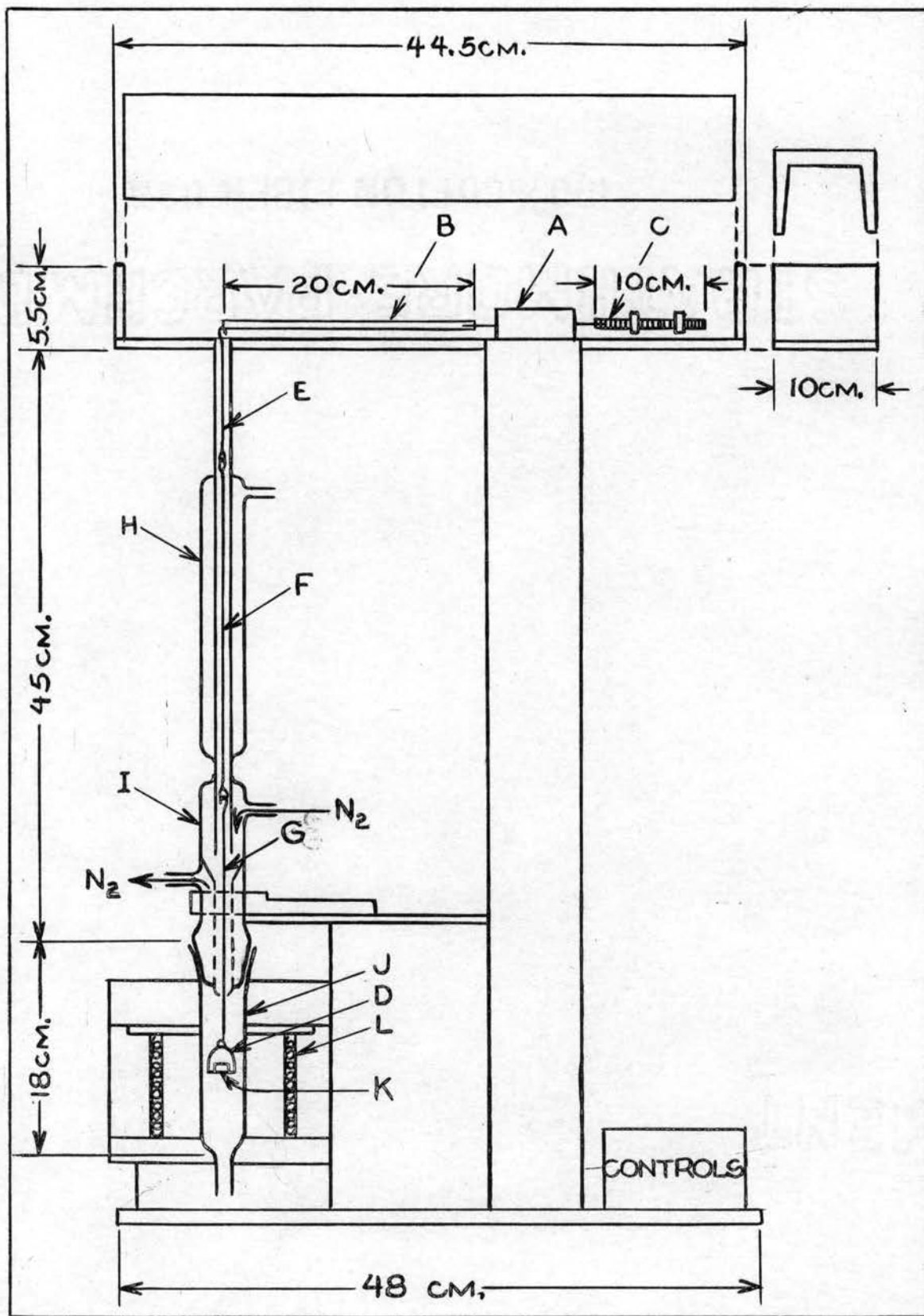
Figure 4. The Thermobalance

in diameter. It joined to the Pyrex assembly by a standard-taper 29/42 Vycor joint.

The quartz sample dish, K, was 12 mm in diameter and 2 mm in height.

The furnace was constructed using a 2-lb. coffee can and chromel-A heating elements, L, with 30 ohms resistance. The furnace was insulated top and bottom with 3/4-inch thick asbestos board insulation. Johns-Mansville Celite analytical filter aid was used as insulation around the sides of the furnace.

The power supply for the furnace was a motor-driven 1 KVA Variac. Three gear ratios were available so the heating rate could be 16°C. per minute, 8.9°C. per minute, or 7.5°C. per minute. The latter rate was the one used in this investigation.

The circuit for the thermobalance was very similar to the one used by Wendlandt (44).

The signal from the strain gauge was recorded by a Sargent Model SR recorder with a 1.0 mv. range plug and using a chart speed of 0.1 inch per minute. Difficulty was encountered with the pen supplied with the recorder so it was replaced by a K&E Leroy pen. Very good traces were then obtained.

The automatic titration apparatus used in this investigation consisted essentially of a motor-driven 10 cc. hypodermic syringe and a Beckman Zeromatic pH Meter used as a potentiometer. A small electric motor operated a worm-gear plunger which moved the syringe plunger. The syringe had a No. 19 hypodermic needle which was extended into the titration vessel through a serum rubber stopper.

The titration vessel was a 200 ml. tall-form electrolytic beaker with a small side arm sealed into it 2 cm. from the bottom of the beaker.

The side arm had an internal diameter of 6 mm and was 1 cm. in length, and was closed by the serum rubber stopper.

A high-pH glass electrode was used in the titration of tributylamine. A regular glass electrode and a silver wire were used as the electrodes in the chloride determination.

The syringe was calibrated "to deliver" with a standard acid and a standard base, the assumption being made (and later verified) that the bore of the syringe was uniform. Various delivery rates were available through varying the gear ratio between the motor and the worm gear. The fastest delivery rate was 10 cc. per minute and the slowest rate was 10 cc. per 50 minutes. By trial-and-error it was found that a delivery rate of 10 cc. per 5 minutes was optimum for this investigation.

The signal from the Beckman Zeromatic first was recorded by a Sargent Model SR recorder used at a sensitivity of 125 mv. per 10 inches to record the iR-drop across a 620-ohm resistor in the pH meter circuit. The change in the signal at the end point did not give a large enough deflection on the recorder chart; therefore the original 620-ohm resistor was replaced by a 1,500-ohm resistor. This alteration gave a signal of the proper magnitude.

A Sargent Model XV polarograph with a Sargent Model A IR-Compensator was used for the amperometric titrations. The polarographic cell used was the one described under Sargent Catalog No. S-29322, with two saturated calomel electrodes. The titrant was added from a certified 10.00 ml. buret.

All pipets used in this investigation were calibrated in this laboratory using the procedure given by Ayres (2), pp. 296-8.

CHAPTER IV

REAGENTS

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

Bacto-agar – "Difco" standard grade prepared by the Difco Laboratories was used without further purification.

Carbon Tetrachloride – J. T. Baker N. F. Grade was used without further purification.

Cupric Chloride Dihydrate – Fisher Scientific reagent grade was used without further purification.

Cupric Sulfate Pentahydrate – Fisher Scientific reagent grade was used without further purification.

Diethyl Ether – U. S. Industrial Chemical U. S. P. grade was used without further purification.

Hydrazine Sulfate – Eastman Kodak 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.

Lithium Chloride – Fisher Scientific reagent grade was used without further purification.

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

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

Nitrogen – Linde laboratory grade nitrogen was used without further purification for the thermobalance. For the amperometric titrations, Linde laboratory grade nitrogen was used after being passed through two towers of chromous sulfate-sulfuric acid-amalgamated zinc, a column of glass wool, a column of silica gel drying agent, and two presaturator towers filled with 2-propanol.

Potassium Carbonate - J. T. Baker anhydrous purified 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.

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.

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

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

Sodium Nitrate - Fisher Scientific reagent grade was used without further purification.

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

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

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

CHAPTER V

EXPERIMENTATION

The invention of the iR-compensator by Dr. Paul Arthur made possi-
ble the extension of the electroanalytical technique of amperometric
titrations to nonaqueous solvents. It was while an attempt was being
made to use organic amines as titrants for cupric ion in alcholic solu-
tion that an unexpected phenomenon was observed -- namely, that although
the titration proceeded as expected up to a certain point, when this
point was reached, the diffusion current continued gradually to decrease
without any further addition of titrant. This gradual decrease of dif-
fusion current plus the fact that a turbidity slowly developed, suggested
the formation of an insoluble complex. Preliminary results of the am-
perometric titrations indicated that the copper (II) was exhibiting a
coordination number with the amine of 1.5. This is radically different
from the coordination numbers reported for this ion in aqueous media.

Since in these titrations, amine, water (from the $CuCl_2 \cdot 2H_2O$), and
2-propanol all were present, it was obvious that many complexes might
be formed. It was decided, therefore, to investigate this complex by
both chemical analysis and thermogravimetric analysis. The chemical
analysis would reveal the mole ratio of copper to amine and to chloride,
while it was hoped that thermogravimetric analysis of the freshly-
precipitated complex would indicate (1) whether or not the 2-propanol
was acting as a ligand, and (2) whether any of the alcohol or amine

24

was loosely bound, with the rest more firmly bound.

Since the preliminary investigations had been done with n-butyla-
mine as the titrant, it was decided additional information could be
obtained by using tributylamine as titrant for this study.

