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Chelation of two polyhydroxyamines with copper (II) ion

David H. Powell

CHELATION OF TWO POLYHYDROXYAMINES WITH COPPER (II) ION.

by

David H. Powell

THESIS

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ABSTRACT

Two polyamines, 2,8-bishydroxymethyl-2,8-dimethyl-3,7-diaza-1,5,9-nonanetriol and 2,8-bishydroxymethyl-2,8-dimethyl-3,7-diaza-1,9-nonanediol, were prepared and the coordination of these compounds with Cu (II) ions in solution was investigated. Spectrophotometric study of the solutions of these compounds gives evidence of the formation of two complexes, containing one mole of ligand per metal ion and two moles of ligand per metal ion, respectively. The two stability constants for these complexes and the basicity constants for these ligands were calculated from potentiometric titrations at 30°C. A comparison of the stability constants and basicity constants for the two compounds was made to determine the effect of the central hydroxy group in chelation.

ACKNOWLEDGMENTS

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I. HISTORY

The chemistry of complexes was born in 1704 with the discovery of Prussian blue by Diesbach. From the time of Diesbach's investigations until 1893 much data on complex compounds accumulated, but little successful theoretical work was presented to explain the existence and properties of these compounds. In 1847, F. A. Genth (28) performed the first reliable research on cobalt (III) ammine complexes. Other prominent workers during this period were Woolcott Gibbs, Christian Wilhelm Blomstrand, and Sophus Mads Jørgensen. Blomstrand, Jørgensen, and others produced several interesting but wholly unsuccessful theories; however, the value of these early investigations should not be underestimated. Only through the painstaking accumulation of data was the first correct explanation of coordination compounds obtained.

The accepted theory of complex compounds in 1891 was the chain theory first presented by Blomstrand (11, 12) and later extended and modified by Jørgensen. In order to appreciate fully Blomstrand's theory, we must realize that until the work of Raoult and van't Hoff about 1882, the only method for molecular weight determinations was from measurement of vapor densities, and no reliable method existed for non-volatile compounds (31). The cobalt (III) ammine complexes will serve to illustrate Blomstrand's

theory. At that time, the non-volatile cobalt (III) chloride was considered to have a dimeric structure, Co_2Cl_6, by analogy with volatile Fe_2Cl_6, and the cobalt (III) ammines were assumed to have the structure $Co_2Cl_6 \cdot 12NH_3$. Blomstrand proposed the following structure for the luteo salt

$$Co_2 \begin{cases} NH_3\text{-}NH_3\text{-}Cl \\ NH_3\text{-}NH_3\text{-}Cl \\ NH_3\text{-}NH_3\text{-}Cl \\ NH_3\text{-}NH_3\text{-}Cl \\ NH_3\text{-}NH_3\text{-}Cl \\ NH_3\text{-}NH_3\text{-}Cl. \end{cases}$$

Jørgensen extended Blomstrand's theory to account for the fact that on heating the luteo salt loses one-sixth of its ammonia and is converted to the purpureo salt. In the purpureo salt only two-thirds of the chlorine can be precipitated by silver nitrate, whereas in the luteo salt all of the chlorine is precipitated by silver nitrate. Jørgensen proposed that halogens attached to the metal through other groups such as ammonia are less strongly bound than those directly attached to the metal and can be precipitated by silver nitrate (29). He also proposed that chain formation was the most stable arrangement and the maximum number of ammonia molecules that could form a chain was four. Therefore, he proposed the following arrangements for the luteo and purpureo salts

$$Co_2\left\{\begin{matrix}NH_3Cl\\NH_3Cl\\NH_3NH_3NH_3NH_3Cl\\NH_3NH_3NH_3NH_3Cl\\NH_3Cl\\NH_3Cl\end{matrix}\right. \xrightarrow{heat} Co_2\left\{\begin{matrix}Cl\\NH_3Cl\\NH_3NH_3NH_3NH_3Cl\\NH_3NH_3NH_3NH_3Cl\\NH_3Cl\\Cl\end{matrix}\right.$$

Jørgensen (30) in 1890 and Petersen (38) in 1892 deduced evidence for monomeric molecular weights by freezing points and conductivity measurements, and the proposed formulas were halved to

$$Co\left\{\begin{matrix}NH_3Cl\\NH_3NH_3NH_3NH_3Cl\\NH_3Cl\end{matrix}\right. \xrightarrow{heat} Co\left\{\begin{matrix}NH_3Cl\\NH_3NH_3NH_3NH_3Cl\\Cl\end{matrix}\right.$$

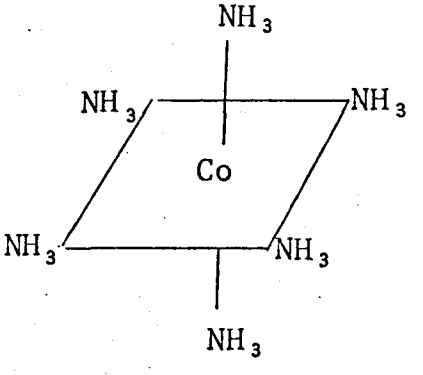
In the early 1890's a chemical genius named Alfred Werner began working in this field and brought a previously unknown continuity to the great mass of experimental data that had accumulated before him. There are several stories about how Werner arrived at his striking new theory of complexes. He was a twenty-six year old Privat-Dozent (28) at the University of Zurich when he was told by retiring Professor Hantzsch that he could have a full professorship if his ideas on complexes were more widely known. Werner retired to a room with a box full of cigars and did not emerge until the cigars were gone and the paper was finished. The paper (9) was published the following year in 1893. That is the account given by N. Bjerrum (10); a somewhat different version is presented by Pfeiffer (41) and Berl (3). According to their account, Werner awoke from a dream at two

one morning with the entire solution in his mind. He immediately got up and wrote until five in the afternoon to complete a monograph on his theory. Regardless of which account is true, these anecdotes serve to illustrate the dynamic character of Alfred Werner's personality.

The basic ideas of Werner's theory of complexes are as follows:

1. Metals have two types of valency; primary (ionizable) and secondary (non-ionizable).
2. All metals have a fixed number of secondary or non-ionizable valencies which are directed in space and correspond to the coordination number of the element.
3. Primary valencies are satisfied by negative ions. The secondary valencies are satisfied by negative groups or neutral molecules. Also, a limited number of positive groups may occupy coordination positions, but the coordination number of the metal must be fulfilled.

Werner abandoned the chain approach of Jørgensen and considered that the ammonia molecules of the luteo cobaltic chloride complex were arranged symmetrically about the cobalt ion.



At first, there was much opposition to Werner's theory and many of the attacks came from Jørgensen. Both Jørgensen's and Werner's structures were compatible with the experimental evidence at the time Werner made his radical approach; however, Werner regarded the chlorine atoms as ions - a concept considered quite revolutionary at the time. What ensued was one of the classic battles of science. After a long series of brilliant experiments by Werner, his theory finally won acceptance. In 1907, when Werner (31) succeeded in preparing the missing violeo (cis) series of dichlorotetraamine cobalt (III) salts whose existence was a necessary condition of Werner's theory but not of Jørgensen's chain theory, Jørgensen promptly acknowledged the validity of Werner's views. Werner also acknowledged his indebtedness to Jørgensen's experimental data; regretably the two great adversaries never met.

On November 12, 1913, Werner received the following telegram: "Nobel Prize for Chemistry awarded you. Letter follows - Aurivillius." (32)

Although Werner's theory cleared up much of the mystery surrounding coordination complexes, it did not adequately explain the complexes by any means. Since Werner's time, many advances have been made. These advances include crystal-field theory, ligand-field theory, and molecular-orbital theory, all of which have greatly expanded and improved our understanding of complexes; nevertheless, no completely satisfactory understanding of complexes yet exists.

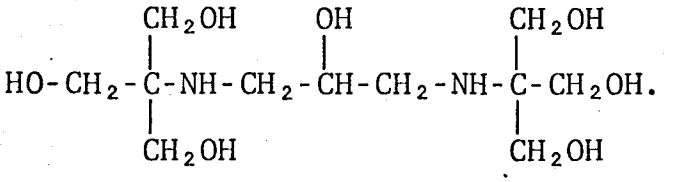
One of the most interesting aspects of coordination compounds has been the determination of their equilibrium constants in solution. At the turn of the century, the first applications of Guldberg and Waage's law of mass action (22) were made in the determination of equilibrium constants of complexes. Much of this first work was carried out by G. Bodlander and his co-workers and involved determining the overall stability constant of the ultimate complex. The first step-wise stability constants were determined by H. N. Morse (36) in 1902 for the mercury (II) chloride system using solubility measurements.

In 1915 Niels Bjerrum helped advance the study of complex equilibria by his work in the chromium (III) thiocyanate complexes. This system consists of six different complexes $CrSCN^{2+}$ through $Cr(SCN)_6^{3-}$. Bjerrum was able to compute each of the step-wise stability constants. The complexes are very inert, and Bjerrum was able to analyze for each separate component in solution and therefore to calculate the average number of ligands bound to each metal ion, designated $\bar{n}$, and the fraction of the total metal present as a single complex, designated α_c. Bjerrum's work was later applied to more labile complexes, and general methods for computing step-wise constants were developed by J. Bjerrum (6) and I. Leden (33) in the early 1940's. These efforts have been expanded and improved by G. Schwarzenbach, L. G. Sillen, F. J. C. Rossotti, and H. Rossotti. Extensive tables of stability constants of

metal-ion complexes with organic and inorganic ligands have been prepared by J. Bjerrum, Schwarzenbach, and Sillen (7, 8).

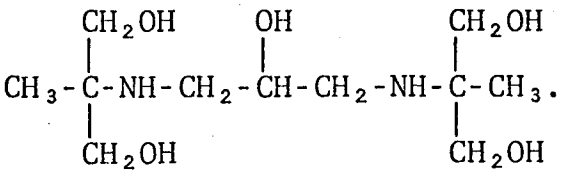
II. INTRODUCTION

In 1944 Pierce and Wotiz (39) synthesized a number of polyhydroxyamines. One of these compounds, 2,2,8,8-tetrakishydroxymethyl-3,7-diaza-1,5,9-nonanetriol, they called "Disec,"



This compound proved to be an excellent chelating agent with ions of the transition series elements and was studied extensively by Gladding (20), Erdmanis (16), Moore (35), Jackson (26), Davis (14), and Fones (17).

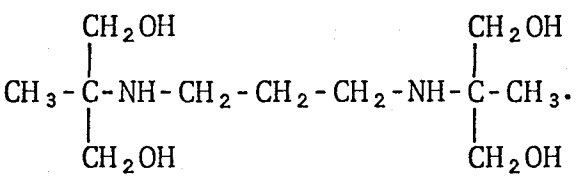
Continuing with this work O'Rear (37) in 1960 studied the effect of removing one hydroxy group from both ends of Disec. He synthesized and studied the chelation of 2,8-bishydroxymethyl-2,8-dimethyl-3,7-diaza-1,5,9-nonanetriol



with elements of the first transition series. O'Rear's compound is designated Compound 1. Garrett (18) has also studied the properties of the ultraviolet-visible spectra of these complexes.

It was suggested by Fernelius (4, 5) that the central hydroxy group might have an even greater effect on the chelating properties of these compounds. The central hydroxy group would be constrained by the two nitrogen-metal bonds in a position favorable for the formation of another metal-ligand bond. This possibility can be explored by synthesizing the compound in which the central hydroxy group is absent and comparing the chelation of this new compound with that of Compound 1.

This thesis presents the synthesis and purification of this new compound, 2,8-bishydroxymethyl-2,8-dimethyl-3,7-diaza-1,9-nonanediol

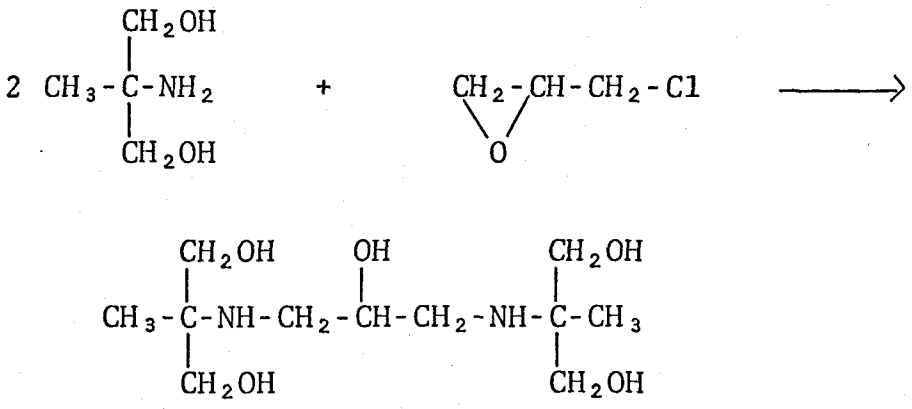


This compound is designated Compound 2. The results of an investigation of the coordination properties of Compound 2 with copper (II) ion are presented. Also, the work on Compound 1 was reinterpreted. Compound 1 was synthesized and purified and the coordination properties of Compound 1 with copper (II) ion are presented.

III. EXPERIMENTAL

A. Synthesis of 2,8-bishydroxymethyl-2,8-dimethyl-3,7-diaza-1,5,9-nonanetriol. (Compound 1)

Compound 1 was synthesized by the dropwise addition of one mole of epichlorohydrin dissolved in absolute ethanol to a slurry of two moles of 2-amino-2-methyl-1,3-propanediol in absolute ethanol. During the addition of the epichlorohydrin the temperature was kept below 20°C. by immersion of the flask in an ice-water bath. The solution was refluxed for seven hours after the last addition of epichlorohydrin.



Since the free base showed no tendency to crystallize it was converted to the dihydrochloride salt by bubbling hydrogen chloride gas through the solution. The compound was recrystallized from ethanol several times, and white crystals were obtained. The compound melted sharply at 198-199°C. The yield of the compound was only fair (60 per cent) due to loss during purification.

The infrared and nuclear magnetic resonance spectra were obtained for the compound and are presented on the following pages.

For a more detailed discussion of the synthesis of Compound 1, see Appendix A.

A sample of Compound 1 was analyzed for its carbon, hydrogen, and nitrogen content. The results of the analysis are presented below together with the theoretical values.

	% C	% H	% N
Theoretical	39.05	8.28	8.28
Found	39.03	8.28	8.12

REMARKS

ORIGIN RECRYSTALLIZATION OF COMPOUND 1

PURITY

PHASE KBr Pellet

CONCENTRATION

THICKNESS

DATE April 6, 1972

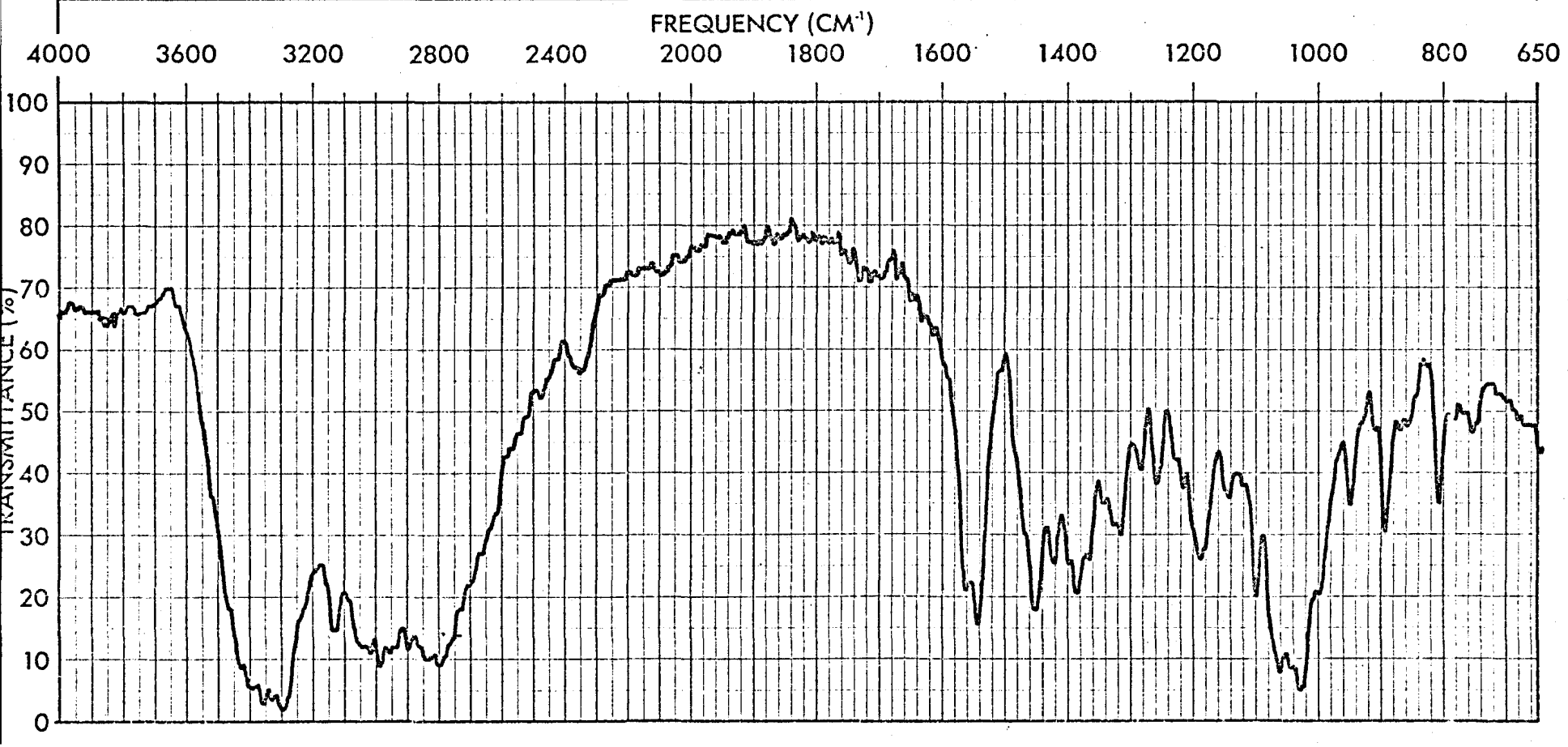
OPERATOR David H. Powell

PERKIN-ELMER
MODEL 700

SPECTRUM NO. 1

SAMPLE 1 COMPOUND 1

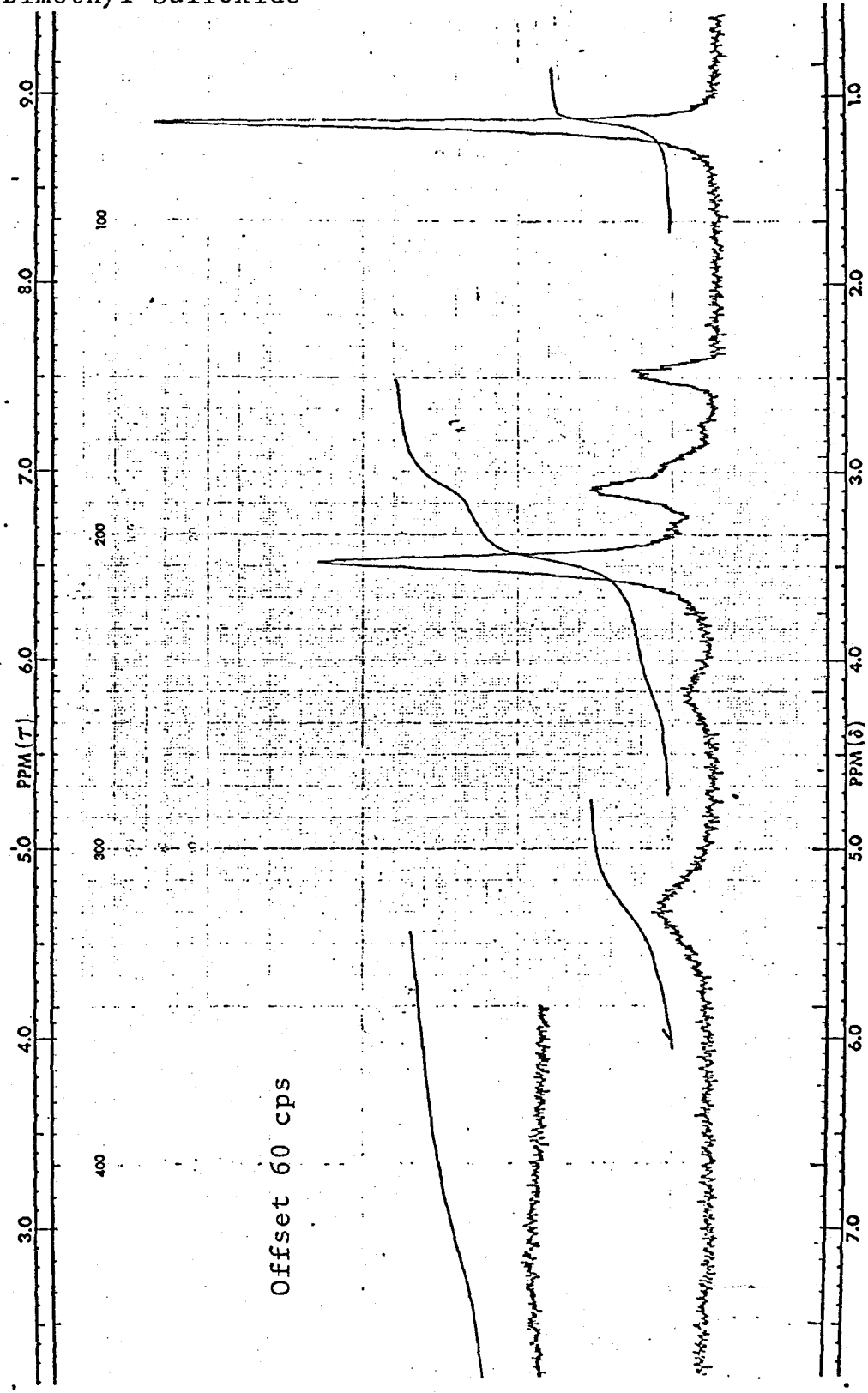
SAMPLE 2



SAMPLE COMPOUND 1 SPECTRUM NO. 1.