Chemical Analysis

Preparation of Copper-Tributylamine Complex

The copper-tributylamine complex, which was analyzed for copper,
tributylamine, and chloride by chemical methods, was prepared from so-
lutions of cupric chloride dihydrate and tributylamine in 2-propanol
which was 0.1M in lithium chloride. The complex was prepared by two
methods which differed only in whether the cupric chloride solution
was added to the tributylamine solution or the tributylamine solution
was added to the cupric chloride. The complex had the same physical
appearance regardless of the order of mixing the solutions. However,
the complex precipitated almost immediately when the cupric chloride
solution was added to the tributylamine solution. This compares to a
thirty minute to one hour waiting period which was necessary for the
precipitate to form when the tributylamine solution was added to the
cupric chloride solution.

As previously mentioned, the precipitation of this copper-amine
complex was first noted during an amperometric titration. In order to
duplicate the conditions of an amperometric titration in the prepara-
tion of the complex for chemical analysis, the cupric chloride and
tributylamine solutions were made up in 0.1M lithium chloride solution
in 2-propanol since lithium chloride or another electrolyte is neces-
sary in amperometric titrations.

The steps in preparing the complex for chemical analysis were as follows:

(1) 300 ml. of 0.01M tributylamine in 2-propanol 0.1M with lithium chloride were placed in a 500 ml. Erlenmeyer flask on a magnetic stirrer. A 2-propanol solution of 200 ml. of 0.01M cupric chloride dihydrate (also in 2-propanol 0.1M with lithium chloride) was added, in 50.0 ml. portions, to the tributylamine solution with stirring.

An alternate first step was also used in which a solution of 200 ml. of 0.01M cupric chloride dihydrate (in 0.1M lithium chloride in 2-propanol) was placed in a 500 ml. Erlenmeyer flask on a magnetic stirrer. A solution of 300 ml. of 0.01M tributylamine (in 0.1M lithium chloride in 2-propanol) was added, in 50 ml. portions, to the cupric chloride dihydrate.

(2) The solution was divided between two 250 ml. centrifuge bottles and allowed to stand until the complex precipitate was well formed.

(3) The precipitate was then centrifuged and the liquid decanted. The precipitate was washed five times with 50 ml. portions of 2-propanol by centrifuging and decanting.

(4) The precipitated copper-amine complex from each bottle was dissolved in distilled water with the aid of three drops of concentrated sulfuric acid, each transferred to a 100 ml. volumetric flask, and diluted to volume. Aliquots to be analyzed were taken from the volumetric flasks.

In the above preparation procedure the washing of the precipitated complex with 2-propanol was done to rid the precipitate of excess chloride from the lithium chloride which might have adhered to its surface. The decision to wash the complex five times was made after conducting

an experiment in which the washings were tested for chloride with silver nitrate. This experiment was conducted by taking two 10 ml. samples from the wash solution. Five milliliters of 1.0M silver nitrate were added to the first sample and the second sample was saved to be compared with a sample from the second wash solution. After the two 10 ml. samples were collected from the second wash solution, 5 ml. of silver nitrate each were added to the second sample from washing I and the first sample from washing II. This process was continued until there was no turbidity produced by the silver nitrate as shown by comparing the second sample of one washing with the first sample of the next washing. It was found that five washings with 50 ml. portions of 2-propanol would rid the sample of all excess chloride.

The copper-tributylamine complex which was used for thermogravimetric analysis was prepared by a somewhat different method, the cupric chloride dihydrate and tributylamine solutions used in the preparation being in pure 2-propanol with no lithium chloride supporting electrolyte present.

The steps in the preparation of the complex were as follows:

(1) A 100 ml. solution of 0.01M cupric chloride dihydrate was placed in a 250 ml. Erlenmeyer flask on a magnetic stirrer. A solution of 150 ml. of 0.01M tributylamine was added, in 25 ml. portions, to the cupric chloride dihydrate solution.

(2) The solution was transferred to a 250 ml. centrifuge bottle and allowed to stand until the precipitate had formed.

(3) The complex was centrifuged and the supernatant liquid was decanted.

(4) The precipitated complex was washed once with 2-propanol,

centrifuged, and the wash solution decanted.

(5) The centrifuge bottle was inverted and allowed to drain for two to three minutes.

(6) The sample for the thermogravimetric analysis was taken directly from the centrifuge bottle while still wet and placed on the balance pan. The sample size was usually about 50 mg.

It may be noted that the complex prepared for thermogravimetric analysis was washed only one time as compared to washing the precipitated complex five times for chemical analysis. This was done because no lithium chloride (supporting electrolyte) was present in the solutions used to prepare the complex. One washing was considered to be sufficient to rid the complex of any appreciable amount of foreign ions or excess amine which might have adhered to it.

In this study it was necessary to analyze for three components, the amine, chloride, and copper. It was thought, at first, that conventional wet chemical methods would be adequate for the analyses. This was not the case.

Amine Analysis.

The Kjeldahl analysis for nitrogen was first attempted for the determination of tributylamine. A standard sample of tributylamine in 50% 2-propanol and 50% water was used in testing this analysis. The sample was very difficult to digest. One milliliter of standard sample was placed in a micro-Kjeldahl flask and one milliliter of concentrated sulfuric acid and a selenium granule were added. This solution was digested for approximately two hours. At the end of this period a large carbon residue still was present. Three drops of hydrogen peroxide (30%) added six different times with a short period of heating in

between each addition did not destroy the carbon residue. Additional concentrated sulfuric acid and potassium sulfate (0.1g.) then were added and the digestion was continued for a period of six hours. With this treatment the carbon residue was eliminated but the sample had a turbid appearance rather than being clear as it should have been.

Since a more rapid method was wanted for the tributylamine determination, a steam distillation from strongly alkaline solution was tried. Again a standard amine sample from a 50% water and 50% 2-propanol solution was used. The distillation was to be followed by a titration of the free amine with hydrochloric acid. The distillation did not give quantitative or reproducible results.

There seemed reason to feel that the poor results of the method involving digestion might be due to the abnormal length of time required for the digestion. A suspicion that the large carbon residue was due to the sulfuric acid attacking the 2-propanol was confirmed by running a blank consisting of one milliliter of 50% water and 50% 2-propanol solution. After about 15 minutes of digestion the large, black residue of carbon was present.

In order to eliminate the excessively large carbon residue, another one milliliter sample was run in which the sample was first acidified with 2 drops of concentrated sulfuric acid to convert the free amine to the salt and then evaporated to about one-third the original volume. To this sample were then added 2 ml. of concentrated sulfuric acid with a selenium granule as a catalyst. After a few hours digestion the carbon residue was still present. Hydrogen peroxide had no visible effect upon this residue.

Another 1 ml. sample of the standard tributylamine solution was

taken, acidified with 3 drops of concentrated sulfuric acid, and evaporated to one-third the original volume. Three ml. of concentrated sulfuric acid and two selenium granules were than added and the sample was digested for two hours. The carbon residue was present at the end of this period. The sample was then heated very vigorously for one-half hour. At the end of this period the solution was clear. However, this analysis was not rapid enough.

It was then decided to try a potentiometric titration to determine tributylamine. A manual titration of tributylamine with 0.100N hyrdochloric acid using a buret and pH meter showed the titration curve to be quite suitable. The automatic titration apparatus, described in a previous section, was then used to titrate the tributylamine. Various speeds of titration and concentration of solutions had to be tried before the correct combination was found.

This potentiometric titration gave the desired results for the free amine but it was realized that in the unknown samples the tributylamine would be in the form of salts. It was also found that tributylamine interfered with the chloride and copper analyses. It was decided, therefore, to separate the amine from the others by making the aqueous layer basic and extracting with an immiscible solvent.

For this extraction a solvent was needed which would separate from the basic aqueous phase rapidly so the extraction could be repeated three or four times in a short period. Also, in order to eliminate a time-consuming step of evaporating the solvent and then adding the 2-propanol to perform the titration, a solvent was needed which, diluted with an equal volume of 2-propanol, would serve as a suitable solvent for the potentiometric titration.

Diethyl ether, the first extracting solvent tried, proved to be unsatisfactory because not only was it partly miscible with the aqueous layer, but also the time required for the ether layer to separate made the extraction process too time consuming.

Carbon tetrachloride was the next extracting solvent used. The solvent separated nicely from the aqueous layer thus speeding the extraction process; however, an attempt to perform the potentiometric titration in a 50% 2-propanol and 50% carbon tetrachloride solution met with difficulty. With a glass electrode as an indicator electrode and a calomel electrode as the reference electrode, a stable response could not be obtained, probably through the nonaqueous layer interfering with the asbestos fiber of the calomel reference electrode.

A new reference electrode consisting basically of a silver-silver chloride electrode was substituted for the calomel. The electrode, Figure 5, consisted of a silver wire with a coat of silver chloride (A) surrounded by a 1.0M aqueous solution of lithium chloride (E). This solution was contained in a glass sleeve sealed at its lower end with a coarse glass frit (B). An agar plug (C), prepared by dissolving 3.5g. of agar in 100 ml. of aqueous 1M lithium chloride, was placed over the glass frit. This sleeve was in turn surrounded by a glass sleeve (F) with an asbestos fiber sealed in the end. A 2-propanol solution of 1.0M lithium chloride was placed in this outside sleeve.

A number of attempts were made to use this electrode in the potentiometric titration of tributylamine in 50% 2-propanol and 50% carbon tetrachloride. An erratic electrode potential was encountered in each case. It was thought that the nonaqueous layer was again interfering with the asbestos fiber. However, after the fiber was rinsed

with acetone and soaked in a 1.0M lithium chloride solution in 2-propanol, the response was still erratic. The use of carbon tetrachloride as an extracting solvent was then abandoned.
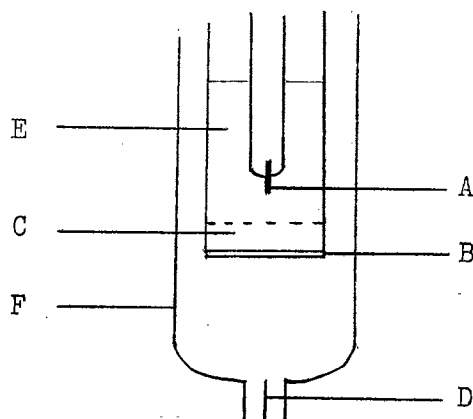

Figure 5. Illustrating the Silver-Silver
Chloride Electrode with Sleeves

Isooctane, which was next tried as an extracting solvent, worked excellently. It separated rapidly from the aqueous layer and potentiometric titrations of tributylamine performed in a 50% 2-propanol and 50% isooctane solution with glass and calomel electrodes gave good results. The calomel electrode was protected with a glass sleeve having an asbestos fiber sealed in its end. This sleeve was filled with 0.1M aqueous lithium chloride.

In order to extract the amine from the aqueous layer the solution must first be made basic. Potassium hydroxide was first used for this purpose but it gave a precipitate of cupric hydroxide thus introducing another phase during the extraction. To eliminate this precipitate, ammonium hydroxide was used. To make certain that ammonia would not be extracted with the tributylamine, a blank was run. This consisted of a 0.001M solution of ammonium hydroxide. A 75 ml. sample of the

ammonium hydroxide was extracted and analyzed by the same method as that used in analyzing for the amine. The results indicated that the ammonium hydroxide was not extracted appreciably by the isooctane.

The final analysis procedure adopted for tributylamine was as follows:

(1) An aliquot of the unknown sample was pipetted into a 125 ml. separatory funnel.

(2) The sample was made basic with 1:1 ammonium hydroxide, the ammonium hydroxide being added until the odor of ammonia was slightly detectable over the solution.

(3) The basic sample was extracted three times with 20 ml. portions of practical grade isooctane and the extracts collected. The aqueous layer was set aside to be analyzed for copper.

(4) The isooctane layer was transferred to an automatic titration vessel, fresh isooctane being used to rinse the collection vessel.

(5) The isooctane solution was evaporated to a volume of 50 ml. and then diluted with 50 ml. of 0.2M lithium chloride in 2-propanol. The evaporation of the sample was expedited by passing nitrogen gas over the sample while it was on a hot plate in the hood.

(6) The diluted sample was then titrated in the automatic titration apparatus with standard 0.1N HCl in 2-propanol solution. In the titration a glass electrode was used as the indicator electrode and a calomel electrode fitted with the 0.1M lithium chloride (aqueous) sleeve was used as the reference electrode.

A check was made on the accuracy of this procedure by analyzing a sample containing known concentrations of amine, copper, and chloride. It was found that the method gave an average error of 1.8% which is

sufficiently accurate for this investigation.

Copper Analysis

Copper was the next component for which to analyze. The method used was similar to the one given by Ayres (2).

In the first attempts at analyzing the sample, the tributylamine was left in the solution. It was found, however, that the amine interfered with the starch indicator used in the copper titration; consequently, the separation of the amine from the copper by extraction as described above was employed.

Earlier, an attempt was made to reduce the copper to the metal, filter it from solution, redissolve it and perform the analysis by the iodometric method. The copper reduction was carried out by using hydrazine sulfate in a basic solution and heating for a short period on a water bath. The excess hydrazine sulfate was destroyed with hydrogen peroxide and the excess hydrogen peroxide was destroyed by boiling the solution. The copper was then filtered, and the analysis performed. Fair results were obtained but the procedure was too time consuming so it was abandoned.

The final analysis procedure adopted for copper was as follows:

(1) The pH of the aqueous layer from the tributylamine extraction procedure was adjusted to 2.0 with 3N sulfuric acid, pHydrion paper, and a glass stirring rod being employed.

(2) Approximately one gram of potassium iodide was added to the sample and dissolved.

(3) The sample was titrated to a straw-yellow color with a standard 0.1N sodium thiosulfate solution using a 10.00 ml. microburet.

(4) Approximately one gram of potassium thiocyanate was added to

the solution and dissolved.

(5) One milliliter of starch indicator was then added to the sample.

(6) The titration with sodium thiosulfate was continued until the disappearance of the blue color.

A check was made on the accuracy of this analysis by analyzing a sample containing a known concentration of copper, tributylamine, and chloride. It was found that the method gave an error of 0.6% which is sufficiently accurate for this investigation.

Chloride Analysis

Chloride was the remaining component for which to analyze. The first analytical method attempted was the Mohr method as described by Ayres (3).

Difficulty was encountered in detecting the end-point since the titration was being done on a solution whose chloride concentration was approximately 0.004M. By using a yellow light in a darkened room, excellent results were obtained for a solution which contained only chloride. When a solution containing copper was analyzed, however, the end-point could not be reproduced because of the interference of the blue color of the cupric ion.

Due to the nature of the difficulties encountered in the Mohr method, it was decided not to attempt the Fajans or Volhard methods, but to determine the chloride by a potentiometric titration. The method used was similar to one given by Reilley and Sawyer (39). A silver wire was used as the indicator electrode and a glass electrode was used as the reference electrode. The automatic titration apparatus with pH meter and recorder were used in this determination.

A direct titration of the unknown chloride with silver nitrate was first attempted. Difficulty was encountered when the silver nitrate reacted with something in the syringe needle forming a precipitate. The syringe and needle were washed thoroughly with acid and water but the precipitate still formed. It was then decided to use a back-titration method.

The resistor, which was used in the pH meter for the tributylamine determination, also gave a nice inflection point for this titration curve. Also, the delivery rate of the titrant had to be adjusted by a trial-and-error method in order to get a good titration curve. This was done by changing the gears on the syringe drive.

The final analytical procedure for chloride determination was as follows:

(1) An aliquot (usually 25 ml.) of the unknown sample was pipetted into the automatic titration vessel.

(2) Ten drops of 6N nitric acid were added to the sample.

(3) Excess standardized 0.100N silver nitrate was added to the sample.

(4) The sample was diluted to a volume of 100 ml. with distilled water.

(5) The excess silver nitrate was then titrated potentiometrically with standard 0.100N potassium chloride.

A check was made on the accuracy of the procedure by analyzing samples of known chloride concentration. The samples contained copper and tributylamine in addition to the chloride. It was found that the method gave an average error of 0.6% with a deviation of 2 parts per thousand.

Results of Chemical Analysis of Complex

The copper-tributylamine complex, prepared by each of the methods described previously, was analyzed giving the results recorded in Table I.

The copper-tributylamine complex was again prepared by the previously described methods except, in this case, the 0.01M cupric chloride and 0.01M tributylamine solutions were not 0.1M in lithium chloride. Also, the precipitated complex was washed only one time with 2-propanol. The chemical analysis gave the results recorded in Table II.

TABLE I

RESULTS OF THE CHEMICAL ANALYSIS OF THE COPPER-
TRIBUTYLAMINE COMPLEX PRECIPITATED
FROM 0.1M LiCl SOLUTION

Method of Preparation	Ratio: Cu:Cl:Tributylamine
Added tributylamine to cupric chloride	1.00:0.49:0.0133
Added cupric chloride to tributylamine	1.00:0.46:0.0153

TABLE II

RESULTS OF THE CHEMICAL ANALYSIS OF THE COPPER-
TRIBUTYLAMINE COMPLEX PRECIPITATED
FROM PURE 2-PROPANOL SOLUTION

Method of Preparation	Ratio: Cu:Cl:Tributylamine
Added tributylamine to cupric chloride	1.00:0.66:0.0372
Added cupric chloride to tributylamine	1.00:0.64:0.0322

In the chemical analyses results, the ratios were based upon the copper concentration. This was done because the cupric ion is the nucleus of the complex.

It may be seen, from Table I, that regardless of the method of preparation the results were very nearly the same. The reason the tributylamine is present in a small amount was thought, at first, to be due to the amine being extracted with the wash solution during the washing process. The increase in amine with less washing (Table II) was not large, however, as will be shown later, other reasons for the low amine are more probable.

Amperometric Titrations

Experiments

Amperometric titrations were performed between cupric chloride dihydrate and tributylamine in 2-propanol solution. The apparatus used for these titrations is described in the apparatus section of this paper.

In the amperometric titrations a complete polarogram was run after each addition of titrant. The polarograms usually were found to have three waves. For each wave, a voltage was selected which would top the wave and the change in diffusion current was plotted as in a regular amperometric titration. The voltages selected were -0.15, -0.75, and -1.83

The results of these titrations were corrected for residual current and dilution. The dilution correction was made by applying the following formula:

$$\text{Corrected } i_d = \frac{V_I + V_T}{V_I} \, i_d$$

Where V_i is the initial volume of the sample; V_T is the volume of tit-

rant added; and i_d is the measured diffusion current.

It is known that the diffusion current of most metal ions increases

about 2% per degree rise in the temperature in aqueous solutions. It

was thought that this would not be the same for a 2-propanol solution

so an experiment was conducted to determine the relationship between

temperature and the diffusion current.

A 75.00 ml. sample of 1.056×10^{-3}M cupric chloride in 2-propanol

was placed in the Sargent polarographic cell used in the amperometric

titrations. The cell was immersed in an oil bath and the temperature

elevated. When the temperature of the bath and sample reached equili-

brium the diffusion current was measured. This temperature was 32.45°C.

The cell was then cooled with a water bath until equilibrium was again

attained and the diffusion current was measured. The lower temperature

was 23.90°C. The diffusion current at the higher temperature was 3.7 μ

A. and at the lower temperature it was 3.2 μA., showing a decrease of

0.5 μA. Thus, the diffusion current increases 1.9% for each degree

rise in temperature. Therefore, the temperature-diffusion current re-

lationship is the same for the cupric ion in 2-propanol as in aqueous

solutions.