Nuclear Magnetic Resonance Spectrum of Compound 1

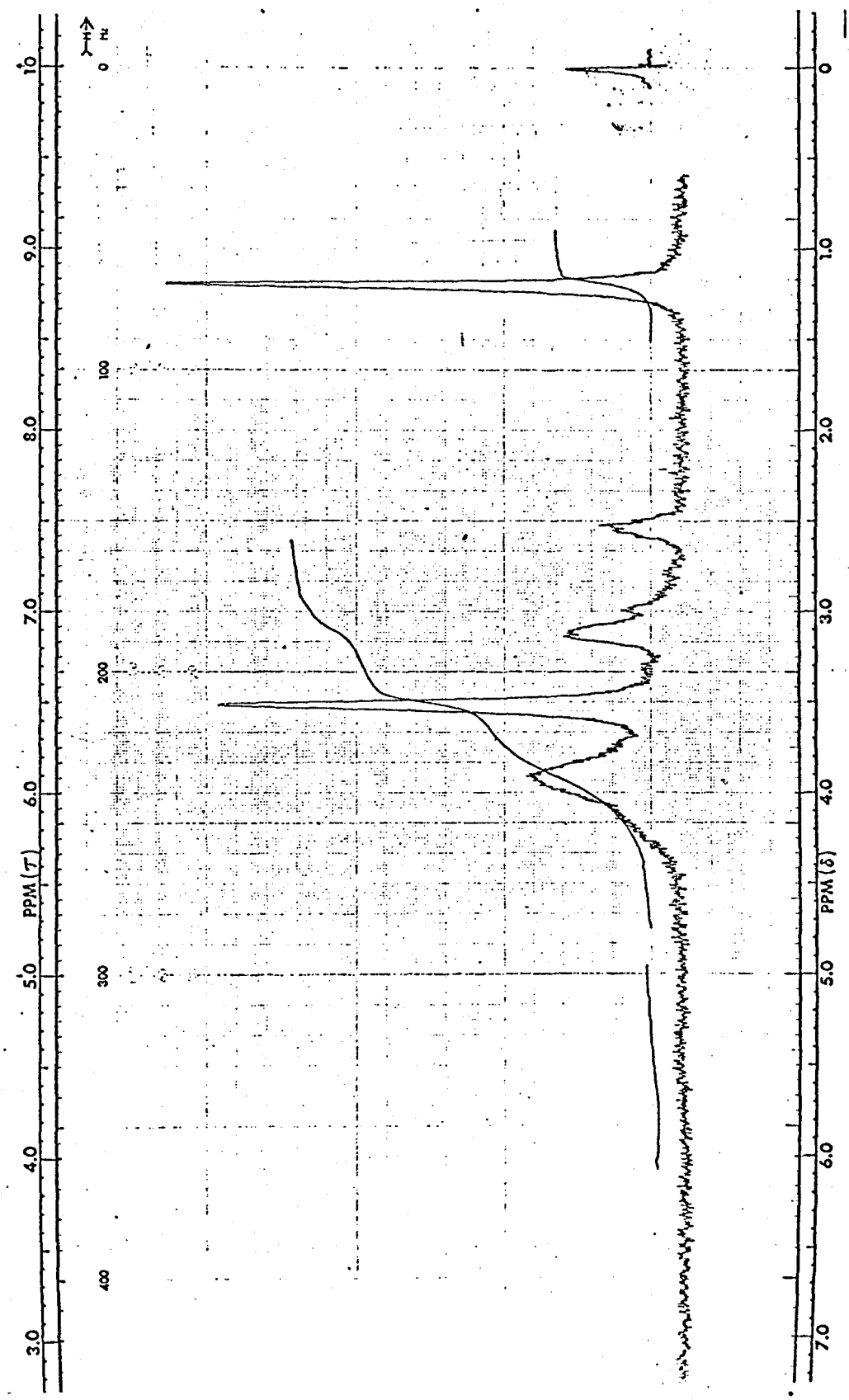
in Dimethyl Sulfoxide



(See page 20 for peak assignments.)

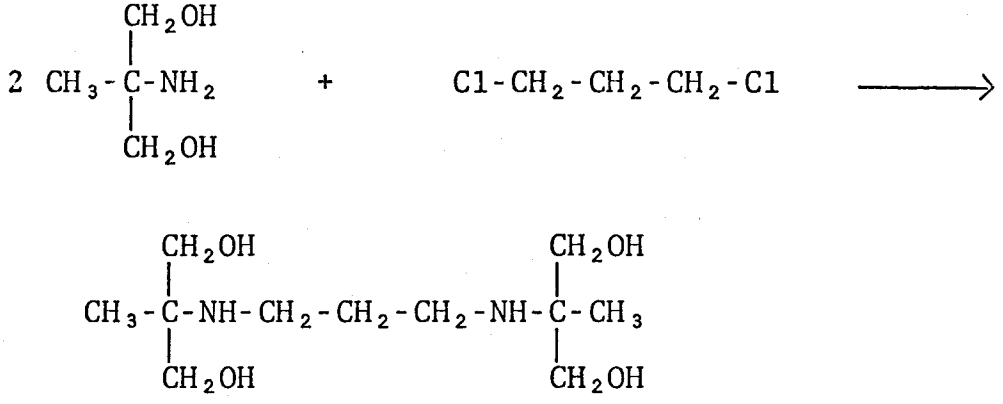
Nuclear Magnetic Resonance Spectrum of Compound 1

in Dimethyl Sulfoxide with D_2O added



B. Synthesis of 2,8-bishydroxymethyl-2,8-dimethyl-3,7-diaza-1,9-nonanediol. (Compound 2)

Compound 2 was synthesized by a method similar to that used for Compound 1. One mole of 1,3-dichloropropane dissolved in absolute ethanol was added dropwise to a slurry of 2-amino-2-methyl-1,3-propanediol. During the addition of the dichloropropane the temperature was kept below 20°C. by immersion of the reaction flask in an ice-water bath. The solution was refluxed for seven hours after the final addition of dichloropropane.



The free base was converted to the dihydrochloride salt by bubbling hydrogen chloride gas through the solution.

The compound was crystallized by bubbling hydrogen chloride gas through a solution of Compound 2 in an ethanol-petroleum ether mixture. The compound was recrystallized several times and washed with absolute ethanol. White crystals were obtained which melted sharply at 164-165°C. The yield of Compound 2 was fair (60 per cent) due to loss during purification.

The infrared and nuclear magnetic resonance spectra were obtained and are presented on the following pages.

For a more detailed discussion of the synthesis of Compound 2, see Appendix B.

A sample of Compound 2 was analyzed for its carbon, hydrogen, and nitrogen content. The results of the analysis are presented below together with the theoretical values.

	% C	% H	% N
Theoretical	40.99	8.70	8.70
Found	40.69	8.74	8.52

REMARKS

ORIGIN RECRYSTALLIZATION OF COMPOUND 2

PURITY

PHASE KBr Pellet

CONCENTRATION

THICKNESS

DATE April 6, 1972

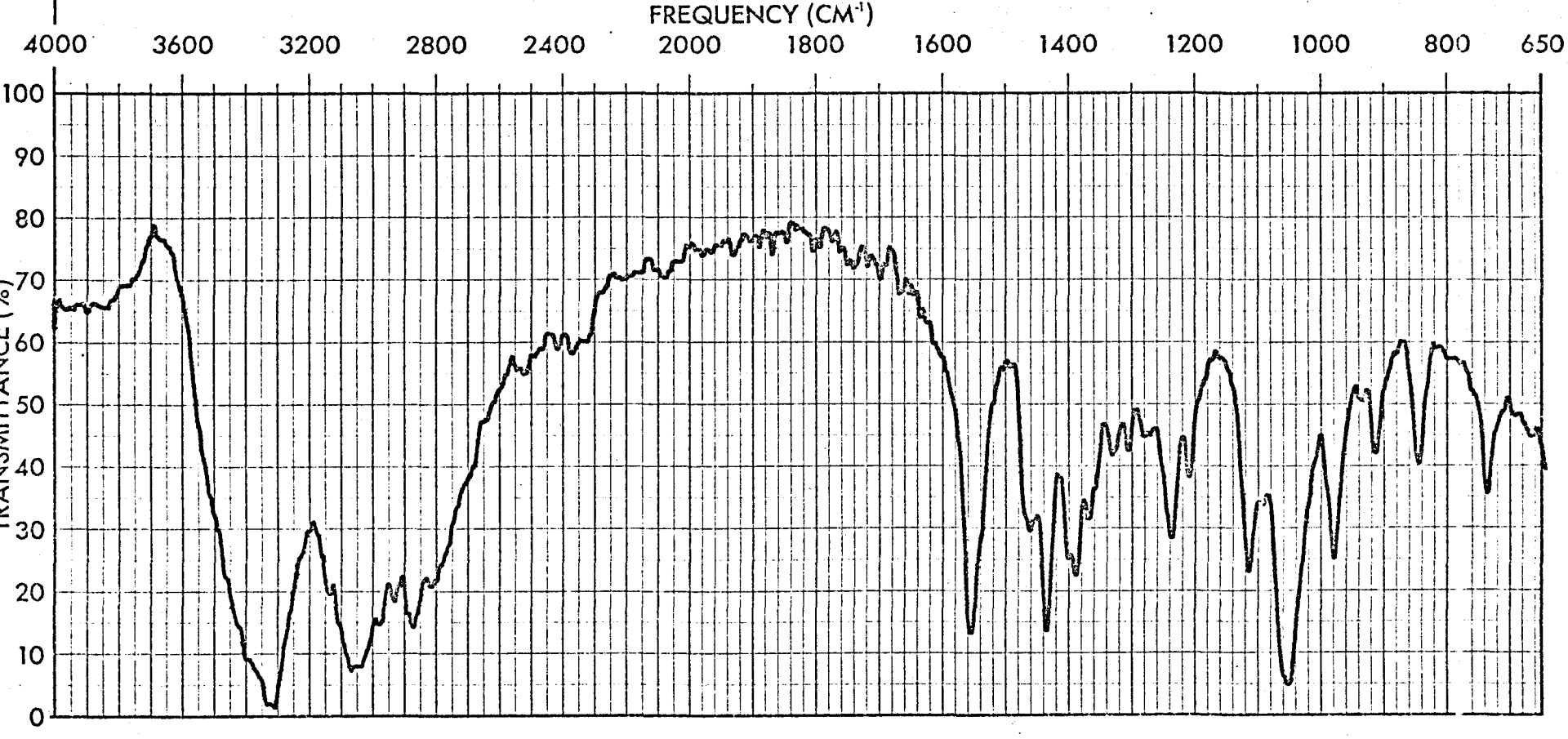
OPERATOR David H. POwell

PERKIN-ELMER
MODEL 700

SPECTRUM NO. 2

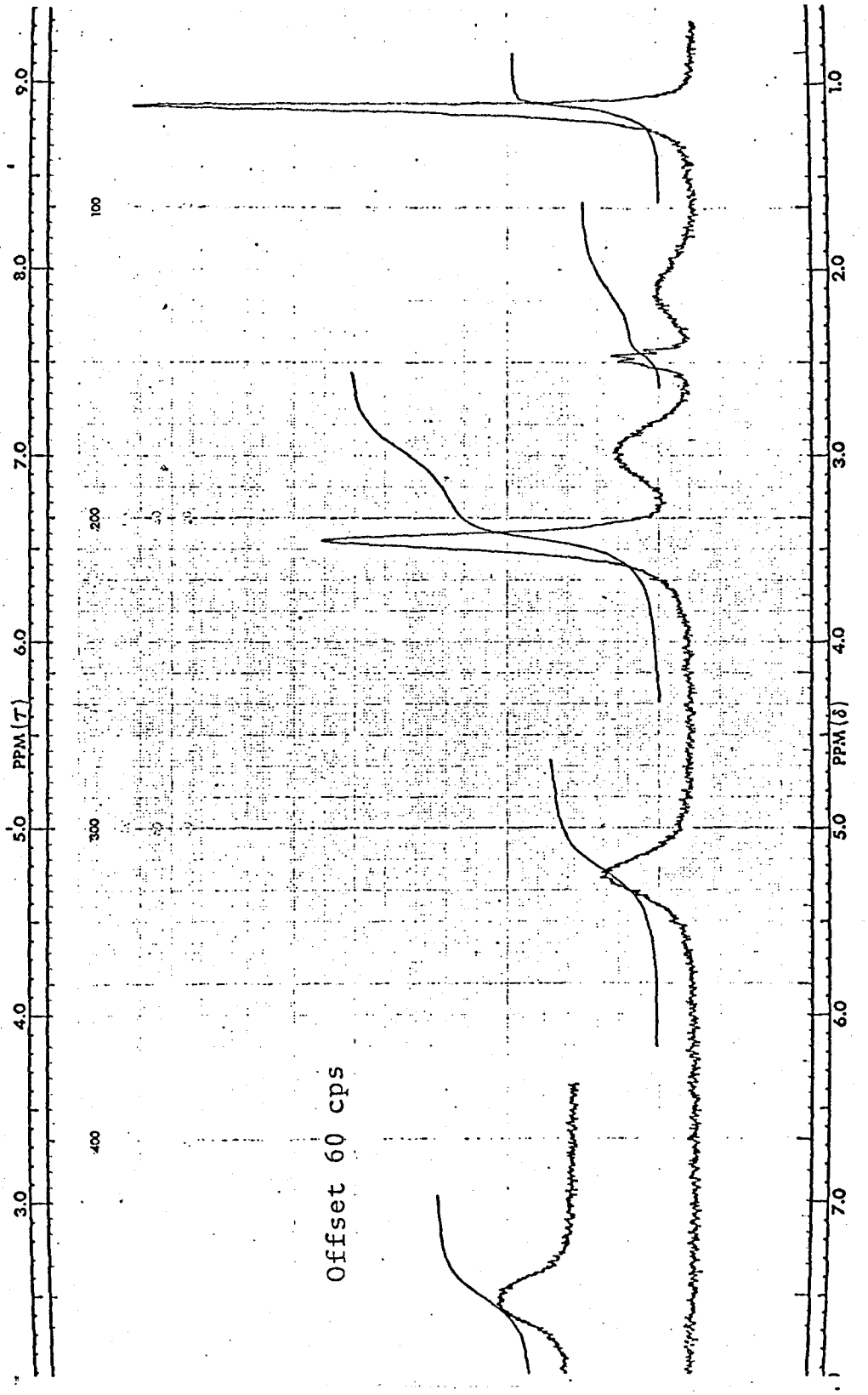
SAMPLE 1 COMPOUND 2

SAMPLE 2



SAMPLE COMPOUND 2 SPECTRUM NO. 2.

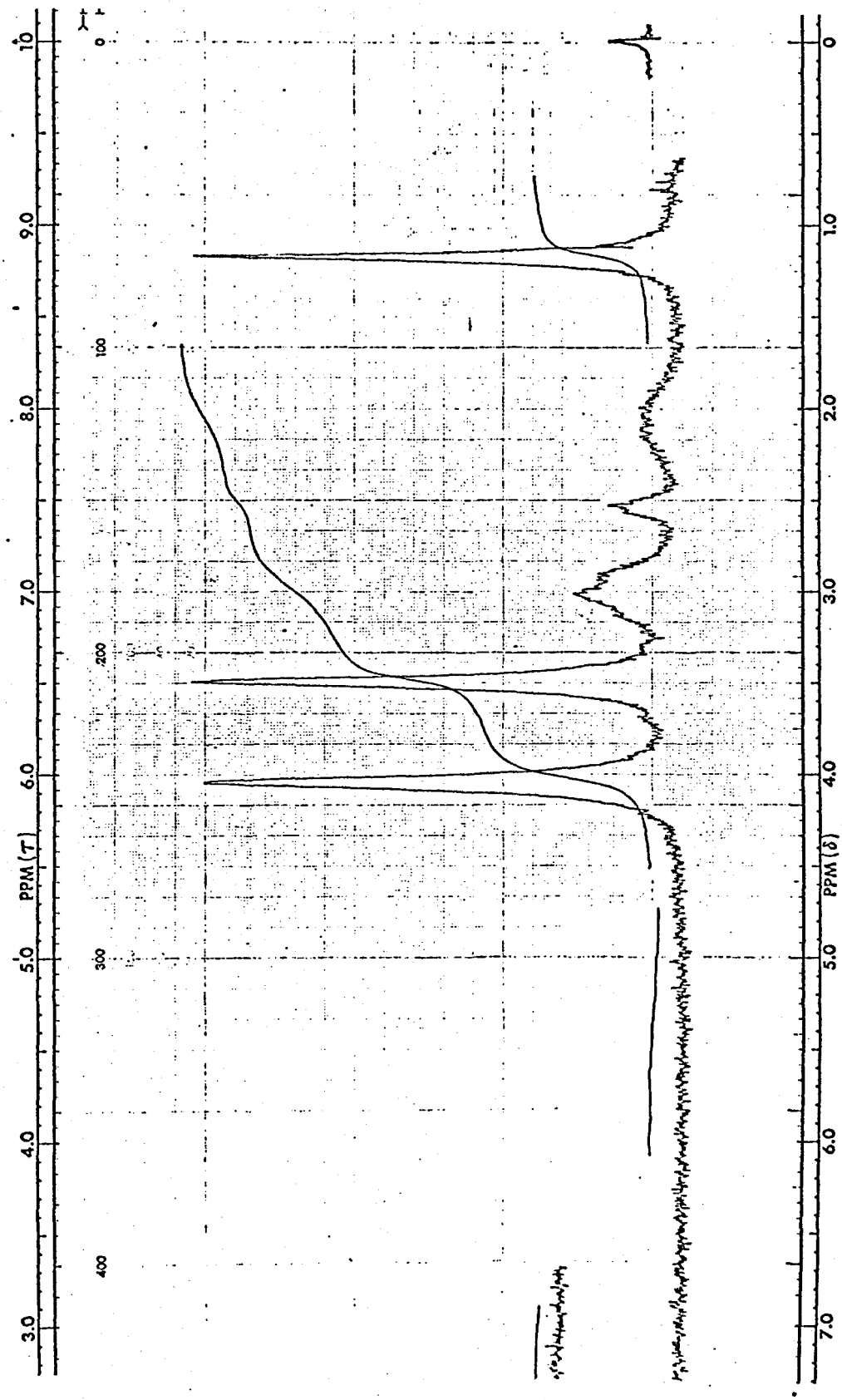
Nuclear Magnetic Resonance Spectrum of Compound 2 in Dimethyl Sulfoxide



(See page 20 for peak assignments.)