As the above experiment indicated the diffusion current could be

read with 1% accuracy for a temperature range of $\pm$ 0.5 degree centigrade.

Consequently, the polarographic cell used in these titrations was not

immersed in a constant-temperature bath because little difficulty was

encountered in controlling the temperature within a $\pm$ 0.5 degree range.

The few points that fell outside this temperature range were corrected

for the variation in diffusion current.

Results of Amperometric Titrations

In all, six amperometric titrations were performed. Three of these were conducted by titrating 75.00 ml. of 0.998×10^{-3}M tributylamine with 0.0212M cupric chloride dihydrate. A total of 7.200 ml. of titrant was added in 0.400 ml. increments. Three titrations were then performed by using the tributylamine as titrant. In this latter case, 75.00 ml. of 1.056×10^{-3}M cupric chloride dihydrate were titrated with 7.200 ml. of 0.01996M tributylamine. Again the titrant was added in 0.400 ml. increments. The results of the above titrations are recorded graphically in Figures 6 - 11.

Figures 6 through 11 are regular amperometric titration curves where the diffusion current is plotted against the milliliters of titrant added. The dashed-vertical lines indicate the ratio of copper to tribytylamine at the indicated points in the titration. In Figures 6 through 8 the curve labeled "No. 1" is from a titration which was performed much more slowly than the other two titrations. Therefore, it could represent a different stage in the equilibrium between the tributylamine and cupric chloride.

In Figure 6, two of the curves showed inflection points where 4.700 ml. of titrant had been added. This point corresponded to a copper-to-amine ratio of 1.00:0.751. The curve for titration No. 1 showed no inflection.

In Figure 7, titration No. 1 gave an inflection point corresponding to a copper-to-tributylamine ratio of 1.00:1.177. Titrations No. 2 and No. 3 had inflection points corresponding to a copper-to-tributylamine ratio of 1.00:1.765.

In Figure 8, titration No. 1 was the only one which had an inflection.

It occurred at a point corresponding to a copper-to-tributylamine ratio of 1.00:1.765.

The data from the amperometric titration of tributylamine with cupric chloride did not indicate that the copper combined with the tributylamine on a whole mole basis. That is, the ratios of copper-to-tributylamine of 1:1, 1:2, etc. were not observed. It appeared that copper exhibited a coordination number which was not a whole number for the tributylamine.

In Figure 9, titration No. 1 gave inflection points corresponding to ratios of 1.00:0.605 and 1.00:1.210 for copper-to-amine. The data for titrations 2 and 3 were not as complete as that for No. 1 due to the interference of a maximum in the polarographic wave. However, these titrations showed the same inflection at a point corresponding to a copper-to-tributylamine ratio of 1.00:1.210 as did titration No. 1.

In Figure 10, there was only one inflection point and it was shown by all the titrations. It corresponded to a copper-to-tributylamine ratio of 1.00:1.260.

In Figure 11, titration No. 1 showed an inflection at a point corresponding to a ratio of copper-to-tributylamine of 1.00:1.210. Titration No. 2 gave an inflection at a point corresponding to a ratio of 1.00:1.109 and titration No. 3 gave an inflection at a ratio of 1.00:1.00.

Thus in the data from the amperometric titration of cupric chloride with tributylamine, copper seemed to exhibit a coordination number with the tributylamine which was a whole number only one time. The remainder of the data again indicated copper to exhibit a fractional coordination number.
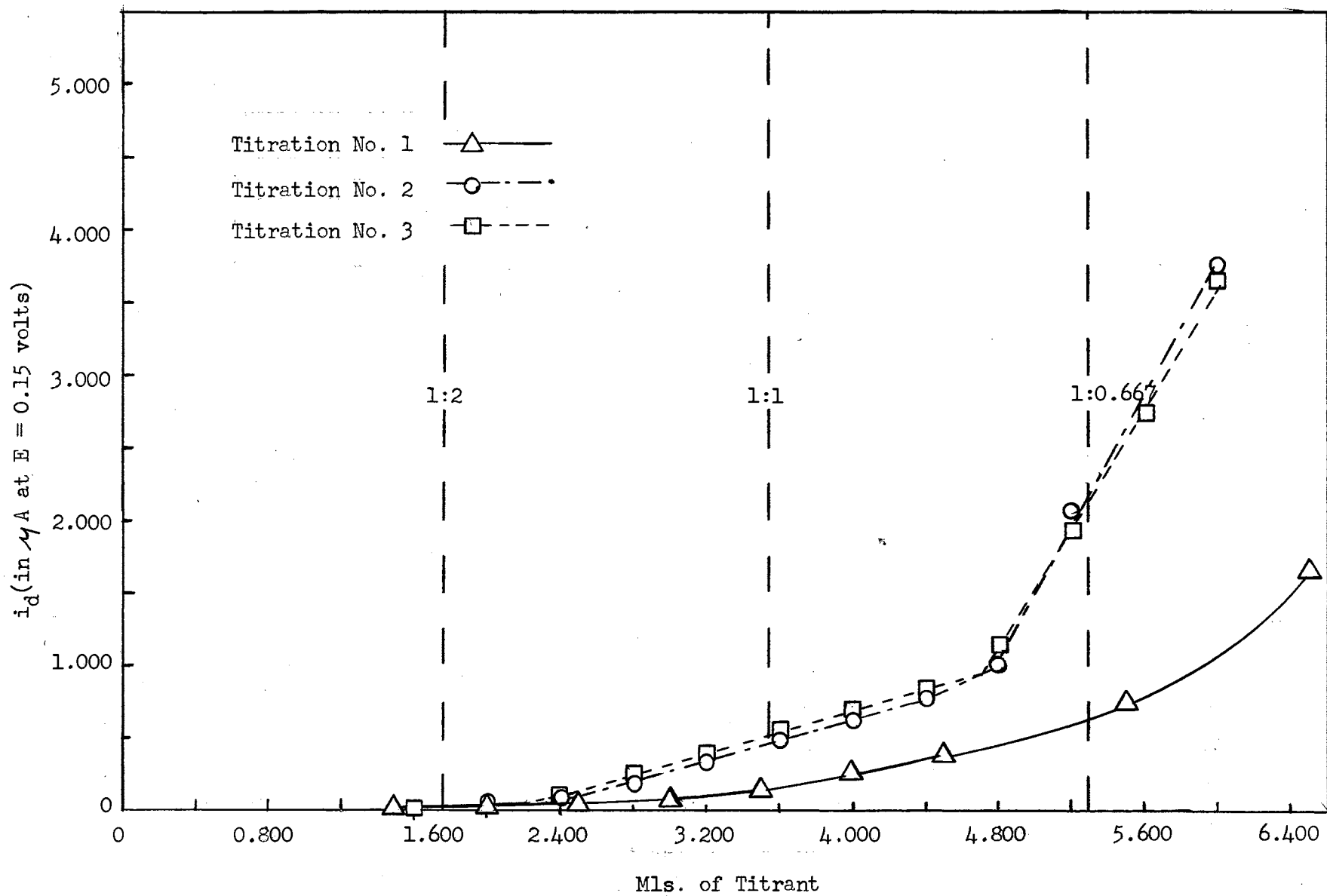
Figure 6. Amperometric Titration of 0.998×10^{-3}M Tributylamine with 0.0212M $CuCl_2 \cdot 2H_2O$

Figure 7. Amperometric Titration of 0.998 X 10^{-3}M Tributylamine with 0.0212M CuCl$_2 \cdot$2H$_2$O
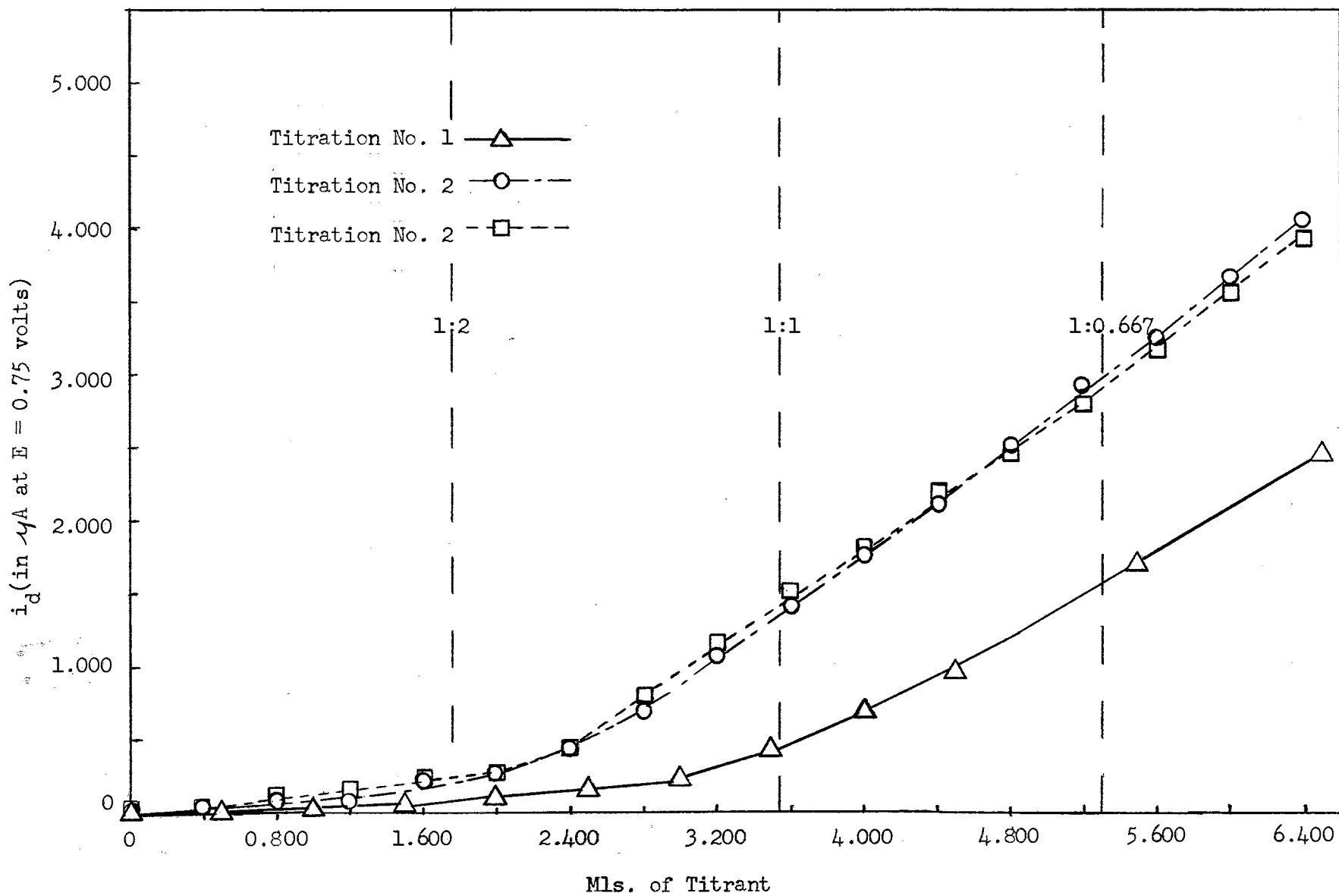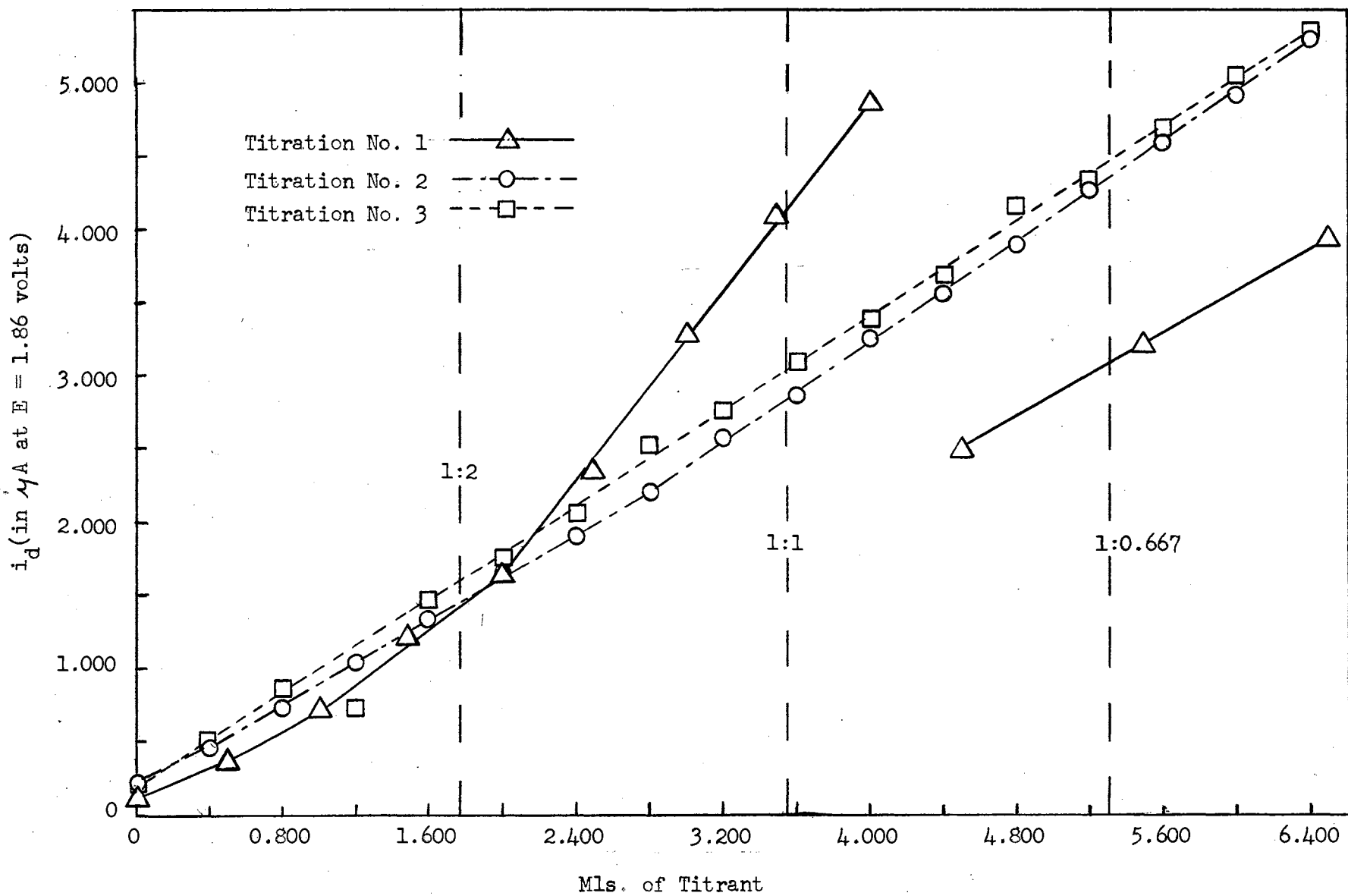
Figure 8. Amperometric Titration of 0.998 X 10^{-3}M Tributylamine with 0.0212M $CuCl_2 \cdot 2H_2O$

Figure 9. Amperometric Titration of 1.056 X 10^{-3}M CuCl$_2$·2H$_2$O with 0.01996M Tributylamine

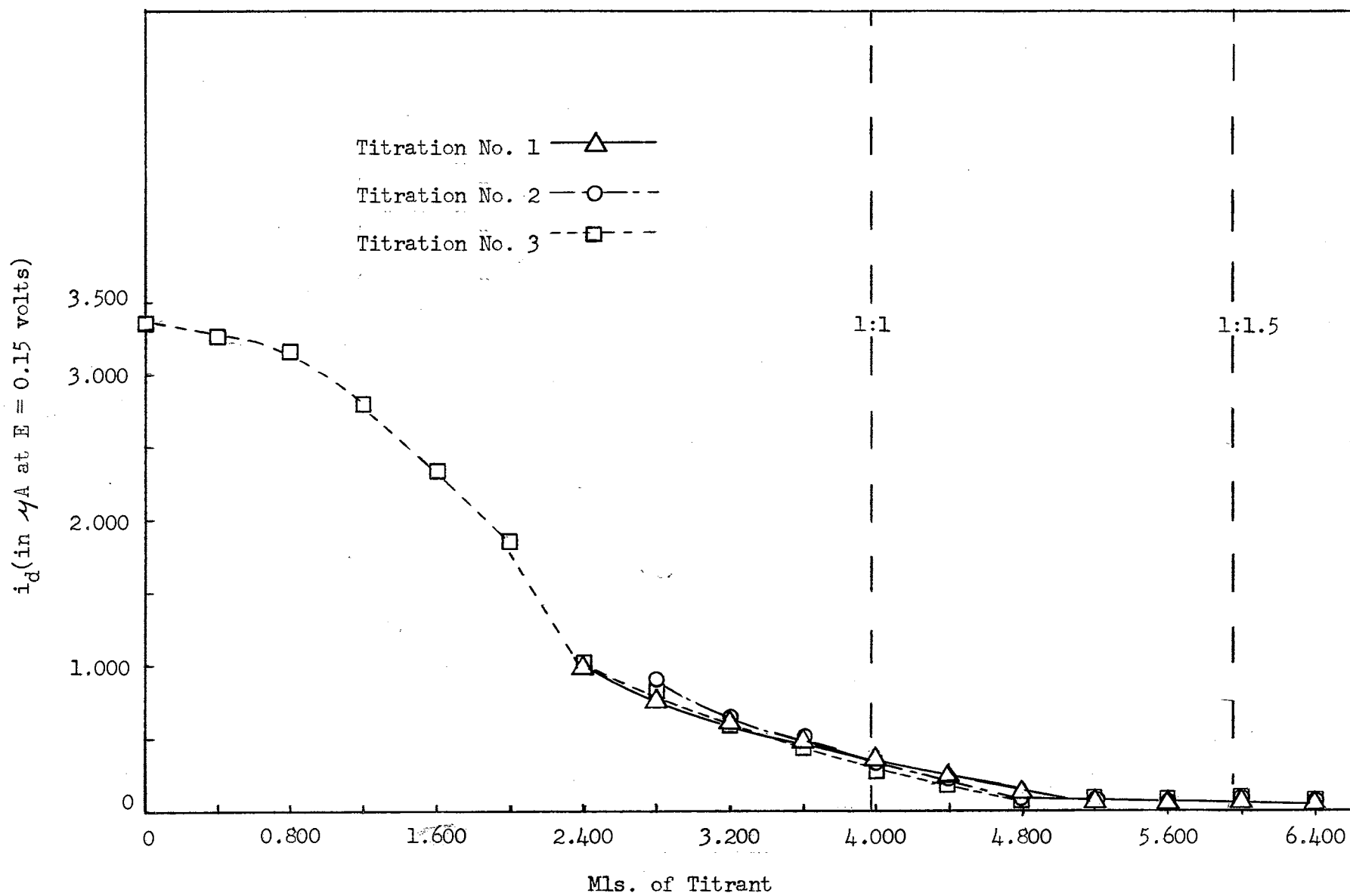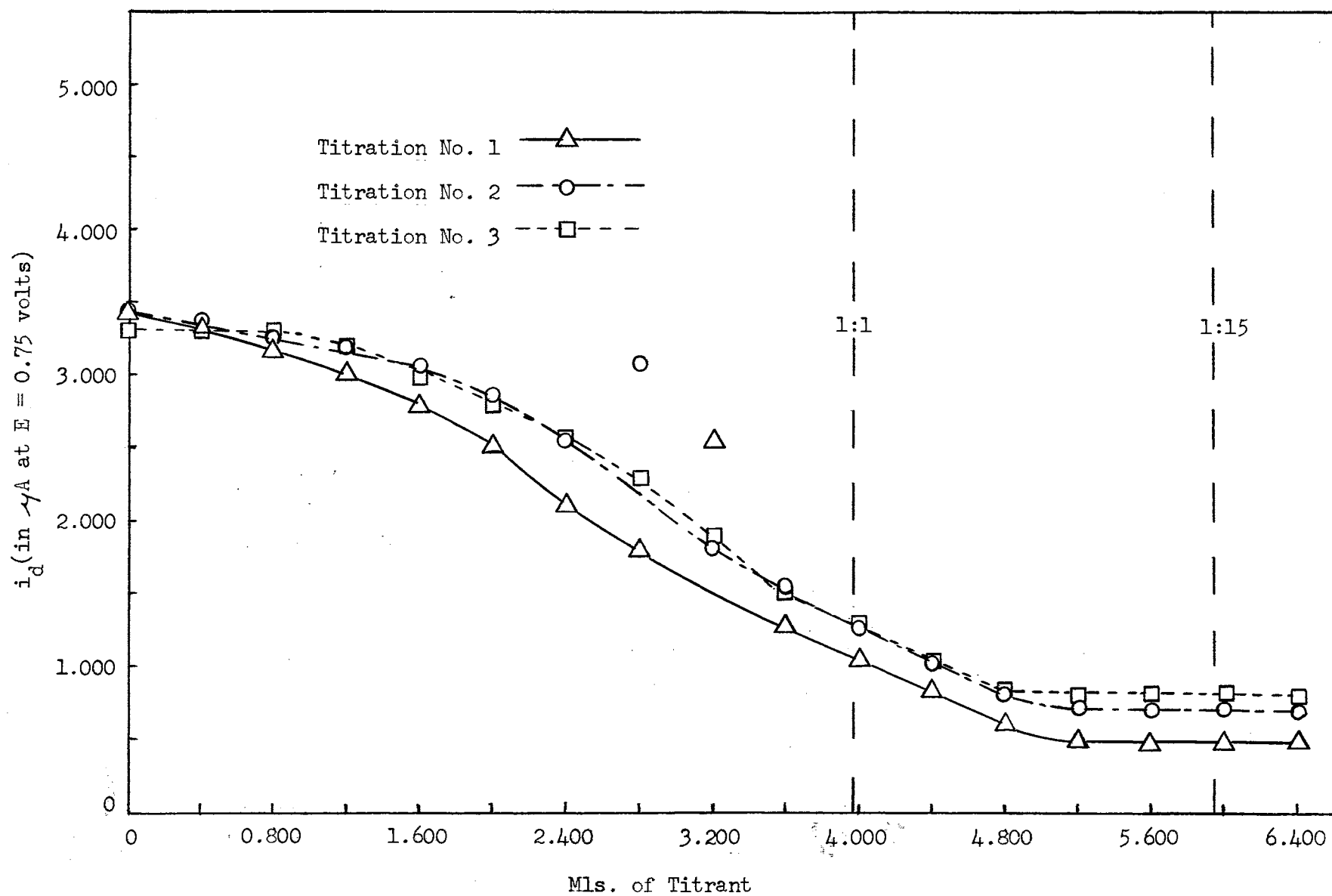Figure 10. Amperometric Titration of 1.056 X 10^{-3}M CuCl$_2 \cdot$2H$_2$O with 0.01996M Tributylamine