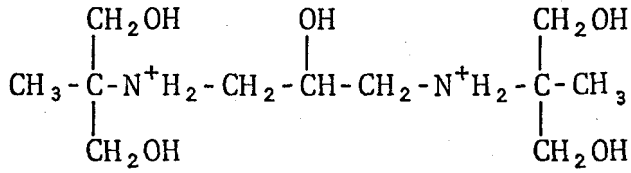
Nuclear Magnetic Resonance Spectrum of Compound 2

in Dimethyl Sulfoxide with D_2O added



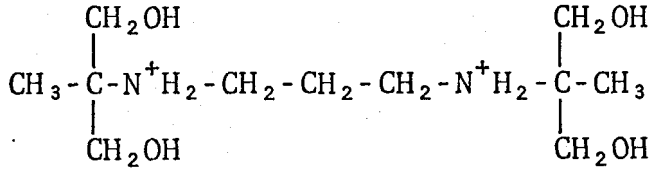
Peak assignments for the nmr spectra.

Compound 1



Functional Group	Chemical Shift	Integration
2 $-CH_3$	δ1.17	6 H
6 $-CH_2-$ and 1 CH	δ2.70 - δ3.90	13 H
central -OH	δ4.18	1 H
4 -OH	δ5.34	4 H
2 $-N^+H_2-$	δ7.70 - δ9.00	4 H

Compound 2



Functional Group	Chemical Shift	Integration
2 $-CH_3$	δ1.15	6 H
central $-CH_2-$	δ2.15	2 H
2 $-CH_2-$	δ3.02	4 H
4 $-CH_2-$	δ3.49	8 H
4 -OH	δ5.28	4 H
2 $-N^+H_2-$	δ8.54	4 H

The peaks at δ5.28 and δ8.54 are removed on addition of D_2O.

C. Spectral Studies

The absorbance of aqueous solutions containing constant overall concentrations of Cu^{2+} and Compound 1 was measured at various pH values. The molar absorptivity increases with pH. It was found that the wavelength maximum shifted from 618 nm. at pH = 4.3 to 597 nm. at pH = 11.80. (See spectra on page 23.) O'Rear (37) observed a similar shift and also carried out a Job's method of continuous variations for pH = 5.0 and at a wavelength of 610 nm. The point of maximum absorbance occurred at $\frac{(m)}{(m)+(L)}$ of 0.45 indicating a small amount of complex containing two moles of ligand per mole of copper (II) ion. The hypsochromic shift with increasing pH also indicates the formation of a small amount of this 2:1 complex.

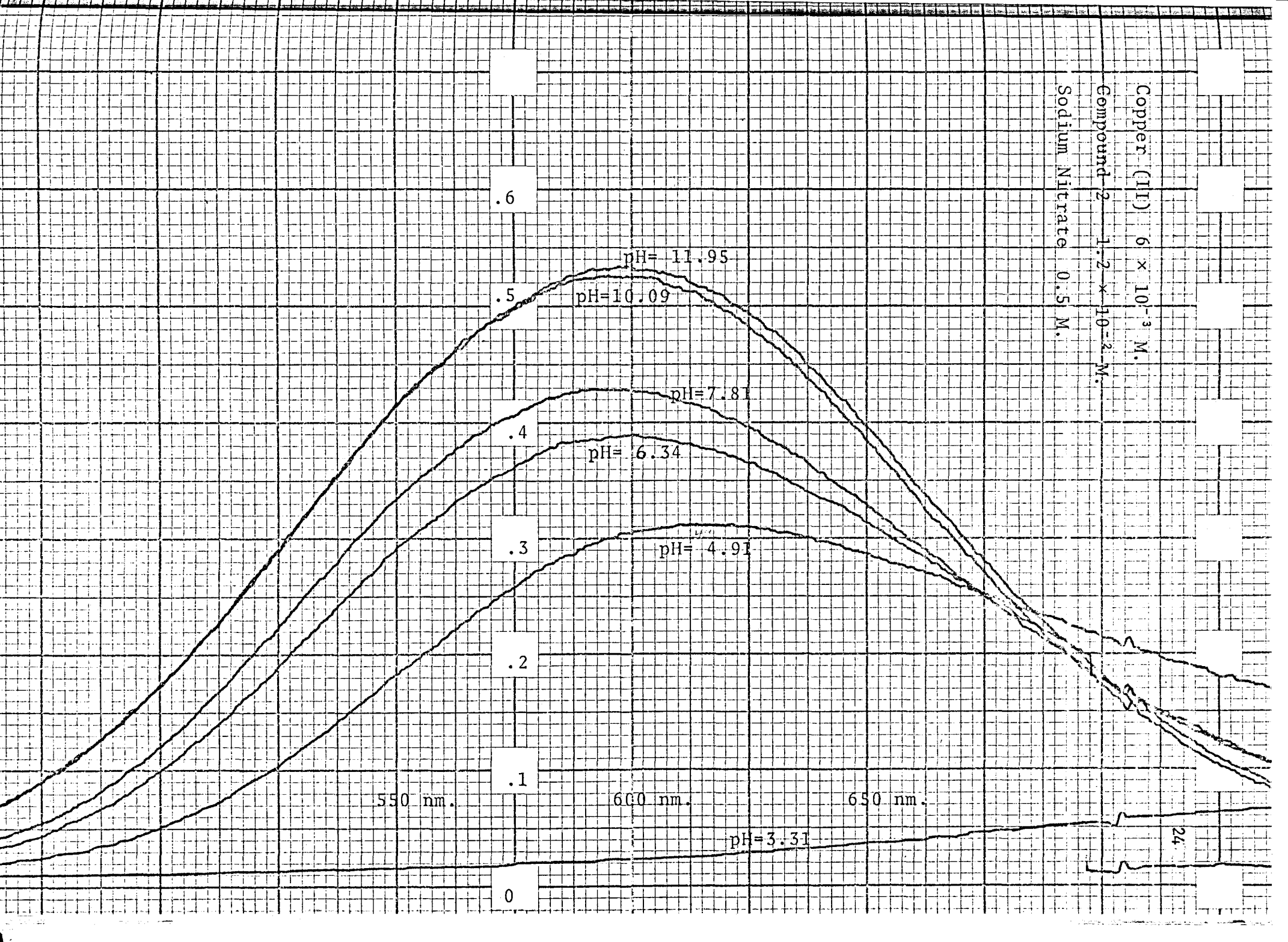
Compound 2 also exhibited this shift in absorption maximum with increasing pH. The point of maximum absorption shifted from 620 nm. at pH = 4.91 to 600 nm. at pH = 11.95. (See spectra on page 24.) A Job's method of continuous variations was also performed on Compound 2. The maximum absorbance occurred at $\frac{(m)}{(m)+(L)}$ at 0.48 indicating the presence of a small amount of complex containing two moles of Compound 2 per mole of copper (II). (See page 25.) Circles are used to emphasize the points on the Job's method graph and on all other graphs presented in this paper. The size

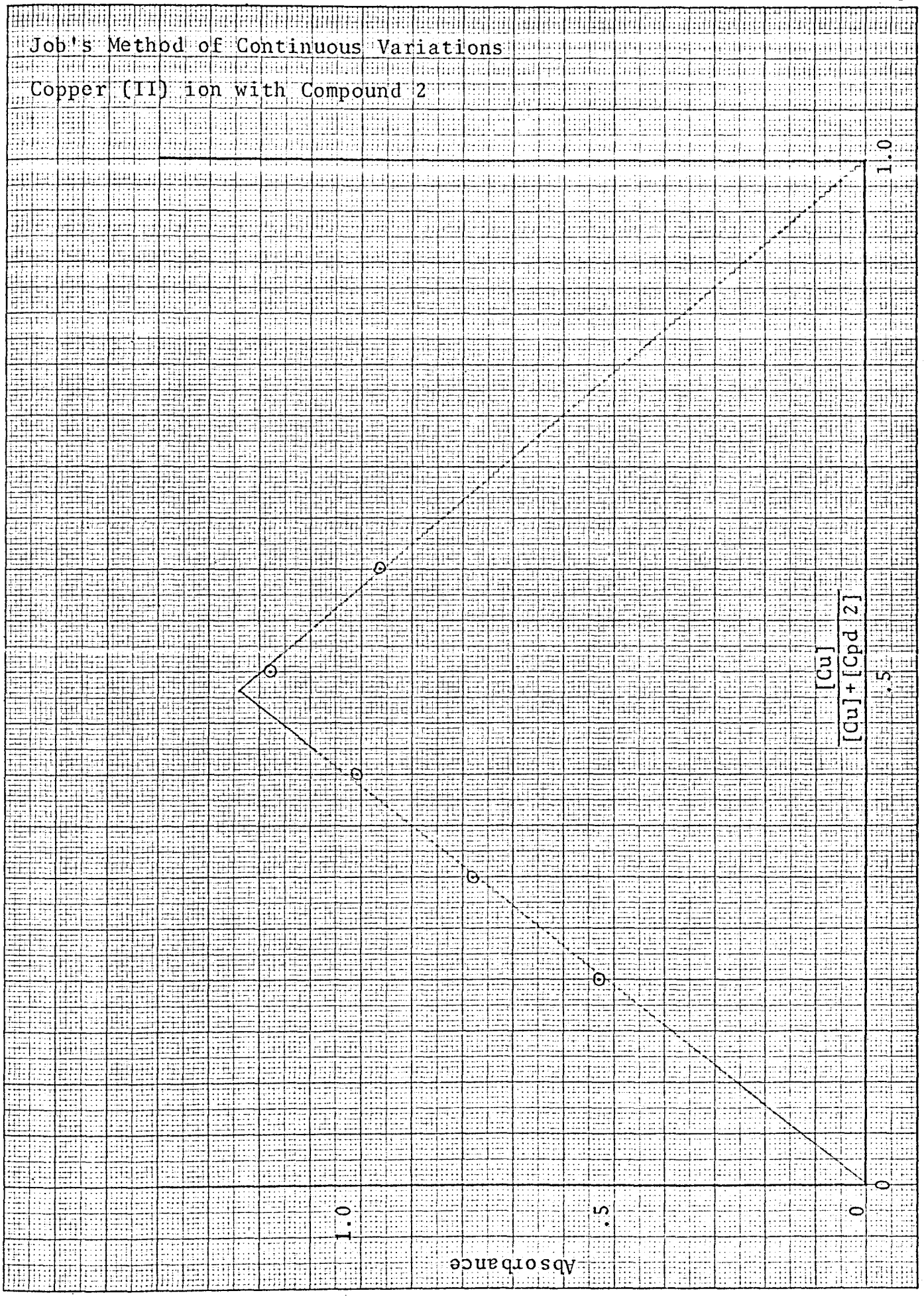
of the circles is not intended to indicate the precision of the measurements.

Copper (II) 6×10^{-3}M.

Compound 1 1.2×10^{-2}M.

Sodium Nitrate 0.5 M.


Copper (II) 6 × 10⁻³ M.
Compound 2 1.2 × 10⁻² M.
Sodium Nitrate 0.5 M.
.6
.5
.4
.3
.2
.1
0
pH= 11.95
pH=10.09
pH=7.81
pH= 6.34
pH= 4.91
pH=3.31
550 nm.
600 nm.
650 nm.
24


Job's Method of Continuous Variations
Copper (II) ion with Compound 2
Absorbance
0
.5
1.0
0
.5
1.0
[Cu] / [Cu] + [Cpd 2]

D. Basicity Constants of the Ligand

Both Compound 1 and Compound 2 can react with hydrogen ions in solution according to the following equations where Z represents the ligand species and H represents the hydrogen ions:

$$H + Z \longrightarrow HZ \qquad K^{H}_{HZ} = \frac{(HZ)}{(Z)(H)} \qquad (1)$$

$$HZ + H \longrightarrow H_2Z \qquad K^{H}_{H_2Z} = \frac{(H_2Z)}{(H)(HZ)} \qquad (2)$$

The overall reaction is

$$2H + Z \longrightarrow H_2Z \qquad \overline{K}^{H}_{H_2Z} = K^{H}_{HZ}\, K^{H}_{H_2Z} \qquad (3)$$

Since the above equilibria also occur when the ligand is in equilibrium with a metal ion in solution, the basicity constants K^{H}_{HZ} and $K^{H}_{H_2Z}$ must be determined for each ligand and are used in the calculation of the stability constants.

The basicity constants were determined by measuring the hydrogen-ion concentration in a solution containing known amounts of ligand, perchloric acid, sodium hydroxide, and sodium nitrate. The experiments were performed as titrations with sodium hydroxide starting with fixed amounts of ligand, perchloric acid, and sodium nitrate. The pH was measured at each point of the titration.

The derivation of the method of calculation (17) is as follows. The total ligand concentration $(Z)_t$ is defined by

$$(Z)_t = (Z) + (HZ) + (H_2Z) \qquad (4)$$

where (Z) is the free ligand concentration and (HZ) and (H_2Z) are the bound ligand concentrations.

The total hydrogen ion concentration $(H)_t$ is defined by

$$(H)_t = (Z)_t(2 - a) = (H) - (OH) + (HZ) + 2(H_2Z) \qquad (5)$$

where the 2 is the maximum number of hydrogen ions per ligand, i.e. m of H_mZ^{m+}, and a is the apparent degree of neutralization of hydrogen ions bound to the ligand. Let

$$g = \frac{(HZ) + 2(H_2Z)}{(Z)_t}. \qquad (6)$$

From equation (5)

$$(HZ) + 2(H_2Z) = (Z)_t(2 - a) - (H) + (OH). \qquad (7)$$

Substituting the right side of equation (7) for the numerator on the right side of equation (6), we obtain

$$g = (2 - a) + \frac{(OH) - (H)}{(Z)_t} \qquad (8)$$

which can be used for the calculation of g from the experimental titration curve.

From equation (4) we can substitute for $(Z)_t$ in equation (6) and obtain

$$g = \frac{(HZ) + 2(H_2Z)}{(Z) + (HZ) + (H_2Z)}$$

which on rearrangement gives

$$g(Z) + g(HZ) + g(H_2Z) = (HZ) + 2(H_2Z)$$

or

$$g(Z) + (g - 1)(HZ) + (g - 2)(H_2Z) = 0.$$

Dividing by (Z) yields

$$g + (g - 1)\frac{(HZ)}{(Z)} + (g - 2)\frac{(H_2Z)}{(Z)} = 0. \qquad (9)$$

From equations (1) and (3) we see that

$$\frac{[HZ]}{[Z]} = [H]K^{H}_{HZ} \quad \text{and} \quad \frac{[H_2Z]}{[Z]} = [H]^2\overline{K}^{H}_{H_2Z}$$

which can be substituted into equation (9) to give

$$g + (g - 1)(H)K^{H}_{HZ} + (g - 2)(H)^2\overline{K}^{H}_{H_2Z} = 0. \qquad (10)$$

Schwarzenbach used this equation to obtain the basicity constants by choosing pairs of points on the titration curve and setting up pairs of simultaneous equations and solving them by the method of determinants. Since the choice of points is somewhat arbitrary and points that are too close on the titration curve may be ill conditioned, a different method of solution was chosen.

Equation (10) may be rearranged to the form of a straight line $y = mx + b$.

$$g + (g - 1)(H)K^{H}_{HZ} = -(g - 2)(H)^{2}\bar{K}^{H}_{H_2Z}$$

$$\frac{g}{-(g - 2)(H)^{2}} = K^{H}_{HZ}\,\frac{(g - 1)}{(g - 2)(H)} + \bar{K}^{H}_{H_2Z}$$

$$y = m\,x + b$$

A computer program was written to calculate the values of x and y in the above equation for each titration. The computer used was the Wang Model 500, and the program and instructions for its use are presented in Appendix H.

For the linear regression analysis to calculate K^{H}_{HZ} and $\bar{K}^{H}_{H_2Z}$ a program from the Wang Program Library (19) was modified to give an output in scientific notation.

The values of the basicity constants of Compound 1 and Compound 2 are presented in the table below together with the 95% confidence interval of the determinations reported as the ± values after each constant.

	Compound 1	Compound 2
$\log K^{H}_{HZ}$	8.69 ± 0.03	9.51 ± 0.01
$\log K^{H}_{H_2Z}$	7.11 ± 0.03	7.68 ± 0.01
$\log \bar{K}^{H}_{H_2Z}$	15.80 ± 0.04	17.19 ± 0.00

E. Stability Constants

The stability constants were determined from potentiometric titrations with standard sodium hydroxide of solutions containing known amounts of ligand, metal ion, perchloric acid, and sodium nitrate. These solutions contained a ligand to metal ratio of 2:1. The sodium nitrate was added to avoid difficulties due to changes in activity coefficients. Several titrations were carried out for each ligand, and all titrations were performed in an atmosphere of nitrogen and at a temperature of 30°C. A Beckman research pH meter was used, and the variable speed magnetic stirrer was turned off each time a pH reading was taken. The data for the stability constant titrations are presented in Appendix E for Compound 1 and in Appendix G for Compound 2.

The method used to calculate the stability constants is essentially the method derived by Bjerrum (6) and later used by Schwarzenbach and Baur (44). Their approach involved the determination of the complex formation curve, $\bar{n}$ vs pZ where $\bar{n}$ is the average number of ligand molecules bound per metal ion and pZ is the logarithm of the ligand concentration. Irving and Rossotti (25) modified and improved Bjerrum's method by rearranging his equations to the form of a straight line and obtaining the stability constants from a linear regression analysis.

The derivation of the method is as follows. Various functions are first defined.

$$(M)_t = (M) + (MZ) + (MZ_2) \qquad (1)$$

where $(M)_t$ = the total metal concentration

(M) = the free metal ion concentration

(MZ) = the concentration of metal bound to one ligand

(MZ_2) = the concentration of metal bound to two ligands

$$(Z)_t = (Z) + (MZ) + 2(MZ_2) \qquad (2)$$

where $(Z)_t$ = the total ligand concentration

$$\alpha = 1 + [H]\cdot K^H_{HZ} + [H]^2 \overline{K}^H_{H_2Z} \qquad (2a)$$

(Z) = the free ligand concentration

$$(H)_t = 2(Z)_t - (NaOH) = (H) - (OH) + \beta(Z) \qquad (3)$$

where $(NaOH)$ = the concentration of NaOH added during the titration

$$(NaOH) = \frac{(\text{ml. of NaOH})(\text{Normality of NaOH})}{(\text{Volume of Solution})}$$

$$\beta = H\, K^H_{HZ} + 2(H)^2 \overline{K}^H_{H_2Z}$$

Substitution from the definition of K^H_{HZ} and $\overline{K}^H_{H_2Z}$ yields

$$\beta = \frac{(HZ) + 2(H_2Z)}{(Z)} \qquad (4)$$

Similarly we can substitute from the definitions of K^{H}_{HZ} and $\bar{K}^{H}_{H_2Z}$ into equation (2a) for α

$$\alpha = \frac{(Z) + (HZ) + (H_2Z)}{(Z)} \tag{5}$$

Substituting for β in equation (3) and solving for (Z), we obtain

$$(Z) = \frac{2(Z)_t - (NaOH) - (H) + (OH)}{(H)K^{H}_{HZ} + 2(H)^2\bar{K}^{H}_{H_2Z}} \tag{6}$$

Since all the quantities on the right-hand side of equation (6) can be determined experimentally, (Z) can be obtained.

The average number of ligands bound per metal ion $\bar{n}$ is defined by

$$\bar{n} = \frac{(MZ) + 2(MZ_2)}{(M)_t} \tag{7}$$

By rearranging equation (2) and substituting into equation (7), $\bar{n}$ can be readily calculated from

$$\bar{n} = \frac{(Z)_t - \alpha(Z)}{(M)_t} \tag{8}$$

Once the formation curve $\bar{n}$ vs pZ is available the stability constants can be obtained from a number of calculation techniques. The stability constants for the following reactions are defined by

$$Z + M \longrightarrow MZ \qquad K^{M}_{MZ} = \frac{[MZ]}{[M][Z]} \tag{9}$$

$$Z + MZ \longrightarrow MZ_2 \qquad K^{M}_{MZ_2} = \frac{[MZ_2]}{[MZ][Z]} \tag{10}$$

The overall reaction is

$$2Z + M \longrightarrow MZ_2 \qquad \bar{K}^{M}_{MZ_2} = \frac{[MZ_2]}{[MZ][Z]} \tag{11}$$

$$\bar{K}^{M}_{MZ_2} = K^{M}_{MZ} K^{M}_{MZ_2}$$

Using these definitions and equations (1) and (7) the following function can be derived

$$\bar{n} + (\bar{n} - 1)(Z)K^{M}_{MZ} + (\bar{n} - 2)(Z)^2\bar{K}^{M}_{MZ_2} = 0.$$

Irving and Rossotti (25) rearrange this equation to the form of a straight line

$$\frac{\bar{n}}{(\bar{n} - 1)(Z)} = \frac{(2 - \bar{n})(Z)}{(\bar{n} - 1)} \bar{K}^{M}_{MZ_2} - K^{M}_{MZ}$$

The method of "least squares" was used to determine the slope, $\bar{K}^{M}_{MZ_2}$, and the intercept, $-\bar{K}^{M}_{MZ}$, for two reasons:

1. The value of (Z) varies over several powers of ten during titrations to determine $\bar{n}$ and (Z) which makes graphical solution difficult.
2. The method of "least squares" avoids subjective "smoothing" of the data and makes use of all the data.

The one disadvantage of this method of solution is due to the fact that the function $\bar{n}/(\bar{n} - 1)$ and $(2 - \bar{n})/(\bar{n} - 1)$ become very large in the center of the curve where $0.95 < n < 1.05$, and any small experimental errors in $\bar{n}$ have a large effect on the functions. Therefore, points in this small region were rejected.

Appendix H contains a sample calculation of the stability constants for Compound 1 and Compound 2 with copper (II) ion, and the 95% confidence interval is reported as the ± values.

	Compound 1	Compound 2
$\log K^{M}_{MZ}$	9.90 ± 0.14	10.62 ± 0.06
$\log K^{M}_{M_2Z}$	6.09 ± 0.18	7.50 ± 0.17
$\log \bar{K}^{M}_{M_2Z}$	15.98 ± 0.13	17.12 ± 0.25

IV. DISCUSSION

There are three sources of evidence for the formation of both the 1:1, ligand to metal, complex and the 2:1, ligand to metal, complex of Compound 1 and Compound 2 with Cu (II) ion:

1. The shift of the absorption maxima toward shorter wavelengths with increasing pH indicates structural changes in the complex consistent with formation of a 2:1 complex at higher pH. If only the 1:1 complex formed the molar absorptivity would increase with pH, but the position of absorption maxima would remain constant. The absorption maxima would shift to the shorter wavelengths with the formation of a 2:1 complex due to increased ligand field splitting.

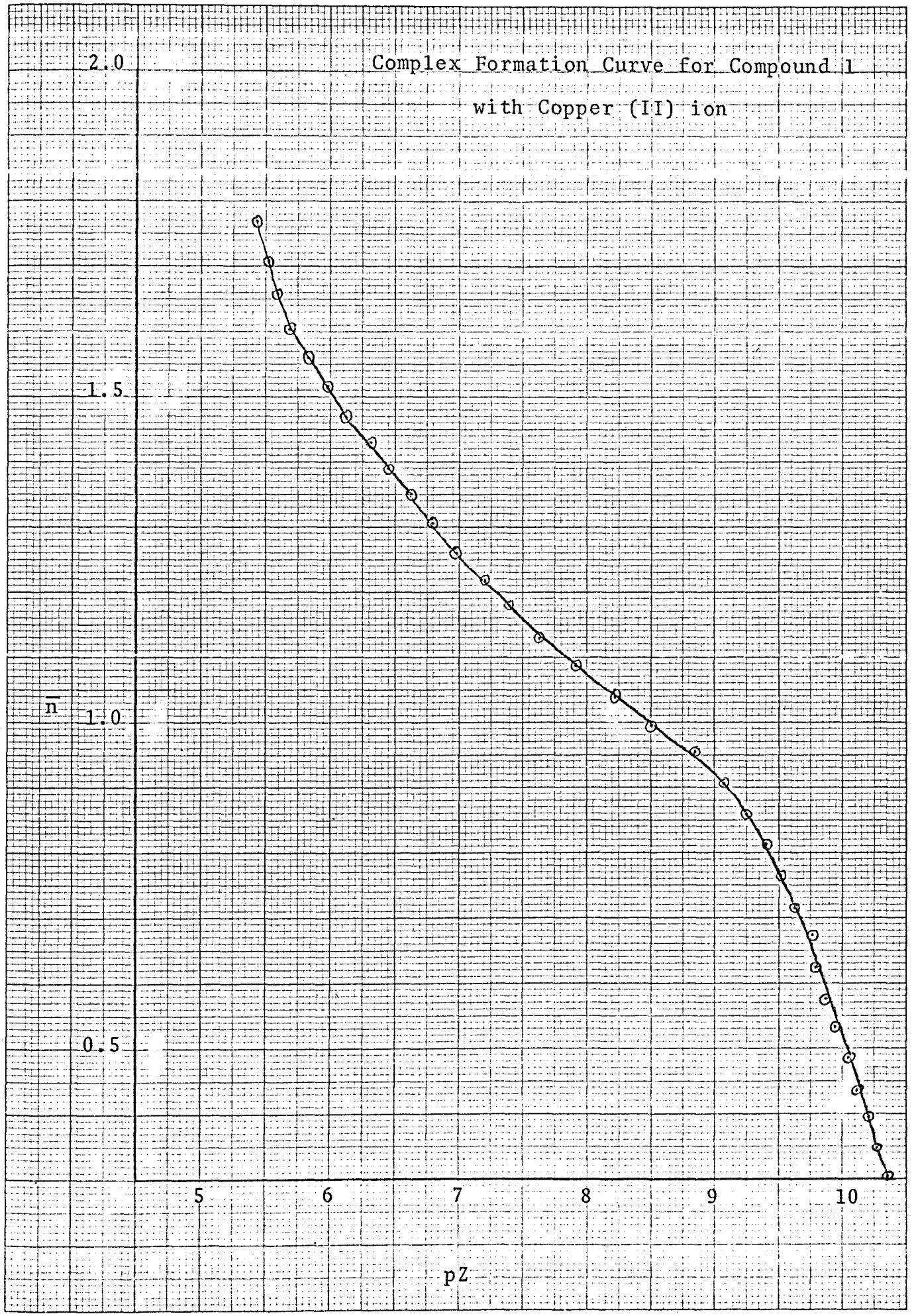
2. In the Job's method, determination of the metal to ligand ratio at maximum absorbance indicates that a small amount of the 2:1 complex forms.

3. Strong evidence for the formation of the 2:1 complex is obtained from complex formation curves, the plots of $\bar{n}$ vs. pZ where $\bar{n}$ is the average number of ligands bound per metal ion and pZ is -log(Z). If $\bar{n} > 1$, then some of the 2:1 complex has to form. The complex formation curves for Compound 1 and Compound 2 with Cu (II) ion are presented on the following pages.

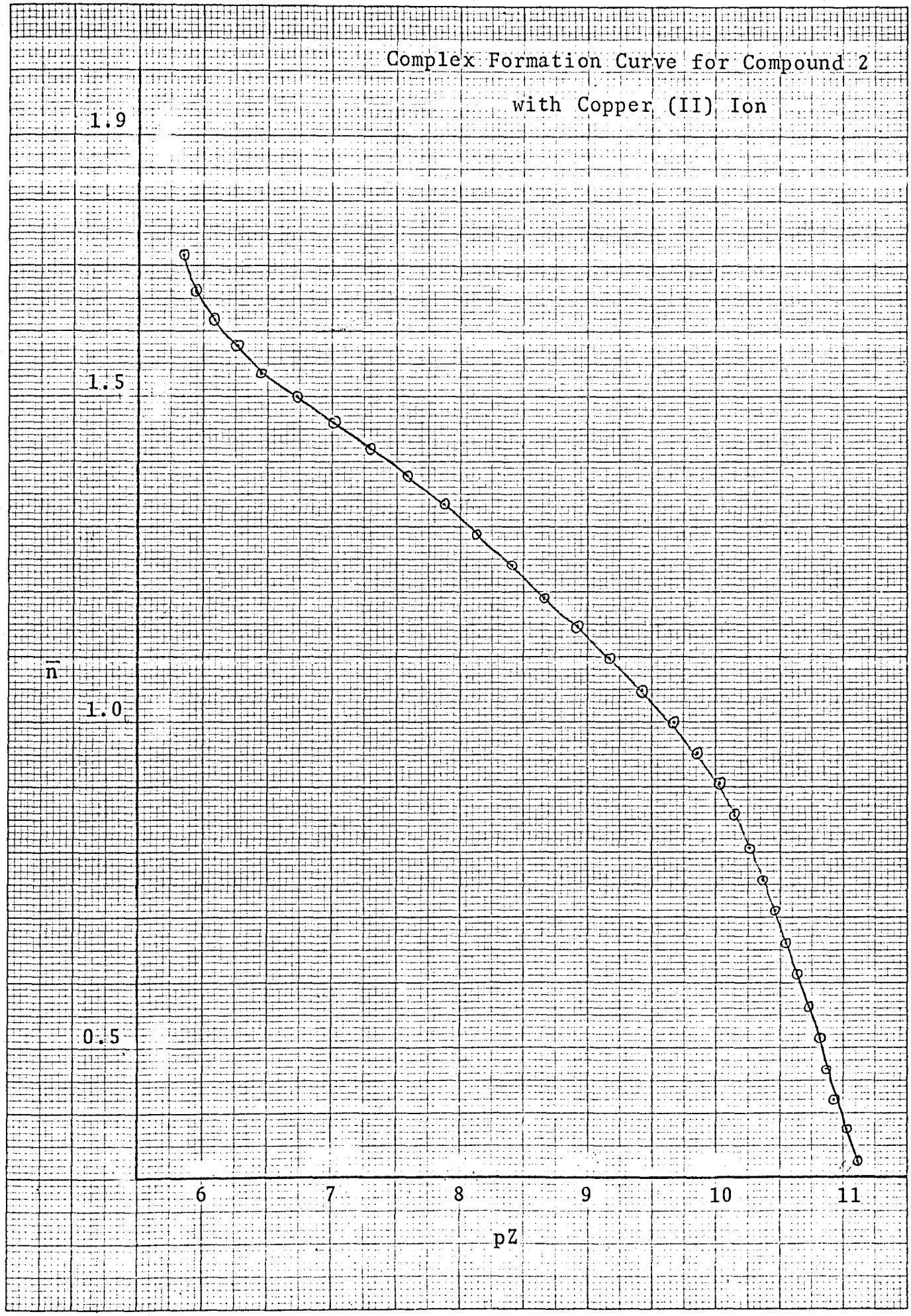
Evidence for the formation of both 1:1 and 2:1 complexes of Compound 1 and Compound 2 with Cu (II) ion is consistent with studies of other diamines and polyhydroxyamines of similar structures with Cu (II) ion. Several examples from the literature are presented in Table I. The values for the stability constants of the compounds in Table I with Cu (II)

Complex Formation Curve for Compound 1

with Copper (II) ion



Complex Formation Curve for Compound 2
with Copper (II) Ion



ion are also presented and are of the same order of magnitude as those calculated for the complexes of Compound 1 and Compound 2.

Table I. Example Compounds from the Literature

		Temperature	Reference
1.	N,N'Dimethylethylenediamine		
	CH_3-NH-CH_2-CH_2-NH-CH_3		
	Cu (II) Z log K_1 = 10.47	25°C.	(15)
	Cu (II) Z_2 log K_2 = 7.63		
2.	N,N'Di-n-propylethylenediamine		
	CH_3-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-CH_3		
	Cu (II) Z log K_1 = 9.30	25°C.	(15)
	Cu (II) Z_2 log K_2 = 6.32		
3.	N-(2-Hydroxyethyl)ethylenediamine		
	HO-CH_2-CH_2-NH-CH_2-CH_2-NH_2		
	Cu (II) Z log K_1 = 10.11	25°C.	(34)
	Cu (II) Z_2 log K_2 = 7.51		
4.	N,N'-Di(2hydroxyethyl)ethylenediamine		
	HO-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-OH		
	Cu (II) Z log K_1 = 9.77	25°C.	(23)
	Cu (II) Z_2 log K_2 = 5.84		
5.	Trimethylenediamine		
	H_2N-CH_2-CH_2-CH_2-NH_2		
	Cu (II) Z log K_1 = 9.62	30°C.	(24)
	Cu (II) Z_2 log K_2 = 7.00		

6. 2,2-Dimethyl-1,3-diaminopropane

$H_2N\text{-}CH_2\text{-}C(CH_3)_2\text{-}CH_2\text{-}NH_2$

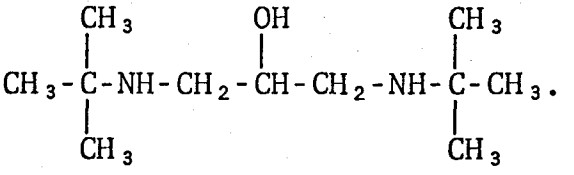
Cu (II) Z $\log K_1 = 9.94$ 30°C. (24)

Cu (II) Z_2 $\log K_2 = 7.45$

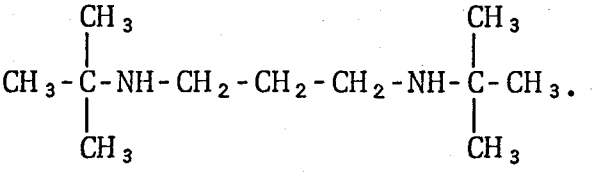
Bertsch, Block, and Fernelius (4,5) studied the coordination properties of 1,3-diamino-2-propanol with Cu (II) ion and reported that only the 1:1 ligand to metal complex formed with the ligand being terdentate.

A comparison of the stability constants of Compound 1 and Compound 2 indicates that the central hydroxy group decreases the stability of Cu (II) complex probably because of the inductive effect of the electronegative oxygen atom. The oxygen withdraws electron density from the nitrogen atoms and decreases their ability to coordinate. The fact that Compound 2 forms a more stable complex with Cu (II) than Compound I with Cu (II) is just the opposite from what would be expected if the central hydroxy group of Compound 1 were involved in chelation.

It would be interesting to study the effect of the terminal hydroxy groups by comparing the stability constants of the Cu (II) complexes of Compound 1 and Compound 2 with their respective analogs containing no terminal hydroxy groups. One of these compounds has been synthesized by Davis (14)



The other compound could be easily synthesized



Nuclear magnetic resonance studies with the europium shift reagents might also shed some light on the configuration of the ligands in complexes and help explain the effect of the central hydroxy group.

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APPENDIX A

Procedure for the Synthesis of 2,8-Bishydroxymethyl-2,8-dimethyl-3,7-diaza-1,5,9-nonanetriol

Compound 1 was prepared by a method similar to that proposed by O'Rear (37). A slurry was made containing two moles (210 grams) of 2-amino-2-methyl-1,3-propanediol in 200 ml. of absolute ethanol. The mixture was placed in a 1000 ml. three necked ground glass round bottom flask with a thermometer and reflux condenser in the side arms. A separatory funnel containing one mole (92.5 grams) of epichlorohydrin diluted with 20 ml. of absolute ethanol was placed in the center neck of the flask, and the epichlorohydrin-ethanol mixture was added to the flask in small increments. After each addition of epichlorohydrin, the flask was shaken vigorously and placed in an ice-water bath to insure that the temperature of the mixture was kept below 20°C.

After the final addition of epichlorohydrin, the mixture was shaken for twenty minutes and then refluxed on a water bath for seven hours. During the reflux period, the mixture was stirred constantly using a magnetic stirrer. When the refluxing was finished, the mixture was allowed to stand overnight at room temperature. Hydrogen chloride gas was bubbled through the solution for fifteen minutes, and most of the ethanol was removed by distillation. A viscous light tan syrup was obtained at this point.

Compound 1 was obtained by dissolving small portions of syrup heated to 50°C. in cold absolute ethanol and allowing the mixture to cool in an ice-water bath. The crystals obtained were washed with absolute ethanol and recrystallized several times. The yield of Compound 1 was approximately 60%.

The melting point of the white crystals was determined by using a Thomas Hoover capillary melting point apparatus. Compound 1 melted sharply at 198-199°C.

APPENDIX B

Procedure for the Synthesis of 2,8-Bishydroxymethyl-2,8-dimethyl-3,7-diaza-1,9-nonanediol

A slurry was made containing two moles (210 grams) of 2-amino-2-methyl-1,3-propanediol in 200 ml. of absolute ethanol. The mixture was placed in a 1000 ml. three necked ground glass round bottom flask with a thermometer and reflux condenser in the side arms. A separatory funnel containing one mole (113 grams) of 1,3-dichloropropane diluted with 20 ml. of absolute ethanol was placed in the center neck of the flask, and the 1,3-dichloropropane-ethanol mixture was added in small increments. After each addition of 1,3-dichloropropane, the flask was shaken vigorously and placed in an ice-water bath to insure that the temperature of the mixture was kept below 20°C.

After the final addition of 1,3-dichloropropane, the mixture was shaken for twenty minutes and then refluxed on a water bath for seven hours. During the reflux period the mixture was stirred constantly using a magnetic stirrer. When the refluxing was finished, the mixture was allowed to stand overnight at room temperature. The mixture was transferred to 2000 ml. beaker and hydrogen chloride gas was bubbled through the solution for fifteen minutes.

Crystallization of Compound 2 proved to be the most difficult phase of the synthesis, since the methods used in the crystallization of Compound 1 proved ineffective when applied

to Compound 2; however, the following technique was successful. The volume of the solution was reduced by one-half by distillation of the ethanol. A viscous light tan syrup was obtained at this point. Portions of the syrup were dissolved in as small amounts of absolute ethanol as possible, and petroleum ether was added dropwise to the solution until the point was reached where a thick white sludge appeared on the surface with each addition of petroleum ether. Precipitation was achieved by cooling the solution while also bubbling hydrogen chloride gas through the solution.

The white crystals obtained were washed with absolute ethanol and recrystallized several times. The yield of Compound 2 was approximately 60%. The melting point of the crystals was determined by using a Thomas Hoover capillary melting apparatus. Compound 2 melted sharply at 164-165°C.