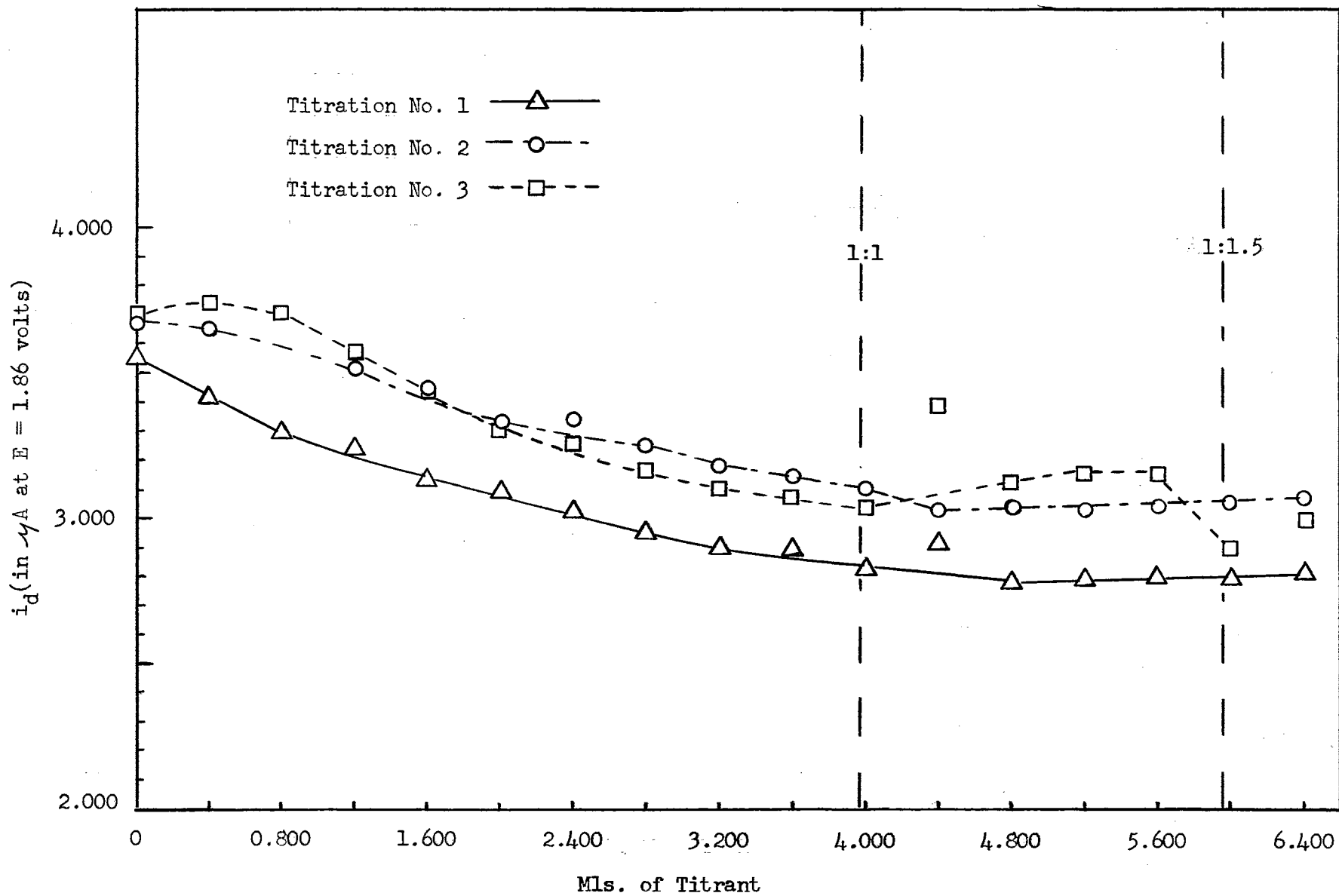Figure 11.   Amperometric Titration of $1.056 \times 10^{-3}M$ $CuCl_2 \cdot 2H_2O$ with 0.01996M Tributylamine

Unless a definite ratio between the copper and tributylamine can be established, this amine can not be used in the determination of copper by amperometric titration. However, it may be noted that the curves from Figures 6 and 10 do closely resemble a well-behaved amperometric titration. That is, the intersection of two straight lines with different slopes is evident.

Thermogravimetric Analysis

The thermobalance used for the thermogravimetric analysis of copper-tributylamine complexes is in this paper in the section on apparatus. It was necessary to calibrate this apparatus to determine the relation between the displacement given by the recorder and the weight change of the sample.

The calibration procedure was as follows:

(1) The strain gauge transducer was activated by applying the 9 V. excitation voltage.

(2) The nitrogen gas flow was adjusted to the proper flow rate.

(3) The transducer was then switched into the recorder circuit with the latter set at a sensitivity of 1 mv. per 250 mm. and the bridge was balanced.

(4) The transducer was then switched out of the recorder circuit and the standard resistor switched into the circuit. At the excitation voltage being used the resistor gave a displacement of 138 mm. on the recorder chart.

(5) The resistor and transducer were switched out of the circuit, the Vycor furnace chamber removed, a Bureau of Standard's 10 mg. weight was added to the balance pan, and the furnace chamber returned to position.

(6) The transducer was switched into the circuit and the displacement given by the 10 mg. weight was measured. It was found to give 112 $\overset{+}{-}$ 1 mm. displacement on the recorder chart at the 9 V. excitation voltage.

The thermobalance was thus calibrated so that a displacement of 112 mm. on the recorder chart would correspond to a 10 mg. change in weight on the sample.

The standard resistor in the circuit served as an additional fine adjustment control for the excitation voltage. The excitation voltage was always adjusted so the standard resistor would give a displacement of 135 to 140 mm. As long as the excitation voltage across the standard resistor gave a displacement in this range, a 10 mg. weight change would give a displacement of 112 $\overset{+}{-}$ 1 mm.