APPENDIX C

Preparation and Standardization of Stock Solutions

1. Compound 1

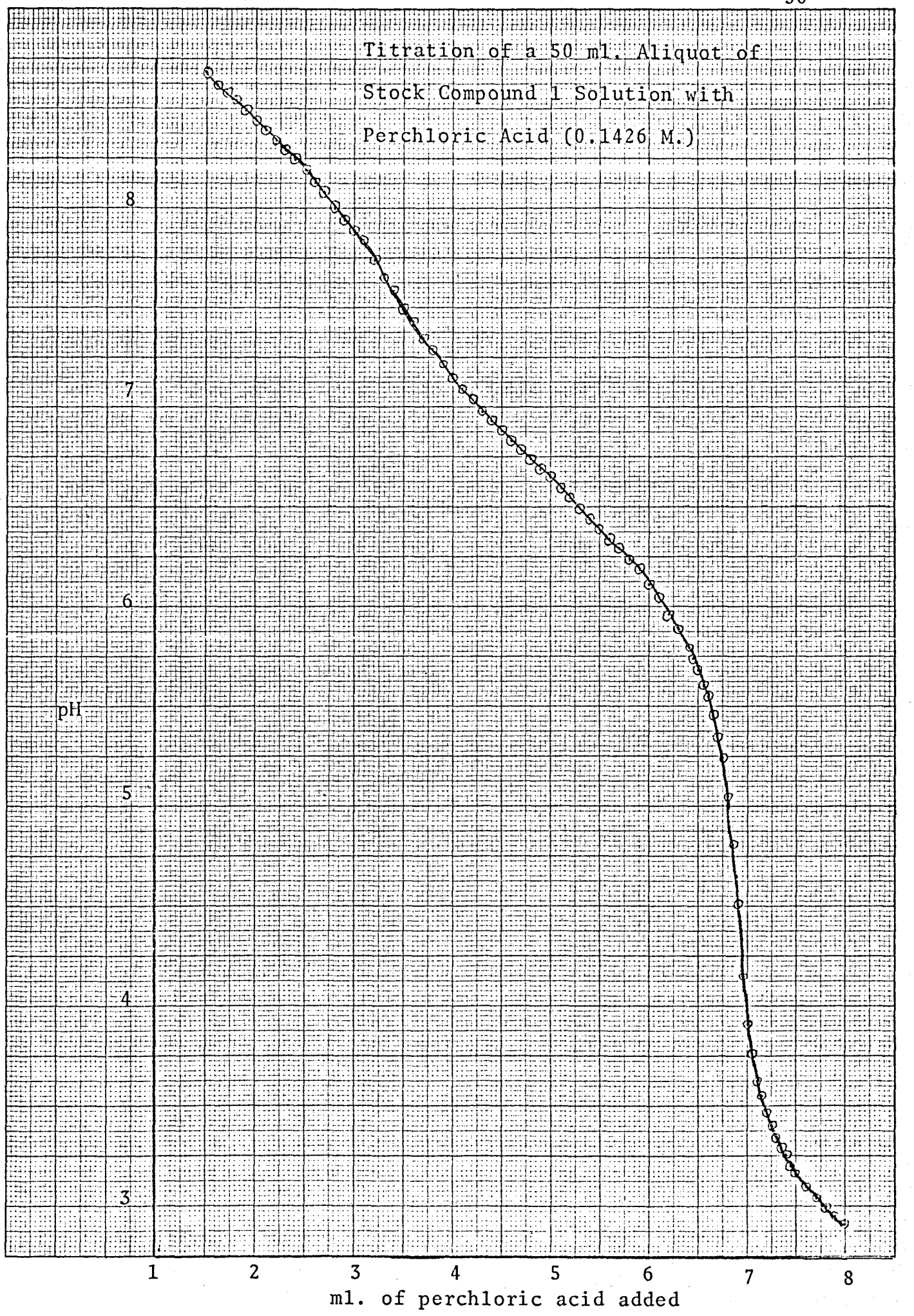
A solution was prepared using 3.4 grams of the dihydrochloride salt of Compound 1 diluted with distilled water to a one liter volume. This solution was then passed through a column containing Amberlite IRA-400 in the OH^- form to convert the hydrochloride to the free base. The column had previously been washed several times with distilled water. 50 ml. aliquots were taken from the resulting solutions and were titrated with a 0.1426 M. perchloric acid solution that had previously been standardized. (See Appendix C-4.)

Two runs were made, and the data were plotted differentially in order to obtain the end point. The data and calculations are presented on the following pages.

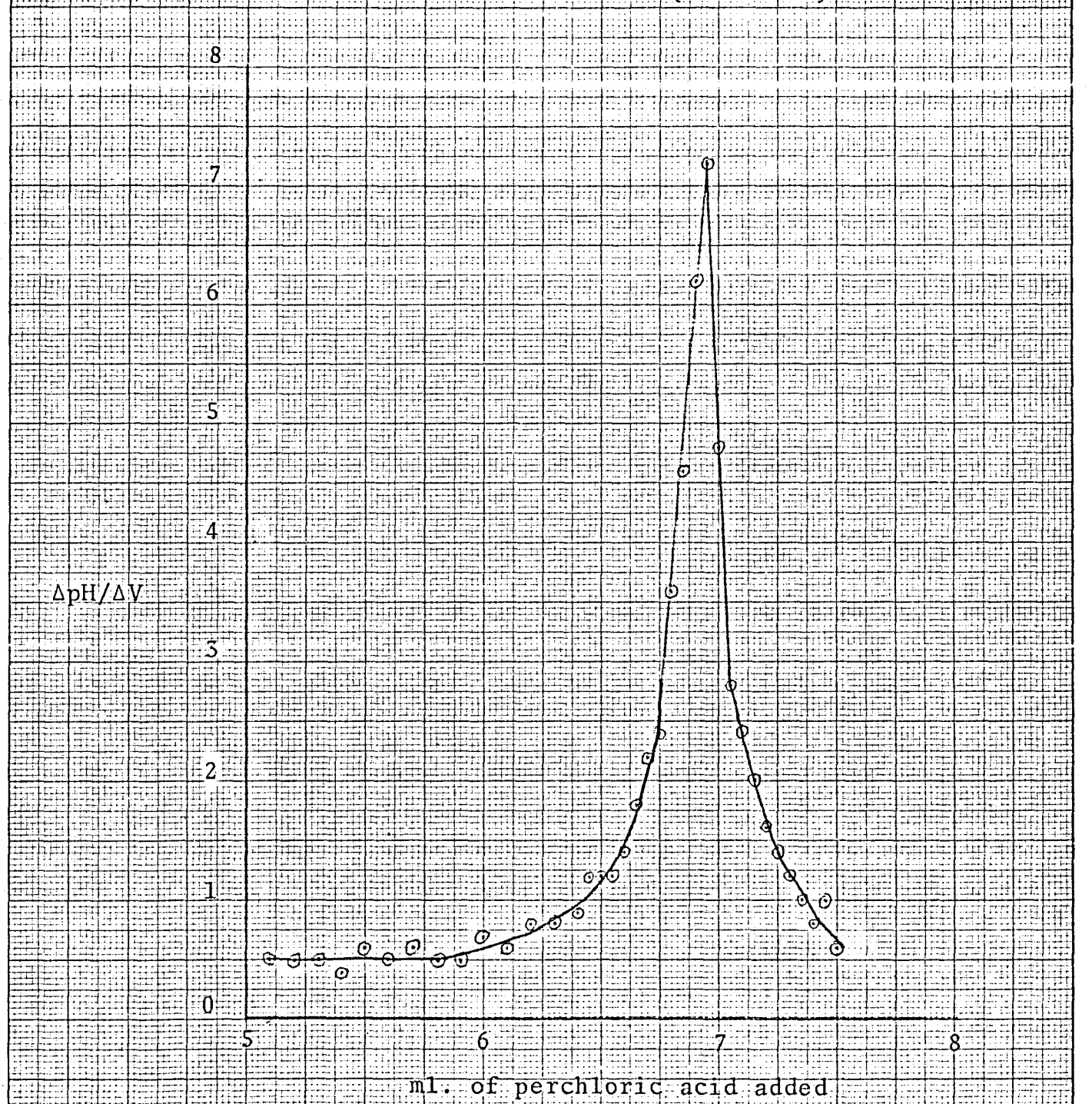
A small aliquot of Compound 1 stock solution was also tested for the presence of chloride ion. No chloride ion was detected.

Titration of a 50 ml. Aliquot of Stock Compound 1 Solution with Perchloric Acid (0.1426 M)

ml. of $HClO_4$ added	pH	ml. of $HClO_4$ added	pH	ml. of $HClO_4$ added	pH
0.00	9.93	3.30	7.65	6.50	5.68
0.10	9.75	3.40	7.58	6.55	5.62
0.20	9.60	3.50	7.49	6.60	5.55
0.30	9.49	3.60	7.43	6.65	5.46
0.40	9.39	3.70	7.35	6.70	5.35
0.50	9.29	3.80	7.29	6.75	5.23
0.60	9.21	3.90	7.22	6.80	5.05
0.70	9.13	4.00	7.15	6.85	4.82
0.80	9.07	4.10	7.09	6.90	4.51
0.90	9.00	4.20	7.04	6.95	4.15
1.00	8.94	4.30	6.98	7.00	3.91
1.10	8.89	4.40	6.93	7.05	3.77
1.20	8.83	4.50	6.88	7.10	3.65
1.30	8.78	4.60	6.83	7.15	3.55
1.40	8.73	4.70	6.78	7.20	3.47
1.50	8.68	4.80	6.73	7.25	3.40
1.60	8.63	4.90	6.68	7.30	3.34
1.70	8.58	5.00	6.64	7.35	3.29
1.80	8.54	5.10	6.59	7.40	3.25
1.90	8.49	5.20	6.54	7.45	3.20
2.00	8.44	5.30	6.49	7.50	3.17
2.10	8.39	5.40	6.45	7.60	3.10
2.20	8.34	5.50	6.39	7.70	3.04
2.30	8.30	5.60	6.34	7.80	2.99
2.40	8.24	5.70	6.29	7.90	2.95
2.50	8.19	5.80	6.23	8.00	2.91
2.60	8.13	5.90	6.18		
2.70	8.07	6.00	6.11		
2.80	8.00	6.10	6.05		
2.90	7.94	6.20	5.97		
3.00	7.88	6.30	5.89		
3.10	7.80	6.40	5.80		
3.20	7.73	6.45	5.74		

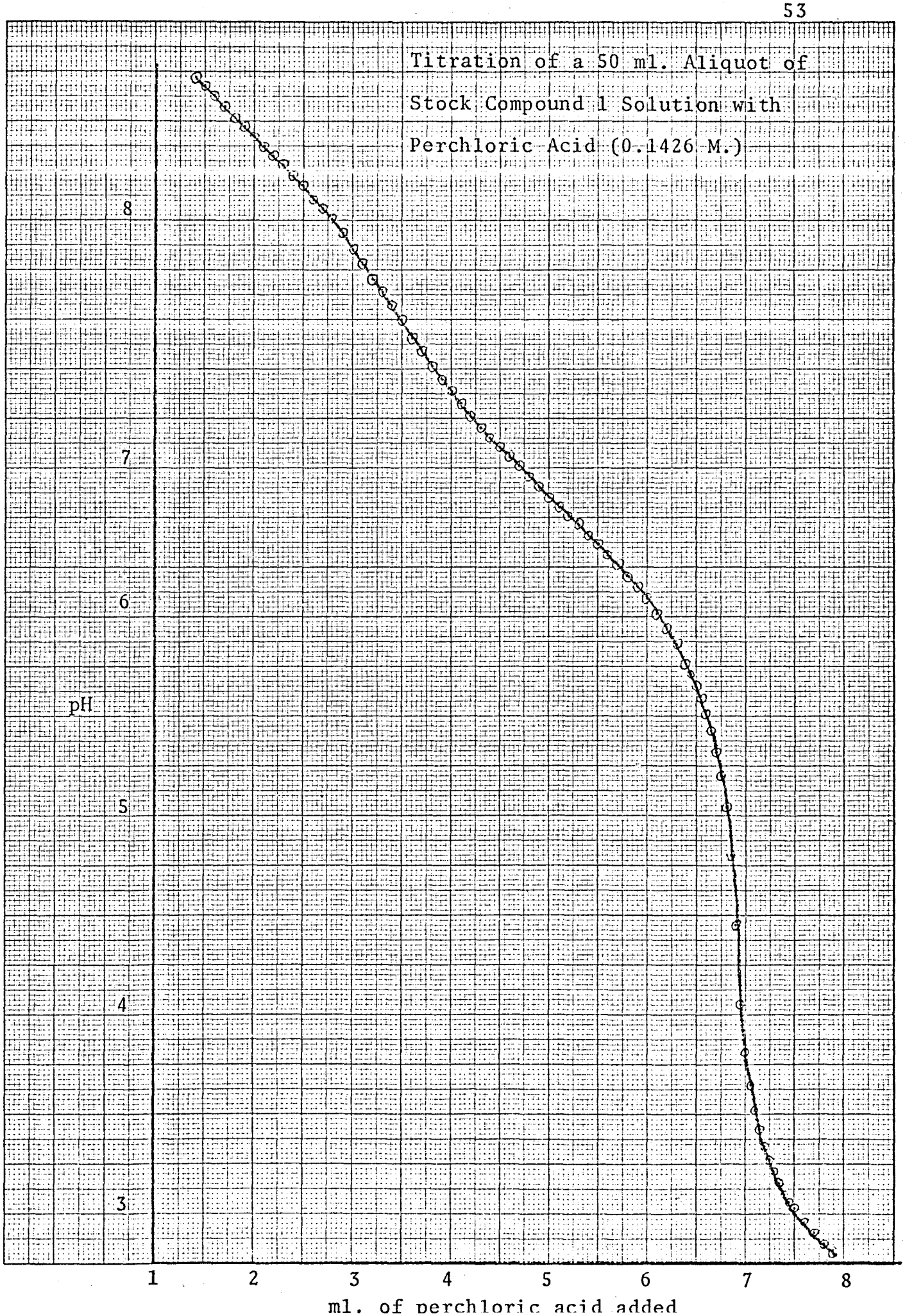

Titration of a 50 ml. Aliquot of
Stock Compound 1 Solution with
Perchloric Acid (0.1426 M.)
pH
8
7
6
5
4
3
1
2
3
4
5
6
7
8
ml. of perchloric acid added

Differential Plot of the Titration of a 50 ml. Aliquot of Stock Compound 1 Solution with Perchloric Acid (0.1426 M.)

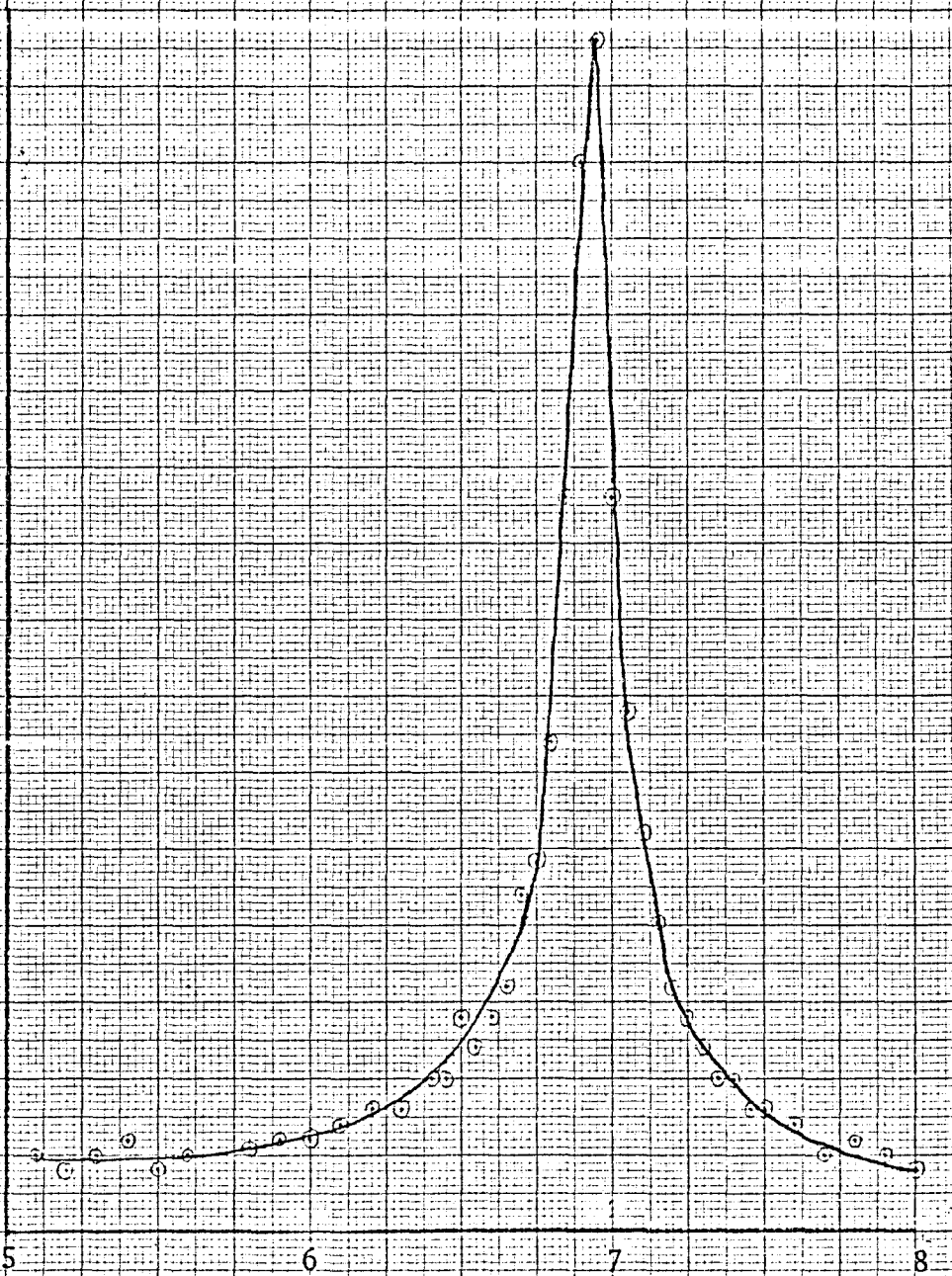


Titration of a 50 ml. Aliquot of Stock Compound 1 Solution with Perchloric Acid (0.1426 M)

ml. of $HClO_4$ added	pH	ml. of $HClO_4$ added	pH	ml. of $HClO_4$ added	pH
0.00	10.00	3.10	7.79	6.20	5.94
0.10	9.79	3.20	7.71	6.30	5.86
0.20	9.63	3.30	7.64	6.40	5.76
0.30	9.50	3.40	7.57	6.45	5.71
0.40	9.39	3.50	7.49	6.50	5.64
0.50	9.29	3.60	7.41	6.55	5.58
0.60	9.21	3.70	7.34	6.60	5.51
0.70	9.13	3.80	7.27	6.65	5.43
0.80	9.07	3.90	7.20	6.70	5.32
0.90	9.00	4.00	7.14	6.75	5.20
1.00	8.94	4.10	7.08	6.80	5.04
1.10	8.89	4.20	7.01	6.85	4.80
1.20	8.83	4.30	6.96	6.90	4.45
1.30	8.78	4.40	6.91	6.95	4.06
1.40	8.73	4.50	6.86	7.00	3.82
1.50	8.68	4.60	6.81	7.05	3.65
1.60	8.63	4.70	6.76	7.10	3.52
1.70	8.58	4.80	6.71	7.15	3.42
1.80	8.53	4.90	6.66	7.20	3.34
1.90	8.48	5.00	6.61	7.25	3.27
2.00	8.43	5.10	6.56	7.30	3.21
2.10	8.38	5.20	6.52	7.35	3.16
2.20	8.33	5.30	6.47	7.40	3.11
2.30	8.28	5.40	6.41	7.45	3.07
2.40	8.23	5.50	6.37	7.50	3.03
2.50	8.18	5.60	6.32	7.60	2.96
2.60	8.11	5.70	6.26	7.70	2.91
2.70	8.06	5.80	6.21	7.80	2.85
2.80	8.00	5.90	6.15	7.90	2.80
2.90	7.93	6.00	6.09	8.00	2.76
3.00	7.86	6.10	6.02		


Titration of a 50 ml. Aliquot of
Stock Compound 1 Solution with
Perchloric Acid (0.1426 M.)
pH
8
7
6
5
4
3
1
2
3
4
5
6
7
8
ml. of perchloric acid added

Differential Plot of the Titration of a 50 ml. Aliquot of Stock Compound 1 Solution with Perchloric Acid (0.1426 M.)



Calculation of the free base concentration of Compound 1 stock solution:

$$\frac{(6.95 \text{ ml.})(0.1426 \text{ M})}{(50 \text{ ml.})} \times 0.5 = 9.91 \times 10^{-3} \text{ M.}$$

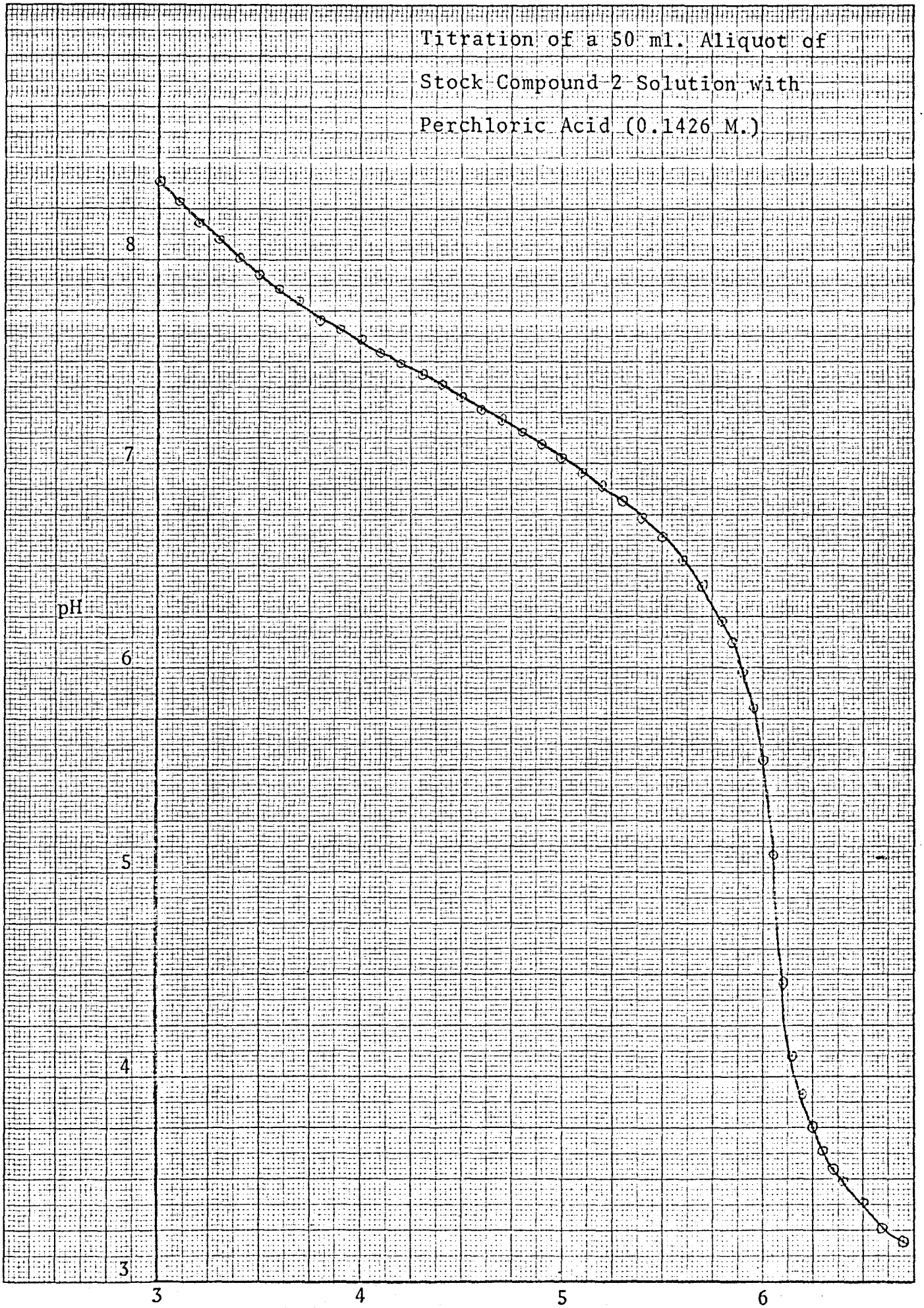
2. Compound 2

The stock solution of Compound 2 was prepared by dissolving 3.3 grams of the dihydrochloride salt of Compound 2 in distilled water and diluting to a one liter volume. After passing the solution through a column containing Amerlite IRA-400 in the OH^- form, 50 ml. aliquots were titrated with 0.1426 M. perchloric acid solution. The data and calculations for these titrations are presented on the following pages.

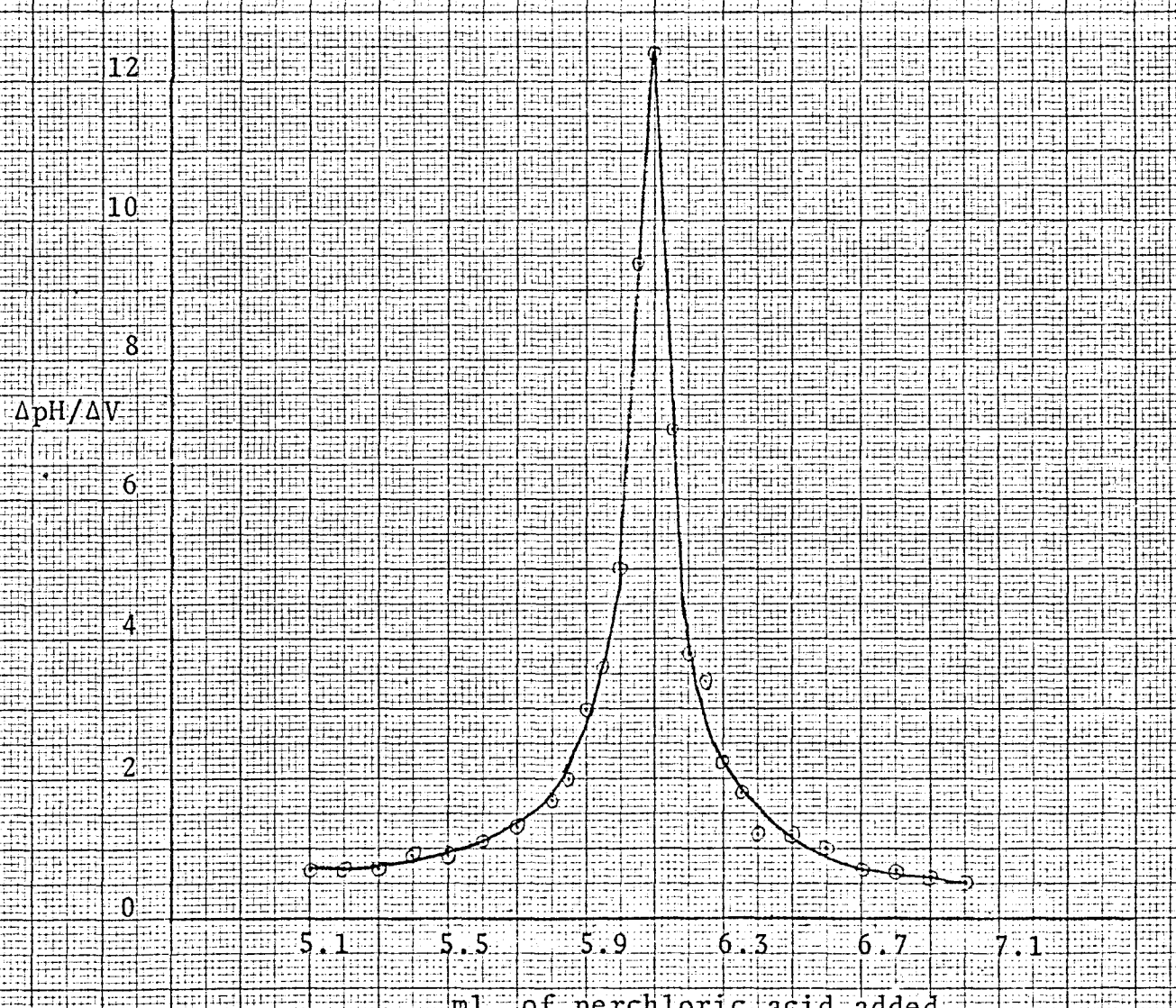
A small aliquot of Compound 2 stock solution was also tested for the presence of chloride ion. No chloride ion was detected.

Titration of a 50 ml. Aliquot of Stock Compound 2 Solution with Perchloric Acid (0.1426 M)

ml. of $HClO_4$ added	pH	ml. of $HClO_4$ added	pH	ml. of $HClO_4$ added	pH
0.00	10.43	2.60	8.76	5.20	6.89
0.10	10.34	2.70	8.67	5.30	6.82
0.20	10.26	2.80	8.58	5.40	6.73
0.30	10.19	2.90	8.48	5.50	6.64
0.40	10.11	3.00	8.39	5.60	6.53
0.50	10.04	3.10	8.29	5.70	6.40
0.60	9.98	3.20	8.18	5.80	6.23
0.70	9.91	3.30	8.10	5.85	6.13
0.80	9.85	3.40	8.01	5.90	5.98
0.90	9.79	3.50	7.93	5.95	5.80
1.00	9.73	3.60	7.86	6.00	5.55
1.10	9.68	3.70	7.80	6.05	5.08
1.20	9.63	3.80	7.71	6.10	4.46
1.30	9.57	3.90	7.67	6.15	4.11
1.40	9.53	4.00	7.61	6.20	3.92
1.50	9.45	4.10	7.55	6.25	3.75
1.60	9.41	4.20	7.49	6.30	3.64
1.70	9.36	4.30	7.43	6.35	3.55
1.80	9.30	4.40	7.38	6.40	3.49
1.90	9.25	4.50	7.32	6.50	3.37
2.00	9.19	4.60	7.26	6.60	3.27
2.10	9.12	4.70	7.21	6.70	3.20
2.20	9.06	4.80	7.15	6.80	3.13
2.30	8.99	4.90	7.09	6.90	3.07
2.40	8.91	5.00	7.03	7.00	3.02
2.50	8.84	5.10	6.96		

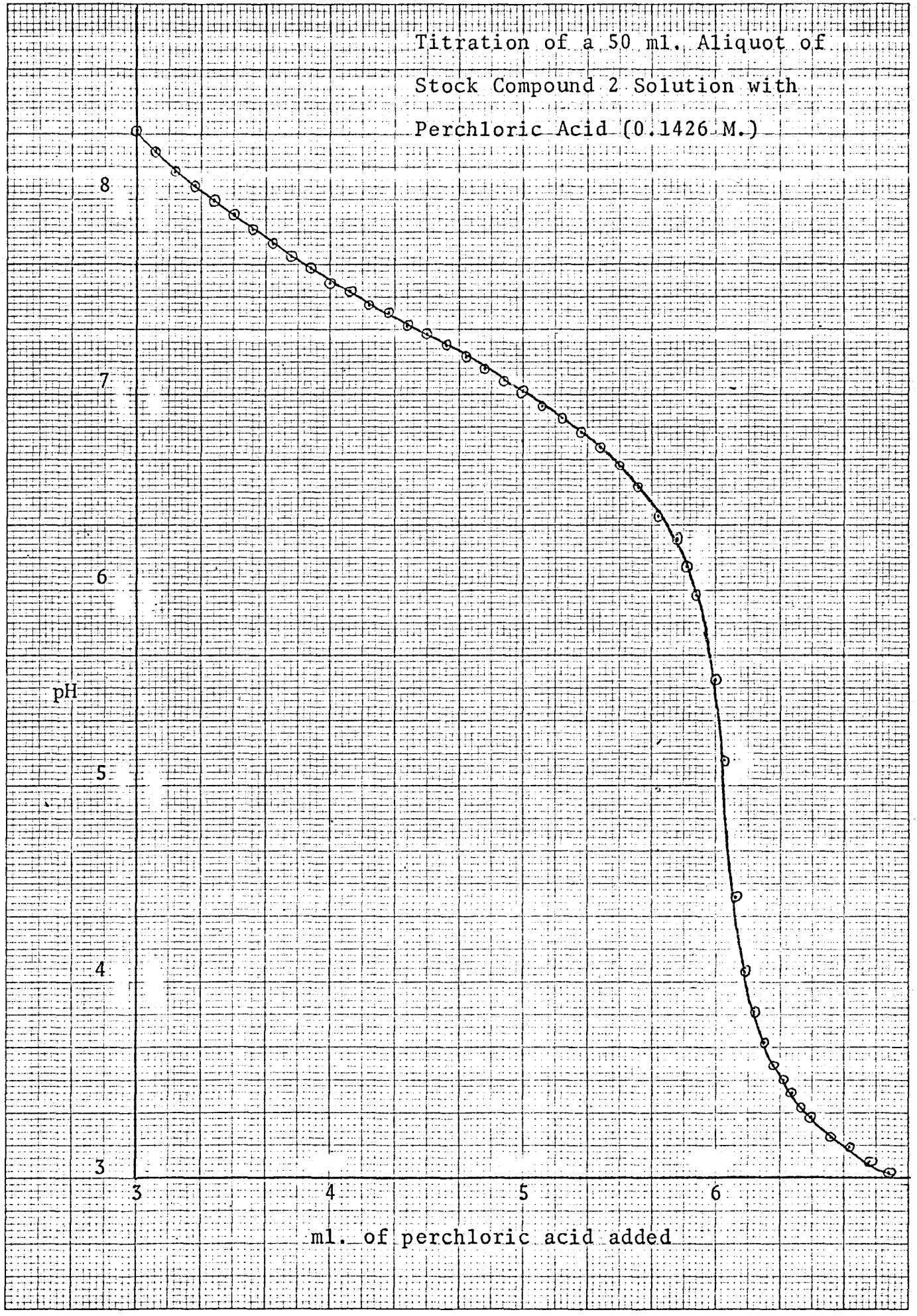

Titration of a 50 ml. Aliquot of
Stock Compound 2 Solution with
Perchloric Acid (0.1426 M.)
pH
8
7
6
5
4
3
3
4
5
6
ml. of perchloric acid added

Differential Plot of the Titration of a 50 ml. Aliquot of Stock Compound 2 Solution with Perchloric Acid (0.1426 M.)

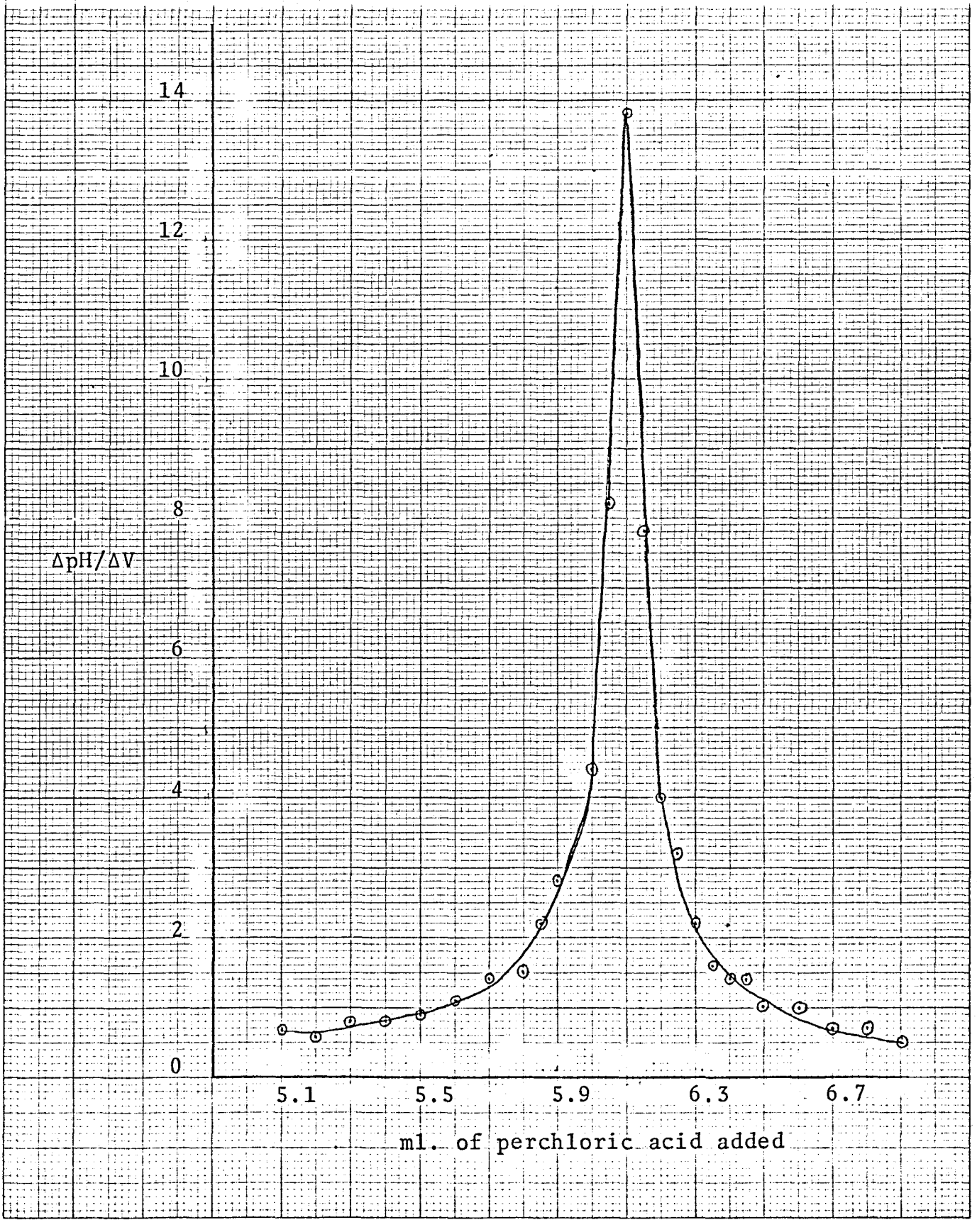


Titration of a 50 ml. Aliquot of Stock Compound 2 Solution with Perchloric Acid (0.1426 M)

ml. of $HClO_4$ added	pH	ml. of $HClO_4$ added	pH	ml. of $HClO_4$ added	pH
0.00	10.42	2.60	8.74	5.20	6.88
0.10	10.31	2.70	8.64	5.30	6.80
0.20	10.24	2.80	8.56	5.40	6.72
0.30	10.16	2.90	8.45	5.50	6.63
0.40	10.09	3.00	8.36	5.60	6.52
0.50	10.01	3.10	8.26	5.70	6.38
0.60	9.95	3.20	8.17	5.80	6.23
0.70	9.89	3.30	8.08	5.85	6.12
0.80	9.83	3.40	7.99	5.90	5.98
0.90	9.77	3.50	7.92	5.95	--
1.00	9.71	3.60	7.85	6.00	5.54
1.10	9.66	3.70	7.78	6.05	5.13
1.20	9.61	3.80	7.71	6.10	4.44
1.30	9.55	3.90	7.65	6.15	4.05
1.40	9.50	4.00	7.58	6.20	3.85
1.50	9.44	4.10	7.53	6.25	3.69
1.60	9.39	4.20	7.47	6.30	3.58
1.70	9.34	4.30	7.42	6.35	3.50
1.80	9.29	4.40	7.36	6.40	3.43
1.90	9.21	4.50	7.31	6.45	3.36
2.00	9.16	4.60	7.25	6.50	3.31
2.10	9.09	4.70	7.19	6.60	3.21
2.20	9.03	4.80	7.13	6.70	3.14
2.30	8.97	4.90	7.08	6.80	3.07
2.40	8.90	5.00	7.01	6.90	3.02
2.50	8.81	5.10	6.94	7.00	2.97


Titration of a 50 ml. Aliquot of
Stock Compound 2 Solution with
Perchloric Acid (0.1426 M.)
8
7
6
pH
5
4
3
3
4
5
6
ml. of perchloric acid added

Differential Plot of the Titration of a 50 ml. Aliquot of Stock Compound 2 Solution with Perchloric Acid (0.1426 M.)



Calculation of the free base concentration of Compound 2 stock solution:

$$\frac{(6.10 \text{ ml.})(0.1426 \text{ M})}{(50 \text{ ml.})} \times 0.5 = 8.70 \times 10^{-3} \text{ M.}$$

3. Standardization of Perchloric Acid Solution

Base Used: NaOH 0.1000 M. ± 0.0001 M.