The furnace used with the thermobalance was also calibrated. The calibration was done by inserting the Vycor thermobalance furnace chamber in the furnace and placing an iron-constantan thermocouple in the chamber. The motor-driven Variac was turned on and the e.m.f. of the thermocouple was recorded with the Sargent SR recorder.

In this investigation the furnace reached a maximum temperature of 700°C.

In making a thermogravimetric analysis of a sample, the excitation voltage was applied and the thermobalance allowed to "warm-up" for at least one hour before starting the analysis. This was found to be necessary in order to get a repeatable response from the instrument.

During the warm-up period, the nitrogen gas flow through the balance sample chamber was adjusted. This was done through the use of a rising bubble flow meter. For this investigation it was not necessary

to know the absolute rate of flow of the nitrogen. After the optimum flow rate was established, through trial-and-error, it was necessary only to be able to reproduce the flow rate. For this purpose the bubble flow meter worked nicely.

Next, the sample was placed in the quartz dish and the dish was placed on the platinum balance pan. The Vycor furnace chamber of the balance was then inserted in the furnace and the entire assembly was lifted over the balance pan and sample.

After the chamber was allowed to degas for 3 to 4 minutes with the side outlet closed, the bottom gas outlet was closed and the side outlet was opened.

The arrests then were removed from the extension arm and the counter-poise of the strain gauge, the cover was replaced to prevent disturbance by air currents, and the bridge was balanced. The pen of the recorder was displaced to one side of the chart with the bridge balance in order to utilize the full width of the chart paper.

When a constant weight had been attained by the sample, the furnace control (the motor-driven Variac) and the recorder were turned on simul-taneously. The thermogravimetric analysis was allowed to proceed to the desired temperature and then the apparatus was turned off. A permanent record of the analysis was made by the recorder.

To test this operational procedure, a sample of cupric sulfate pentahydrate was analyzed. The results obtained agreed very closely with those of Wendlandt (44).

The copper-tributylamine complex, prepared as previously described, was studied using the above procedure. A characteristic record of the results is shown in Figure 12. The average size sample of complex

analyzed was approximately 50 mg.

The vertical line shown at 25°C. is due to the fact the precipitated complex was placed on the balance pan while still wet with 2-propanol. The furnace was not turned on until the sample had reached a constant weight. The furnace was then turned on and the analysis was allowed to proceed to approximately 700°C. where a constant weight was manifest. The residue, quartz dish, and platinum pan were then removed from the balance and weighed on an analytical balance to determine the weight of the residue. From a knowledge of the weight of the residue and application of the calibration of the thermobalance, the total weight of the original sample could be determined.

The residue on the thermobalance pan was dark brown or black in color. It was found to be insoluble in cold concentrated nitric acid and in cold concentrated sulfuric acid. It dissolved readily, however, in concentrated hydrochloric acid, giving a green-colored solution, and less readily in hot nitric acid. A qualitative test for chloride on the nitric acid solution gave negative results. Although no determination was made for copper, the physical appearance of the residue was that of cupric oxide and the color of the hydrochloric acid solution indicated the presence of copper.

In Figure 12, it may be noted that two breaks occur in the weight-versus-temperature curve. Both brakes take place over a wide range of temperature. The first break starts at 50°C. and proceeds until 275°C. From 275° to 400°C. the weight is essentially constant. This is followed by the second break which proceeds between 400° and 675°C. The ratio of the weight losses of the first break to the second break is 1.00:2.42. Taking the sample weight to be the weight of the sample after becoming

constant at room temperature, the first weight loss representa an

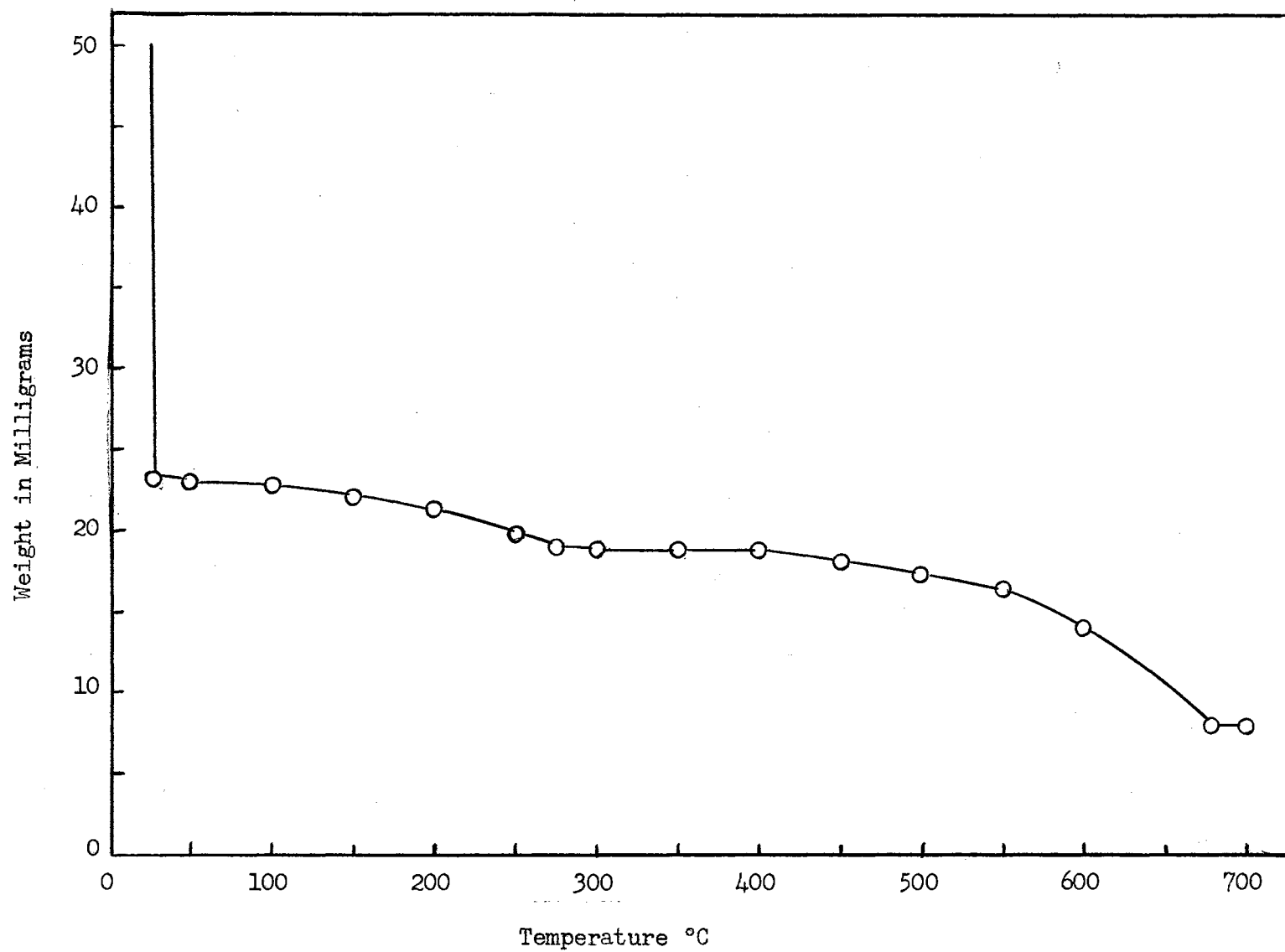18.1% loss and the second break represents a 47.2% loss in weight.

Figure 12. Thermogravimetric Analysis of Copper-Tributylamine Complex
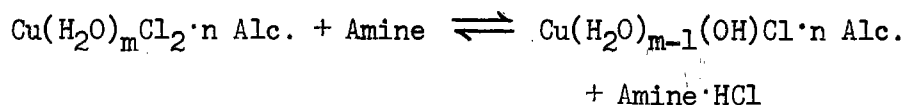
CHAPTER VI

DISCUSSION

The interpretation of the data collected from the chemical analysis, the thermogravimetric analysis, and the amperometric titrations indicates that the precipitate formed when 2-propanol solutions of cupric chloride and tributylamine are mixed is not composed of one compound but is more probably a mixture of two or more compounds. Also, the precipitate contains very little, if any, true copper-tributylamine complex, because the amount of amine shown to be present by the chemical analysis is far too small.

Inflection points obtained in the amperometric titration curves seem to indicate no formation of copper-tributylamine complexes containing simple numbers as the copper-to-amine ratio. The amperometric titration solutions do undergo a color change during the course of the titration, indicating the probable presence of copper-tributylamine complexes in solution. The results seem to indicate that the reactions indicated by the inflection points are not necessarily due to the formation of amine complexes but that some, at least, could be obtained by titrating with any weak base such as tributylamine.

From the weight of the residue in the thermogravimetric analysis of the precipitate and the total percentage weight loss it is possible to postulate a molecular weight for the original compound by making certain assumptions.

If the assumption is made that the residue is entirely CuO, then the molecular weight of the original compound (unless it were polynuclear) would be approximately 229. Of this molecular weight, the substance lost at the first break in the TGA would be represented by 41.5, while the substance lost at the second break would be represented by 108.

Placing the chemical analysis on a whole mole basis shows that for every three moles of copper there are close to 2 moles of chloride. The tributylamine is present in such a small amount in the precipitate that it might even be present due only to coprecipitation of a small amount of amine complex from the solution. Thus in the precipitate there are copper, chloride, almost certainly hydroxyl groups (since it is the only negative ion that possibly could make up for the lack of chloride ions to balance the cupric ions -- or even cuprous ions) and probably water and alcohol molecules. It is highly probable that the precipitate is largely hydrated and/or alcholated $Cu(OH)_2$ and $Cu(OH)Cl$, formed by reaction of the type

$$Cu(H_2O)_m Cl_2 \cdot n \text{ Alc.} + \text{Amine} \rightleftharpoons Cu(H_2O)_{m-1}(OH)Cl \cdot n \text{ Alc.}$$
$$+ \text{ Amine} \cdot HCl$$

and so forth.