Indicator: phenolphthalein

Volume of perchloric acid aliquot: 25 ml.

Run #1 $\frac{(35.66 \text{ ml.})(0.1000 \text{ M})}{25 \text{ ml.}} = 0.1426 \text{ M.}$

Run #2 $\frac{(35.68 \text{ ml.})(0.1000 \text{ M})}{25 \text{ ml.}} = 0.1427 \text{ M.}$

Run #3 $\frac{(35.60 \text{ ml.})(0.1000 \text{ M})}{25 \text{ ml.}} = 0.1424 \text{ M.}$

Average concentration $HClO_4$ = 0.1426 M.

4. Standardization of $Cu(NO_3)_2$ Solution

The method presented by Pierce, Haenisch and Sawyer (40) was followed using electrodeposition of the copper from a 25 ml. aliquot of the stock solution of $Cu(NO_3)_2$. Four trials were made, and the average concentration of the stock solution was found to be 5.15×10^{-2} M. This solution was also used to check the calibration of the ACTA III UV-visible spectrophotometer used in the Job's method. The molar absorptivity

of $Cu(NO_3)_2$ solution at 750 nm. was reported by Warner and Webber (45) to be 10.2. A cell of path length 0.988 cm. was used, and the calculated abosrbance using the stock $Cu(NO_3)_2$ solution was 0.519. The absorbance from the ACTA III's display was 0.521 which was within the instrument's specification of ±0.003.

APPENDIX D

Basicity Constant Titration of Compound 1

Run #1

Compound 1: 1×10^{-3} M. Temperature: 30°C.

$HClO_4$: 2×10^{-3} M. $NaNO_3$: 0.5 M.

NaOH: 0.1000 M.

ml. of NaOH added	pH	ml. of NaOH added	pH	ml. of NaOH added	pH
0.00	5.57	1.10	8.07	2.15	9.83
0.05	5.88	1.15	8.17	2.20	9.91
0.10	6.12	1.20	8.26	2.25	9.98
0.15	6.28	1.25	8.34	2.30	10.03
0.20	6.42	1.30	8.43	2.35	--
0.25	6.53	1.35	8.51	2.40	10.13
0.30	6.64	1.40	8.58	2.45	10.18
0.35	6.74	1.45	8.65	2.50	10.21
0.40	6.82	1.50	8.73	2.60	10.28
0.45	6.91	1.55	8.80	2.70	10.33
0.50	6.99	1.60	8.88	2.80	10.39
0.55	7.06	1.65	8.96	2.90	10.43
0.60	7.14	1.70	9.04	3.00	10.47
0.65	7.23	1.75	9.11	3.25	10.54
0.70	7.32	1.80	9.20	3.50	10.61
0.75	7.40	1.85	9.28	3.75	10.67
0.80	7.49	1.90	9.38	4.00	10.71
0.85	7.58	1.95	9.47	4.50	10.79
0.90	7.68	2.00	9.57	5.00	10.85
0.95	7.77	2.05	9.66	5.50	10.89
1.00	7.88	2.10	9.75	6.00	10.94
1.05	7.98				

Run #2

Compound 1: 1×10^{-3} M. Temperature: 30°C.

$HClO_4$: 2×10^{-3} M. $NaNO_3$: 0.5 M.

NaOH: 0.1000 M.

ml. of NaOH added	pH	ml. of NaOH added	pH	ml. of NaOH added	pH
0.00	5.47	1.10	8.06	2.15	9.80
0.05	5.84	1.15	8.17	2.20	9.88
0.10	6.09	1.20	8.24	2.25	9.94
0.15	6.27	1.25	8.34	2.30	10.00
0.20	6.41	1.30	8.41	2.35	10.05
0.25	6.52	1.35	8.49	2.40	10.10
0.30	6.62	1.40	8.57	2.45	10.15
0.35	6.72	1.45	8.65	2.50	10.18
0.40	6.81	1.50	8.72	2.60	10.26
0.45	6.90	1.55	8.80	2.70	10.31
0.50	6.97	1.60	8.87	2.80	10.36
0.55	7.05	1.65	8.95	2.90	10.40
0.60	7.13	1.70	9.02	3.00	10.44
0.65	7.21	1.75	9.09	3.25	10.52
0.70	7.30	1.80	9.18	3.50	10.59
0.75	7.38	1.85	9.27	3.75	10.65
0.80	7.47	1.90	9.35	4.00	10.69
0.85	7.57	1.95	9.45	4.50	10.77
0.90	7.66	2.00	9.54	5.00	10.83
0.95	7.76	2.05	9.63	5.50	10.88
1.00	7.87	2.10	9.71	6.00	10.92
1.05	7.97				

Run #3

Compound 1: 1×10^{-3} M. Temperature: 30°C.

$HClO_4$: 2×10^{-3} M. $NaNO_3$: 0.5 M.

NaOH: 0.1000 M.

ml. of NaOH added	pH	ml. of NaOH added	pH	ml. of NaOH added	pH
0.00	5.53	1.10	8.09	2.15	9.83
0.05	5.89	1.15	8.18	2.20	9.90
0.10	6.11	1.20	8.27	2.25	9.96
0.15	6.28	1.25	8.36	2.30	10.03
0.20	6.42	1.30	8.44	2.35	10.07
0.25	6.54	1.35	8.51	2.40	10.12
0.30	6.63	1.40	8.59	2.45	10.16
0.35	6.73	1.45	8.67	2.50	10.20
0.40	6.82	1.50	8.74	2.60	10.26
0.45	6.91	1.55	8.81	2.70	10.33
0.50	6.99	1.60	8.89	2.80	10.37
0.55	7.06	1.65	8.96	2.90	10.41
0.60	7.14	1.70	9.04	3.00	10.45
0.65	7.23	1.75	9.12	3.25	10.53
0.70	7.31	1.80	9.21	3.50	10.59
0.75	7.40	1.85	9.29	3.75	10.65
0.80	7.49	1.90	9.38	4.00	10.70
0.85	7.58	1.95	9.47	4.50	10.77
0.90	7.69	2.00	9.57	5.00	10.83
0.95	7.79	2.05	9.66	5.50	10.87
1.00	7.89	2.10	9.75	6.00	10.92
1.05	7.99				

APPENDIX E

Basicity Constant Titration of Compound 2

Run #1

Compound 2: 1×10^{-3} M. Temperature: 30°C.

$HClO_4$: 2×10^{-3} M. $NaNO_3$: 0.5 M.

NaOH: 0.1000 M.

ml. of NaOH added	pH	ml. of NaOH added	pH	ml. of NaOH added	pH
0.00	--	1.10	8.81	2.15	10.08
0.05	6.20	1.15	8.90	2.20	10.12
0.10	6.62	1.20	9.00	2.25	10.16
0.15	6.86	1.25	9.09	2.30	10.19
0.20	7.02	1.30	9.17	2.35	10.22
0.25	7.15	1.35	9.25	2.40	10.25
0.30	7.27	1.40	9.32	2.45	10.28
0.35	7.38	1.45	9.38	2.50	10.31
0.40	7.48	1.50	9.45	2.60	10.36
0.45	7.57	1.55	9.51	2.70	10.41
0.50	7.66	1.60	9.57	2.80	10.45
0.55	7.74	1.65	9.62	2.90	10.49
0.60	7.82	1.70	9.68	3.00	10.52
0.65	7.90	1.75	9.73	3.25	10.60
0.70	7.99	1.80	9.78	3.50	10.66
0.75	8.09	1.85	9.83	3.75	10.72
0.80	8.17	1.90	9.88	4.00	10.76
0.85	8.27	1.95	9.92	4.50	10.84
0.90	8.37	2.00	9.96	5.00	10.90
0.95	8.47	2.05	10.00	5.50	10.95
1.00	8.59	2.10	10.04	6.00	11.00
1.05	8.70				

Run #2

Compound 2: 1×10^{-3} M. Temperature: 30°C.

$HClO_4$: 2×10^{-3} M. $NaNO_3$: 0.5 M.

NaOH: 0.1000 M.

ml. of NaOH added	pH	ml. of NaOH added	pH	ml. of NaOH added	pH
0.00	5.60	1.10	8.80	2.15	10.07
0.05	6.28	1.15	8.90	2.20	10.11
0.10	6.62	1.20	8.99	2.25	10.14
0.15	6.86	1.25	9.08	2.30	10.18
0.20	7.04	1.30	9.16	2.35	10.20
0.25	7.18	1.35	9.24	2.40	10.24
0.30	7.28	1.40	9.31	2.45	10.27
0.35	7.39	1.45	9.37	2.50	10.29
0.40	7.49	1.50	9.43	2.60	10.35
0.45	7.59	1.55	9.50	2.70	10.40
0.50	7.66	1.60	9.55	2.80	10.44
0.55	7.74	1.65	9.61	2.90	10.48
0.60	7.83	1.70	9.66	3.00	10.51
0.65	7.91	1.75	9.71	3.25	10.58
0.70	8.00	1.80	9.77	3.50	10.65
0.75	8.10	1.85	9.81	3.75	10.70
0.80	8.17	1.90	9.86	4.00	10.75
0.85	8.27	1.95	9.90	4.50	10.82
0.90	8.38	2.00	9.94	5.00	10.89
0.95	8.48	2.05	9.99	5.50	10.94
1.00	8.58	2.10	10.03	6.00	10.98
1.05	8.69				

Run #3

Compound 2: 1×10^{-3} M. Temperature: 30°C.

$HClO_4$: 2×10^{-3} M. $NaNO_3$: 0.5 M.

NaOH: 0.1000 M.

ml. of NaOH added	pH	ml. of NaOH added	pH	ml. of NaOH added	pH
0.00	5.29	1.10	8.80	2.15	10.07
0.05	6.20	1.15	8.90	2.20	10.11
0.10	6.61	1.20	9.00	2.25	10.15
0.15	6.84	1.25	9.08	2.30	10.19
0.20	7.02	1.30	9.17	2.35	10.21
0.25	7.16	1.35	9.24	2.40	10.25
0.30	7.29	1.40	9.31	2.45	10.28
0.35	7.39	1.45	9.39	2.50	10.30
0.40	7.49	1.50	9.44	2.60	10.35
0.45	7.57	1.55	9.50	2.70	10.40
0.50	7.66	1.60	9.57	2.80	10.45
0.55	7.75	1.65	9.62	2.90	10.48
0.60	7.83	1.70	9.67	3.00	10.52
0.65	7.92	1.75	9.72	3.25	10.59
0.70	8.00	1.80	9.77	3.50	10.66
0.75	8.09	1.85	9.82	3.75	10.71
0.80	8.17	1.90	9.87	4.00	10.76
0.85	8.27	1.95	9.91	4.50	10.83
0.90	8.37	2.00	9.95	5.00	10.89
0.95	8.47	2.05	10.00	5.50	10.95
1.00	8.58	2.10	10.04	6.00	10.99
1.05	8.70				

APPENDIX F

Stability Constant Titration of Compound 1

Run #1

Compound 1: 1×10^{-3} M. Temperature: 30°C.

$Cu(NO_3)_2$: 5×10^{-4} M. $NaNO_3$: 0.5 M.

$HClO_4$: 2×10^{-3} M. NaOH: 0.1000 M.

ml. of NaOH added	pH	ml. of NaOH added	pH	ml. of NaOH added	pH
0.00	4.02	1.30	6.15	2.55	8.77
0.05	4.08	1.35	6.26	2.60	8.85
0.10	4.12	1.40	6.37	2.65	8.93
0.15	4.17	1.45	6.48	2.70	9.00
0.20	4.22	1.50	6.58	2.75	9.09
0.25	4.26	1.55	6.70	2.80	9.17
0.30	4.30	1.60	6.81	2.85	9.26
0.35	4.35	1.65	6.92	2.90	9.35
0.40	4.40	1.70	7.05	2.95	9.46
0.45	4.44	1.75	7.15	3.00	9.55
0.50	4.49	1.80	7.26	3.10	9.72
0.55	4.53	1.85	7.39	3.20	9.87
0.60	4.58	1.90	7.52	3.30	9.98
0.65	4.61	1.95	7.64	3.40	10.07
0.70	4.69	2.00	7.77	3.50	10.14
0.75	4.75	2.05	7.89	3.60	10.21
0.80	4.82	2.10	8.01	3.70	10.26
0.85	4.90	2.15	8.12	3.80	10.30
0.90	5.00	2.20	8.21	3.90	10.35
0.95	5.12	2.25	8.31	4.00	10.38
1.00	5.30	2.30	8.40	4.25	10.45
1.10	5.62	2.40	8.56	5.00	10.61
1.15	5.77	2.45	8.63	5.50	10.67
1.20	5.90	2.50	8.71	6.00	10.74
1.25	6.02				

Run #2

Compound 1: 1×10^{-3} M. Temperature: 30°C.

$Cu(NO_3)_2$: 5×10^{-4} M. $NaNO_3$: 0.5 M.

$HClO_4$: 2×10^{-3} M. NaOH: 0.1000 M.

ml. of NaOH added	pH	ml. of NaOH added	pH	ml. of NaOH added	pH
0.00	4.00	1.30	6.09	2.55	8.76
0.05	4.04	1.35	6.21	2.60	8.83
0.10	4.09	1.40	6.31	2.65	8.91
0.15	4.14	1.45	6.43	2.70	8.99
0.20	4.19	1.50	6.54	2.75	9.08
0.25	--	1.55	6.64	2.80	9.16
0.30	4.28	1.60	6.75	2.85	9.25
0.35	4.32	1.65	6.86	2.90	9.35
0.40	4.37	1.70	6.97	2.95	9.43
0.45	4.41	1.75	7.08	3.00	9.54
0.50	4.45	1.80	7.20	3.10	9.73
0.55	4.49	1.85	7.33	3.20	9.88
0.60	4.55	1.90	7.45	3.30	10.01
0.65	4.60	1.95	7.58	3.40	10.11
0.70	4.66	2.00	7.71	3.50	10.19
0.75	4.72	2.05	7.83	3.60	10.26
0.80	4.79	2.10	7.95	3.70	10.31
0.85	4.86	2.15	8.07	3.80	10.36
0.90	4.96	2.20	8.17	3.90	10.41
0.95	5.07	2.25	8.27	4.00	10.44
1.00	5.22	2.30	8.36	4.25	10.53
1.05	5.37	2.35	--	4.50	10.59
1.10	5.50	2.40	8.52	5.00	10.69
1.15	5.70	2.45	8.60	5.50	10.76
1.20	5.84	2.50	8.68	6.00	10.81
1.25	5.97				

Run #3

Compound 1: 1×10^{-3} M. Temperature: 30°C.

$Cu(NO_3)_2$: 5×10^{-4} M. $NaNO_3$: 0.5 M.

$HClO_4$: 2×10^{-3} M. NaOH: 0.1000 M.

ml. of NaOH added	pH	ml. of NaOH added	pH	ml. of NaOH added	pH
0.00	4.03	1.30	6.13	2.55	8.75
0.05	4.08	1.35	6.24	2.60	8.83
0.10	4.13	1.40	6.36	2.65	8.90
0.15	4.18	1.45	6.47	2.70	8.98
0.20	4.22	1.50	6.58	2.75	9.05
0.25	4.27	1.55	6.68	2.80	9.14
0.30	4.31	1.60	6.80	2.85	9.23
0.35	4.35	1.65	6.90	2.90	9.32
0.40	4.40	1.70	7.02	2.95	9.41
0.45	4.44	1.75	7.12	3.00	9.50
0.50	4.49	1.80	7.24	3.10	9.68
0.55	4.53	1.85	7.36	3.20	9.82
0.60	4.59	1.90	7.49	3.30	9.94
0.65	4.64	1.95	7.62	3.40	10.04
0.70	4.69	2.00	7.75	3.50	10.11
0.75	4.75	2.05	7.87	3.60	10.17
0.80	4.82	2.10	7.97	3.70	10.22
0.85	4.90	2.15	8.09	3.80	10.27
0.90	5.01	2.20	8.19	3.90	10.31
0.95	5.13	2.25	8.29	4.00	10.35
1.00	5.27	2.30	8.37	4.25	10.42
1.05	5.45	2.35	8.46	4.50	10.48
1.10	5.61	2.40	8.53	5.00	10.58
1.15	5.75	2.45	8.61	5.50	10.64
1.20	5.88	2.50	8.68	6.00	10.70
1.25	6.02				

APPENDIX G

Stability Constant Titration of Compound 2

Run #1

Compound 2: 1×10^{-3} M. Temperature: 30°C.

$Cu(NO_3)_2$: 5×10^{-4} M. $NaNO_3$: 0.5 M.

$HClO_4$: 2×10^{-3} M. NaOH: 0.1000 M.

ml. of NaOH added	pH	ml. of NaOH added	pH	ml. of NaOH added	pH
0.00	4.21	1.30	6.26	2.55	9.21
0.05	4.31	1.35	6.41	2.60	9.28
0.10	4.37	1.40	6.58	2.65	9.36
0.15	4.43	1.45	6.74	2.70	9.43
0.20	4.48	1.50	6.91	2.75	9.51
0.25	4.54	1.55	7.08	2.80	9.57
0.30	4.58	1.60	7.27	2.85	9.64
0.35	4.63	1.65	7.39	2.90	9.70
0.40	4.68	1.70	7.53	2.95	9.77
0.45	4.72	1.75	7.66	3.00	9.82
0.50	4.77	1.80	7.78	3.10	9.93
0.55	4.81	1.85	7.90	3.20	10.03
0.60	4.85	1.90	8.01	3.30	10.12
0.65	4.91	1.95	8.11	3.40	10.19
0.70	4.96	2.00	8.22	3.50	10.26
0.75	5.02	2.05	8.33	3.60	10.31
0.80	5.08	2.10	8.43	3.70	10.38
0.85	5.14	2.15	8.53	3.80	10.41
0.90	5.22	2.20	8.62	3.90	10.45
0.95	5.31	2.25	8.71	4.00	10.48
1.00	5.41	2.30	8.80	4.25	10.56
1.05	5.54	2.35	8.88	4.50	10.63
1.10	5.68	2.40	8.97	5.00	10.73
1.15	5.82	2.45	9.04	5.50	10.80
1.20	5.97	2.50	9.12	6.00	10.86
1.25	6.11				

Run #2

Compound 2: 1×10^{-3} M. Temperature: 30°C.

$Cu(NO_3)_2$: 5×10^{-4} M. $NaNO_3$: 0.5 M.

$HClO_4$: 2×10^{-3} M. NaOH: 0.1000 M.

ml. of NaOH added	pH	ml. of NaOH added	pH	ml. of NaOH added	pH
0.00	4.20	1.30	6.17	2.55	9.15
0.05	4.27	1.35	6.31	2.60	9.24
0.10	4.34	1.40	6.47	2.65	9.31
0.15	4.41	1.45	6.63	2.70	9.39
0.20	4.47	1.50	6.80	2.75	9.46
0.25	4.52	1.55	6.97	2.80	9.53
0.30	4.56	1.60	7.15	2.85	9.60
0.35	4.61	1.65	7.30	2.90	9.66
0.40	4.66	1.70	7.44	2.95	9.73
0.45	4.71	1.75	7.58	3.00	9.79
0.50	4.75	1.80	7.70	3.10	9.90
0.55	4.79	1.85	7.83	3.20	--
0.60	4.84	1.90	7.94	3.30	10.10
0.65	4.89	1.95	8.05	3.40	10.17
0.70	4.94	2.00	8.16	3.50	10.24
0.75	4.99	2.05	8.26	3.60	10.31
0.80	5.05	2.10	8.37	3.70	10.36
0.85	5.11	2.15	8.46	3.80	10.41
0.90	5.18	2.20	8.56	3.90	10.45
0.95	5.26	2.25	8.65	4.00	10.49
1.00	5.35	2.30	8.74	4.25	10.57
1.05	5.47	2.35	8.83	4.50	10.64
1.10	5.60	2.40	8.91	5.00	10.74
1.15	5.74	2.45	8.99	5.50	10.82
1.20	5.88	2.50	9.07	6.00	10.88
1.25	6.02				

Run #3

Compound 2: 1×10^{-3} M. Temperature: 30°C.

$Cu(NO_3)_2$: 5×10^{-4} M. $NaNO_3$: 0.5 M.

$HClO_4$: 2×10^{-3} M. NaOH: 0.1000 M.

ml. of NaOH added	pH	ml. of NaOH added	pH	ml. of NaOH added	pH
0.00	4.19	1.30	6.15	2.55	9.09
0.05	4.26	1.35	6.28	2.60	9.17
0.10	4.34	1.40	6.43	2.65	9.24
0.15	4.40	1.45	6.60	2.70	9.31
0.20	4.45	1.50	6.75	2.75	9.39
0.25	4.51	1.55	6.93	2.80	9.46
0.30	4.56	1.60	7.08	2.85	9.52
0.35	4.61	1.65	7.24	2.90	9.59
0.40	4.65	1.70	7.39	2.95	9.65
0.45	4.70	1.75	7.52	3.00	9.71
0.50	4.74	1.80	7.64	3.10	9.83
0.55	4.79	1.85	7.76	3.20	9.93
0.60	4.83	1.90	7.88	3.30	10.03
0.65	4.88	1.95	7.99	3.40	10.11
0.70	4.94	2.00	8.09	3.50	10.18
0.75	4.99	2.05	8.21	3.60	10.25
0.80	5.04	2.10	8.30	3.70	10.31
0.85	5.11	2.15	8.39	3.80	10.36
0.90	5.18	2.20	8.49	3.90	10.40
0.95	5.25	2.25	8.59	4.00	10.45
1.00	5.35	2.30	8.68	4.25	10.53
1.05	5.46	2.35	8.76	4.50	--
1.10	5.60	2.40	8.85	5.00	10.71
1.15	5.73	2.45	8.93	5.50	10.79
1.20	5.88	2.50	9.01	6.00	10.85
1.25	6.02				

Run #4

Compound 2: 1×10^{-3} M. Temperature: 30°C.

$Cu(NO_3)_2$: 5×10^{-4} M. $NaNO_3$: 0.5 M.

$HClO_4$: 2×10^{-3} M. NaOH: 0.1000 M.

ml. of NaOH added	pH	ml. of NaOH added	pH	ml. of NaOH added	pH
0.00	4.21	1.30	6.24	2.55	9.20
0.05	4.29	1.35	6.39	2.60	9.29
0.10	4.35	1.40	6.55	2.65	9.36
0.15	4.42	1.45	6.72	2.70	9.44
0.20	4.47	1.50	6.88	2.75	9.52
0.25	4.53	1.55	7.07	2.80	9.58
0.30	4.57	1.60	7.24	2.85	9.65
0.35	4.63	1.65	7.38	2.90	9.71
0.40	4.67	1.70	7.51	2.95	9.78
0.45	4.71	1.75	7.65	3.00	9.84
0.50	4.76	1.80	7.77	3.10	9.95
0.55	4.80	1.85	7.88	3.20	10.04
0.60	4.85	1.90	8.00	3.30	10.13
0.65	4.89	1.95	8.11	3.40	10.20
0.70	4.95	2.00	8.21	3.50	10.27
0.75	5.01	2.05	8.32	3.60	10.32
0.80	5.06	2.10	8.42	3.70	10.38
0.85	5.13	2.15	8.51	3.80	10.42
0.90	5.20	2.20	8.61	3.90	10.46
0.95	5.29	2.25	8.70	4.00	10.49
1.00	5.39	2.30	8.79	4.25	10.57
1.05	5.51	2.35	8.88	4.50	10.63
1.10	5.65	2.40	8.96	5.00	10.73
1.15	5.79	2.45	9.04	5.50	10.81
1.20	5.94	2.50	9.12	6.00	10.86
1.25	6.09				

APPENDIX H

Sample Calculations and Programs

A. Sample Calculation for Basicity Constants - Using a Point on the Compound 1 Titration

$$(Z)_t = 1 \times 10^{-3} \text{ M.}$$

$$v_i = 100 \text{ ml.}$$

$$\text{Normality of NaOH} = 0.1000 \text{ N.}$$

$$\text{Volume of NaOH} = 0.5 \text{ ml.}$$

$$\text{Average pH} = 6.98$$

$$g = 2 - \frac{(\text{ml. of NaOH})(\text{N. of NaOH})}{(Z)_t \times v_i} + \frac{(OH) - (H)}{\frac{(Z)_t \times v_i}{v_i + \text{ml. of NaOH}}}$$

$$g = 2 - \frac{(0.50)(0.1000)}{(1 \times 10^{-3})(100)} + \frac{(9.55 \times 10^{-8}) - (1.05 \times 10^{-7})}{\frac{(1 \times 10^{-3})(100)}{(100 + 0.5)}}$$

$$g = 1.500$$

$$x = \frac{(g - 1)}{(g - 2)(H^+)}$$

$$x = \frac{(1.500 - 1)}{(1.500 - 2)(1.05 \times 10^{-7})}$$

$$x = -9.524 \times 10^6$$

$$y = \frac{g}{-(g - 2)(H)^2}$$

$$y = \frac{1.500}{-(1.500 - 2)(1.05 \times 10^{-7})^2}$$

$$y = 2.721 \times 10^{14}$$

The values of x and y are used in the linear regression analysis of the straight line $y = mx + b$ where $K^H_{HZ} = m$ and $K^H_{H_2Z} = b$.

B. Sample Calculation for Stability Constant - Using a Point on the Compound 1 Titration

$(m)_t = 5 \times 10^{-4}$ M. $\quad (Z)_t = 1 \times 10^{-3}$ M.

$HClO_4 = 2 \times 10^{-3}$ M. $\quad NaNO_3 = 0.5$ M.

$pK^H_{HZ} = 8.69$ $\quad p\overline{K}^H_{H_2Z} = 15.80$

pH = 4.48 $\quad$ Temperature: 30°C.

Volume of NaOH added = 0.5 ml.

Normality of NaOH = 0.1000 N.

Initial Volume = 100 ml.

$$[Z] = \{2\left(\frac{(Z)_t V_i}{V_i + \text{ml. of NaOH}}\right) - \frac{(\text{N. of NaOH})(\text{ml. of NaOH})}{V_i + \text{ml. of NaOH}}$$

$$- (H) + (OH)\}/\{(H)K^H_{HZ} - 2(H)^2\overline{K}^H_{H_2Z}\}$$

$$[Z] = \{2\left(\frac{1 \times 10^{-3} \cdot 100}{100 + 0.5}\right) - \left(\frac{.1000 \cdot 0.5}{100 + 0.5}\right) - (3.31 \times 10^{-5})$$

$$+ (3.02 \times 10^{-10})\}/\{(3.31 \times 10^{-5})(4.90 \times 10^{8})$$

$$- 2(3.31 \times 10^{-5})^2(1.20 \times 10^{15})\}$$

$$[Z] = 5.512 \times 10^{-10}$$

$$\alpha = 1 + (H)K^{H}_{HZ} + (H)^2\overline{K}^{H}_{H_2Z}$$

$$\alpha = 1 + (3.31 \times 10^{-5})(4.90 \times 10^{8}) + (3.31 \times 10^{-5})^2(1.20 \times 10^{15})$$

$$\alpha = 1.33 \times 10^{6}$$

$$\bar{n} = \frac{\left(\frac{(Z)_t V_i}{V_i + \text{ml. of NaOH}}\right) - \alpha(Z)}{\left(\frac{(M)_t V_i}{V_i + \text{ml. of NaOH}}\right)}$$

$$\bar{n} = \frac{\left(\frac{1 \times 10^{-3} \cdot 100}{100 + .5}\right) - (1.33 \times 10^{6} \cdot 5.512 \times 10^{-10})}{\left(\frac{5 \times 10^{-4} \cdot 100}{100 + .5}\right)}$$

$$\bar{n} = 0.5243$$

$$x = \frac{(2 - \bar{n})(Z)}{(\bar{n} - 1)}$$

$$x = \frac{(2 - .5243)(5.512 \times 10^{-10})}{(.5243 - 1)}$$

$$x = -1.710 \times 10^{-9}$$

$$y = \frac{\bar{n}}{(\bar{n} - 1)(Z)}$$

$$y = \frac{0.5243}{(0.5243 - 1)(5.512 \times 10^{-10})}$$

$$y = -2.000 \times 10^{9}$$

The values of x and y are used in a linear regression analysis of the line $y = mx + b$.

C. Programs for Calculations

All calculations were carried out on a Wang Model 500 Calculator with Printer. Each program used is presented below together with instructions for its use. The programs are also stored on magnetic tape and are available on request.

1. Program for differential plots - calculation of ΔpH/Δvolume.

```
000   09 00   * LBL M
001   00 01   E 1
002   09 03   * LBL SP
003   08 02   * W
004   01 02   T 2
005   06 00   STO 0
006   06 04   STO 4
007   07 02   RCL 2
008   03 00   - 0
009   08 02   * W
010   04 02   × 2
011   07 04   RCL 4
012   06 02   STO 2
013   09 03   * LBL SP
014   08 02   * W
015   03 02   - 2
016   06 05   STO 5
017   03 03   - 3
018   08 02   * W
019   05 02   ÷ 2
020   06 06   STO 6
021   07 00   RCL 0
022   05 06   ÷ 6
023   08 02   * W
024   06 03   STO 3
025   07 05   RCL 5
026   06 03   STO 3
027   08 02   * W
028   00 15   E IS
029   08 00   * S
030   00 01   E 1
031   09 14   * LBL EP
```

Operating Instructions

STORE 02 first volume
STORE 03 first pH

1. Depress PRINTER ON
2. Key SEARCH 1
3. Key volume$_1$, GO, pH$_1$, GO
   Repeat step 3 for each volume and pH
4. Read: volume labeled by "Y", Δvolume labeled by "B", pH labeled by "A", ΔpH labeled by "C", ΔpH/Δvolume labeled by "D"

Test Data:

STORE 0.00 in 02
STORE 10.00 in 03

1. Depress PRINTER ON
2. Key SEARCH 1
3. Key 1.00, GO, 9.00, GO, 2.00, GO, 7.00, GO
4. Read:

1.00	Y
1.00	B
9.00	A
1.00	C
1.000	D
2.00	Y
1.00	B
7.00	A
2.00	C
2.000	D

2. Program for basicity constants calculation calculates g, x, and y

000	09 00	* M
001	00 01	E 1
002	09 03	* SP
003	08 02	* W
004	15 02	D 2
005	06 05	ST 5
006	06 15	ST 15
007	07 02	RE 2
008	02 05	+ 5
009	05 15	÷ 15
010	07 00	RE 0
011	04 15	× 15
012	07 01	RE 1
013	06 14	ST 14
014	07 05	RE 5
015	05 14	÷ 14
016	07 02	RE 2
017	04 14	× 14
018	05 15	÷ 15
019	07 03	RE 3
020	06 06	ST 6
021	07 15	RE 15
022	03 06	− 6
023	09 03	* SP
024	08 02	* W
025	03 02	− 2
026	00 12	E 12
027	09 11	* 10^x
028	06 15	ST 15
029	07 04	RE 4
030	06 07	ST 7
031	07 15	RE 15
032	05 07	÷ 7
033	07 15	RE 15
034	03 07	− 7
035	07 14	RE 14
036	05 07	÷ 7
037	02 06	+ 6
038	06 08	ST 8
039	06 09	ST 9
040	08 02	* W
041	09 05	* LE
042	07 03	RE 3
043	03 06	− 6
044	00 12	E 12
045	05 08	÷ 8
046	07 15	RE 15
047	08 12	* x^2
048	05 08	÷ 8
049	08 02	* W
050	01 11	T 11
051	00 01	E 1
052	03 09	− 9
053	07 15	RE 15
054	05 09	÷ 9
055	07 06	RE 6
056	05 09	÷ 9
057	08 02	* W
058	00 11	E 11
059	08 02	* W
060	00 15	E 15
061	08 00	* G
062	00 01	E 1
063	09 14	* EP

Operating Instructions

STORE 00 normality of NaOH
STORE 01 $(Z)_t$
STORE 02 initial volume
STORE 07 2
STORE 08 1×10^{-14}

1. Key PRIME, LOAD PROGRAM, VERIFY PROGRAM:
   Display should read 841
2. Depress PRINTER ON
3. Key SEARCH 1
4. Key volume of NaOH, GO, pH, GO
   Repeat step 4 for each titration point
5. Read: Volume of NaOH labeled by "M"
   pH labeled by "A"
   g labeled by "G"
   Y labeled by "Y"
   X labeled by "X"

Test Data:

STORE 00 0.1
STORE 01 1×10^{-3}
STORE 02 100.0
STORE 07 2
STORE 08 1×10^{-14}

1. Key PRIME, LOAD PROGRAM, VERIFY PROGRAM
   Display should read 841
2. Depress PRINTER ON
3. Key SEARCH 1
4. Key 1.55, GO, 9.50, GO
5. Read:

1.55	M
9.50	A
.44999	G
2.903223134+18	Y
1.122098947+09	X

3. Program for Stability Constants Calculations calculates [Z], $\bar{n}$, X, and Y

A complete listing of the program is on the following page.

Operating Instructions

STORE 00 $(Z)_t$
STORE 01 Normality of NaOH
STORE 02 Initial Volume
STORE 03 $(M)_t$
STORE 04 K^H_{HZ}
STORE 05 $K^H_{H_2Z}$
STORE 06 1×10^{-14}

1. Key PRIME, LOAD PROGRAM, VERIFY PROGRAM
   Display should read 1219.
2. Depress PRINTER ON
3. Key SEARCH 2
4. Key Volume of NaOH, GO, pH, GC
5. Read: Volume of NaOH labeled by "B"
   pH labeled by "A"
   $\underline{(Z)}$ labeled by "Z"
   $\bar{n}$ labeled by "M"
   X labeled by "A"
   Y labeled by "Y"

Test Data:

STORE 00 1×10^{-3}
STORE 01 0.100
STORE 02 100.0
STORE 03 5×10^{-4}
STORE 04 6.1982×10^{8}
STORE 05 6.3050×10^{15}
STORE 06 1×10^{-14}

1. Key PRIME, LOAD PROGRAM, VERIFY PROGRAM
   Display should read 1219.
2. Depress PRINTER ON
3. Key SEARCH 2
4. Key 0.10, GO, 4.11, GO
5. Read:

.10	B
4.11	A
2.594392098-11	Z
1.765483953-01	M
-5.302145026-11	X
-3.954311246+09	Y

000	09	00	* M
001	00	02	E 2
002	09	03	* SP
003	08	02	* W
004	04	02	× 2
005	06	15	ST 15
006	06	14	ST 14
007	07	01	RE 1
008	04	15	× 15
009	07	02	RE 2
010	02	14	+ 14
011	05	15	÷ 15
012	07	00	RE 0
013	06	07	ST 7
014	07	02	RE 2
015	04	07	× 7
016	07	14	RE 14
017	05	07	÷ 7
018	06	10	ST 10
019	00	02	E 2
020	04	07	× 7
021	07	15	RE 15
022	03	07	− 7
023	07	03	RE 3
024	06	08	ST 8
025	07	02	RE 2
026	04	08	× 8
027	07	14	RE 14
028	05	08	÷ 8
029	09	03	* SP
030	08	02	* W
031	03	02	− 2
032	00	12	E 12
033	09	11	* W*
034	06	15	ST 15
035	03	07	− 7
036	07	06	RE 6
037	06	14	ST 14
038	07	15	RE 15
039	05	14	÷ 14
040	02	07	+ 7
041	07	15	RE 15
042	08	12	* x^2
043	06	14	ST 14
044	07	05	RE 5
045	04	14	× 14
046	06	09	ST 9
047	07	04	RE 4
048	04	15	× 15
049	02	09	+ 9
050	00	01	E 1
051	02	09	+ 9
052	00	02	E 2
053	04	14	× 14
054	02	15	+ 15
055	05	07	÷ 7
056	08	02	* W
057	02	11	+ 11
058	08	05	* J+
059	08	00	* S
060	00	03	E 3
061	04	09	× 9
062	03	10	− 10
063	07	08	RE 8
064	05	10	÷ 10
065	08	02	* W
066	15	11	D 11
067	06	11	ST 11
068	00	02	E 2
069	06	12	ST 12
070	07	11	RE 11
071	03	12	− 12
072	00	01	E 1
073	03	11	− 11
074	05	12	÷ 12
075	07	07	RE 7
076	04	12	× 12
077	08	02	* W
078	00	11	E 11
079	07	07	RE 7
080	04	11	× 11
081	05	10	÷ 10
082	08	02	* W
083	01	11	T 11
084	08	02	* W
085	00	15	E 15
086	08	00	* S
087	00	02	E 2
088	09	00	* M
089	00	03	E 3
090	00	09	E 9
091	00	09	E 9
092	00	09	E 9
093	08	02	* W
094	07	00	RE 0
095	09	14	* EP

4. The linear regression analyses were performed using a program (19) from the Wang Model 500 Program Library. The program was modified by Dr. James E. Worsham, Jr. to give output in scientific notation, and the verify number was therefore changed from 2133 to 2145. A complete description of the program and operating procedure is presented in the reference noted above.

APPENDIX I

List of Equipment and Reagents Used

A. Equipment

1. Beckman Research pH Meter with Standard Beckman Glass Electrode and Saturated Calomel Electrode

   Beckman Instruments, Inc.
   Fullerton, California

2. Sargent Thermonitor Controlled Temperature Water Bath

   E. H. Sargent and Company
   Chicago, Illinois

3. Sealed Magnetic Stirrer

   Courtesy of Reynolds Metals Company
   Richmond, Virginia

4. Sargent-Slomin Electrolytic Analyzer

   E. H. Sargent and Company
   Chicago, Illinois

5. Beckman ACTA III UV-Visible Spectrophotometer

   Beckman Instruments, Inc.
   Fullerton, California

6. Wang Model 500 Advanced Programmable Calculator

   Wang Laboratories, Inc.
   Tewksbury, Massachusetts

7. Perkin-Elmer 210 Infrared Spectrophotometer

   The Perkin-Elmer Corporation
   Norwalk, Connecticut

8. Varian A60-A Nuclear Magnetic Resonance Spectrophotometer

   Varian Associates
   Palo Alto, California

B. Reagents

1. Epichlorohydrin

   Code L099

   J. T. Baker Chemical Company
   Phillipsberg, New Jersey

2. 2-Amino-2-methyl-1,3-propanediol

   Code A890, Lot 1-5196

   J. T. Baker Chemical Company
   Phillipsberg, New Jersey

3. 1,3-Dichloropropane

   Code H272, Lot 9-99

   J. T. Baker Chemical Company
   Phillipsberg, New Jersey

4. Hydrogen Chloride (anhydrous)

   Code 6390

   J. T. Baker Chemical Company
   Phillipsberg, New Jersey

5. Sodium Hydroxide - Carbonate Free
   (Standard Volumetric Solution)

   Anachemia Chemicals Limited
   Champlain, New York

6. Cupric Nitrate

   Code 1800, Lot 38520

   J. T. Baker Chemical Company
   Phillipsberg, New Jersey

7. Absolute Ethanol

   Commercial Solvents Corporation
   Terre Haute, Indiana

8. Perchloric Acid

   Code 2764

   Malinckrodt Chemical Works
   St. Louis, Missouri

9. Sodium Nitrate

   Code 3770

   J. T. Baker Chemical Company
   Phillipsberg, New Jersey

10. Amberlite IRA-400

    Code 3335, Lot XKV

    Malinckrodt Chemical Works
    St. Louis, Missouri

AUTOBIOGRAPHY

The author was born in Richmond, Virginia on February 4, 1947, and attended the primary and secondary schools in that city. Upon graduation from high school in June, 1964, he entered the University of Richmond, Virginia and received his B. S. degree in June, 1968.

He entered the service of the United States Army in October, 1968. Upon release from the Army in August, 1970, he entered the Graduate School of the University of Richmond and received the Puryear Fellowship. This thesis is submitted in partial fulfillment of the requirements for the degree of Master of Science.