Postulating a composite formula containing all these components except alcohol it would be $Cu_3(OH)_x Cl_2 \cdot yH_2O$, the Cu:Cl ratio in this being established by the chemical analysis. The molecular weight of the compound calculated from the above would be 229 X 3 = 687, and for the compound to be neutral "x" would need to be equal to 4. To fulfill the molecular weight requirement, then, "y" would need to be equal to 20.

This is probably a mixture of compounds and could be composed of such salts as $Cu(OH)_2 \cdot zH_2O$ and $Cu(Oh)Cl \cdot wH_3O$, where z = 6 and w = 7.

In order to have a material balance the $Cu(OH)Cl \cdot 7H_2O$ would have to be taken twice.

According to the TGA data the properly-weighted summation of molecular weights of the substances lost at the first break would be 18.1% X 687 = 124, while that for the substances lost at the second break would be 47.2% X 687 = 324. The first break would be equivalent to losing 7 molecules of water. The second break would be equivalent to losing 14 molecules of water and 2 molecules of HCl. This, in itself would be improbable since it would indicate a coordination number of 7 for the copper, and a further discrepancy appears when the temperature difference of the breaks is considered. The second break starts at 400°C. and it seems highly improbable that any water of hydration would be so tightly coordinated that it would not evolve until this temperature.

Assuming that the residue from the TGA is finely divided copper metal rather than CuO, and using calculations similar to those given above, a molecular weight of 183, or its multiple, is calculated for the original compound. Following a line of reasoning similar to that used in the previous example a compound such as $Cu_3(OH)_4Cl_2 \cdot 12H_2O$ could be postulated. Again this is probably a mixture of $Cu(OH)_2 \cdot 4H_2O$ and 2 $Cu(OH)Cl \cdot 4H_2O$. In this case the first weight loss would correspond to losing 5.5 molecules of H_2O and the second break would correspond to losing 8 molecules of H_2O, 2 molecules of HCl, and 1 molecule of oxygen— a supposition that is as hard to believe as the first.

If 2-propanol enters into the complex, the results obtained are more reasonable, but the data obtained would not be sufficient to give an adequate picture of the composition of the precipitate. Until chemical analyses are performed on the residue from the TGA and upon the

compound which is stable between 275° and 400°C., it is impossible to determine definitely the compound or compounds in the original precipitate. At the present time another investigation in this laboratory is being conducted to solve this problem.

Conclusions

From the results of this research, it is obvious that the precipitates obtained by mixing amines with $CuCl_2 \cdot 2H_2O$ in 2-propanol are essentially mixtures of solvated (and probably hydrated) cupric hydroxide and cupric hydroxychloride possibly admixed with a small amount of amine complex formed more by coprecipitation than by true reaction. Thus the amine was acting as a weak base rather than as a ligand. This makes the work of others in this field suspect except where actual analysis of precipitates was performed or where the complexes studied remained in solution in sufficiently high concentration.

These results point to the fact also that water, even in traces, cannot be disregarded as a possible reactant; for the ease with which these precipitates formed, even at the low concentrations (both of water and of the other reactants) employed shows that only under truly anhydrous conditions can amines, though they are well known as ligands for copper (II), form complexes with water. In other words, amines in the presence of water, accept protons from the hydrated cation largely in preference to displacing the water as a ligand.

There was inconclusive, but good evidence, however, that copper-amine complexes do form in solution. These need to be studied, therefore, under less competitive conditions.

SELECTED BIBLIOGRAPHY

1. Aumeras, M. and Tamisier, A., Bull. soc chim. 53, 97-113 (1933).

2. Ayres, G. H., Quantitative Chemical Analysis, Harper and Brothers, New York, 1958, pp. 666-70.

3. Ayres, G. H., Ibid, pp. 646-51.

4. Bartlett, E. S. and Williams, D. N., Rev. Sci. Instr. 28, 919 (1957).

5. Bhattacharya, A. K. and Dey, Arun K., Current Sci. 14, 69 (1945).

6. Biltz, W., Z. anorg. Chem. 148, 207 (1925).

7. Brintzinger, H. and Hesse, B., Ibid 252, 293-404 (1944).

8. Broome, F. K., Ralston, A. W. and Thornton, M. H., J. Am. Chem. Soc. 68, 67-9 (1946).

9. Broome, F. K., Ralston, A. W. and Thornton, M. H., J. Am. Chem. Soc. 68, 849-54 (1946).

10. Bruehlmon, R. J. and Verhoek, F. H., J. Am. Chem. Soc. 70, 1401-4 (1948).

11. Brusset, A. R. and Burgaud, J. L., Compt. rend. 254, 4032-3 (1962).

12. Burkin, A. R., J. Chem. Soc. 122-7 (1950).

13. Caglioti, Vincenzo, et al., Gazz. Chim. Ital. 92, 1276-89 (1962).

14. Chattaway, F. W. and Drew, H. D. K., J. Chem. Soc. 947-8 (1937).

15. Chevenard, P. and Wache, R. De la Tullaye, Bull. soc. chim. 11 41-7 (1944).

16. Crowe, C. W.., "Applicability of Solid Microelectrodes to Non-aqueous Amperometric Titrations," M. S. thesis, Oklahoma State University, 1961.

17. Doyle, C. D., Anal. Chem. 33, 77-9 (1961).

18. Dubois, P., PhD. Thesis, University of Paris (1935).

19. Duval, C. L., _Inorganic Thermogravimetric Analysis_, Elsevier Publishing Co., Inc., New York, 1953.

20. Ephraim, F. and Bolle, E., Ber. 48, 1770-7 (1915).

21. Ephraim, F., Ber. 52, 940 (1919).

22. German, W. L. and Jamsett, R. A., J. Chem. Soc. 1337-41 (1939).

23. German, W. L. and Jansett, R. A., Ibid., 1360-2 (1940)

24. Gordon, S. and Campbell, C., Anal. Chem. 28, 124-6 (1956).

25. Gordon, S. and Campbell, C., Ibid., 32, 271R-289R (1960).

26. Guichard, M., Bull. soc. chim. 37, 62 (1925).

27. Haendler, H. M., J. Am. Chem. Soc. 64, 686-8 (1942).

28. Hall, J. L. and Dean, W. E., J. Am. Chem. Soc., 80, 4183-8 (1958).

29. Honda, K., Sci. Reports Tohoku Imp. Univ. 4, 97 (1915).

30. Knobloch, W., Lotos 78, 110-11 (1930).

31. Kolthoff, I. M. and Laitimer, H. A., _pH and Electro Titrations_, 2nd Ed., John Wiley and Sons, Inc., New York, 1941.

32. Korshonov, I. A. and Malyugina, N. I., Zhur. Obschei Khim. 20, 402-6 (1950).

33. Mandal, K. L., Science and Culture 5, 494 (1940).

34. Moran, P. R., "Amperometric Titrations of Selected Petroleum Additives and Sulfonic Acids in Nonaqueous Solutions," Ph.D. thesis, Oklahoma State University, 1959.

35. Neogi, P. and Mandal, K. L., J. Indian Chem. Soc. 16, 433-6 (1939).

36. Parasad, Sarju and Sharma, B. D., J. Proc. Inst. Chemist (India) 30, 245-58 (1958).

37. Pinkston, J. R. and Briscoe, H. T., J. Phys. Chem. 46, 469-73 (1942).

38. Pominov, I. S., Zhur. Fiz. Khim. 31, 2184-90 (1957).

39. Reilley, C. N. and Sawyer, D. T., _Experiments for Instrumental Methods_, McGraw-Hill Book Co., New York, 1961, pp. 30-2.

40. Rencker, Edouard, Bull. soc. chim. 4, 1992-5 (1937).

41. Sturrock, Peter E., Anal. Chem. $\underline{35}$, 1092 (1963).

42. Urazov, G. G., Kirakosyan, A. K. and Galustyan, V. D., Zhur. Neorg.
    Khim. $\underline{2}$, 1094-1114 (1957).

43. Vainshtein, E. E., and Antipova-Karataeva, I. I., Zhur. Neorg.
    Khim. $\underline{4}$, 793-800 (1959).

44. Wendlandt, W. W., J. Chem. Educ. $\underline{38}$, 566-8 (1961).

45. Wendlandt, W. W., J. Inorg. Nucl. Chem. $\underline{25}$, 833-42 (1963).

VITA

Don Adam Carley

Candidate for the Degree of

Master of Science

Thesis: A STUDY OF THE COPPER-TRIBUTYLAMINE COMPLEXES IN 2-PROPANOL

Major Field: Chemistry

Biographical:

    Personal Data: Born in Sapulpa, Oklahoma, February 27, 1939, the son of Nathaniel L. and Cora B. Carley.

    Education: Attended public school in Sapulpa, Oklahoma; graduated from Sapulpa High School in 1957; received the Bachelor of Science degree from Bethany Nazarene College, with a major in Chemistry, in May, 1961; completed requirements for the Master of Science degree in May, 1964.

    Professional Experience: Worked as a laboratory technician in the Biochemistry Department of the Oklahoma University Medical School, Oklahoma City, from February, 1960 to June 1961; worked as a chemist for the Oklahoma Testing Laboratories, Oklahoma City, from June, 1961 to September, 1961; is a member of Phi Delta Lambda, Honorary Scholarship Society of Nazarene Colleges, and Phi Lambda Upsilon, Honorary Chemical Society.