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Synthesis and Application of An Organic Analytical Reagent

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SYNTHESIS AND APPLICATION OF
AN ORGANIC ANALYTICAL REAGENT

being

A thesis presented to the Graduate Faculty
of the Fort Hays Kansas State College in
partial fulfillment of the requirements for
the Degree of Master of Science

by

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Date

July 16, 1959

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ABSTRACT OF THE THESIS

SYNTHESIS AND APPLICATION OF
AN ORGANIC ANALYTICAL REAGENT

by

George W. Mc Court Jr., A.B.

Fort Hays Kansas State College

CONTENT: This work concerns the reaction of the primary amine, 2-amino-2-methyl-1-propanol with carbon disulfide to produce the amine salt of 1-methyl-(1-methylol)-ethylthiocarbamic acid. This salt is then investigated to determine its physical properties and the possibility of use in copper analysis.

A report is given on the reaction, and the purification and analysis of the reaction product

The colored reaction of the amine salt with copper and other metal ions is listed, and an analytical procedure for the determination of trace amounts of copper is given. Using the procedure described, accurate determinations of copper concentration to one ppm. were obtained.

The effect of pH on fading of the colored copper thiocarbamate was investigated and found to be negligible between the range of pH from 4 to 8.

An attempt was made to determine if the colored compound formed by reaction of the amine salt with copper was a chelate. Potentiometric and precipitation titrations were carried out with inconclusive results.

EXPERIMENTAL: The amine salt is best prepared through the reaction of two molar quantities of the amine with one molar quantities of carbon disulfide. The amine is dissolved in absolute ethanol and left at room temperature. The carbon disulfide is added to this solution and the reaction allowed to go to completion. The reaction mixture is then poured into a large evaporation dish and allowed to stand in the hood until a yield of yellow crystals is evident.

Purification of the crude product is carried out through repeated recrystallization from hot water.

For copper analysis, 10 ml. of the unknown copper solution is placed in a separatory funnel followed by 15 ml. of diethyl ether and one ml. of a one per cent solution of the reagent. This mixture is shaken vigorously for 30 seconds and the water layer removed from the funnel. The bottom delivery tube is thoroughly dried and the colored solution delivered into a cuvette. This is inserted into a spectrophotometer calibrated at 440 millimicrons and the per cent transmittance noted. The copper concentration is then obtained from a chart of known concentration plotted against per cent transmittance.

SUMMARY: The preparation of the amine salt of 1-methyl-(1-methylol)-ethylthiocarbamic acid is described. Physical characteristics which have been investigated are reported.

An analytical procedure has been developed for the colorimetric determination of trace amounts of copper. The method as described is sensitive to concentrations of one ppm.

The role of this amine salt as a chelating agent in the formation of the colored precipitate with copper has been investigated.

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INTRODUCTION

The reaction of carbon disulfide with ammonia and with primary or secondary amines ¹ was first studied in the middle of the nineteenth century. It was found that these reactions formed salts of dithiocarbamic or substituted dithiocarbamic acids. Further work showed that these acid salts and substituted acids react with the common metal ions to produce colored precipitates. ^{2, 5, 6, 10, 12} These precipitates found early use in gravimetric determinations of some of the metals; however, with the increasing use and greater convenience of the colorimetric methods of analysis, attention has shifted to this application.

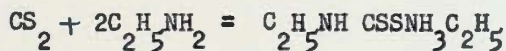
A work by Welcher ¹⁸ on organic analytical reagents lists six members of the dithiocarbamate family that have been used in metals analysis. One of this group, sodium diethyldithiocarbamate, has found extensive use in the quantitative analysis of trace amounts of copper. In the colorimetric method commonly used, ¹⁴ the metal is present in very small quantities. When copper reacts with the dithiocarbamate a colored compound is formed, which is extracted with an organic solvent. The colored extractant is then compared to a known standard using the colorimeter.

The purpose of this investigation was to determine the feasibility of using 2-methyl-2-amino-1-propanol, an amino alcohol prepared by reduction of the corresponding nitro compound (Vanderbilt, Hass, U.S. Pat. 2,174,242; 1940), in a reaction with carbon disulfide to produce a reagent which could be used satisfactorily in the colorimetric determination of trace amounts of copper.

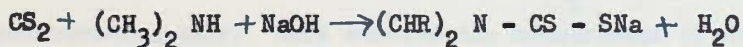
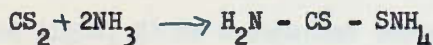
The study divided itself naturally into two phases. The first consisted of a study of the reagent, its formation, purification, description of physical characteristics, and analysis. After this portion of the project was completed, interest turned to the analytical application and study of the colored precipitate. Using copper as the test ion, the sensitivity of the reagent, fading of the colored reaction product, and other factors concerned in the development of a scheme of analysis were studied.

Theory

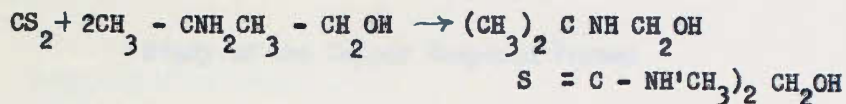
According to von Richter,¹⁶ the amine salts of alkyl dithiocarbamic acids are formed by heating together carbon disulfide and primary or secondary amines in alcoholic solution. The reaction between ethylamine and carbon disulfide is stated¹⁷ to proceed in the following manner:



Further examples of this type of reaction are given by Welcher.¹⁹



From these we can postulate a possible product for the interaction of carbon disulfide with the amine 2-methyl-2-amino-1-propanol:



The product is the amine salt of 1-methyl-(1-methylol)-ethyldithiocarbamic acid. For further confirmation of the identity of this product, the percentage of nitrogen and sulfur actually present in the reagent were determined and the percentages computed and those found were compared.

Analytical Application Theory

The dithiocarbamates give colors instead of precipitates with dilute solutions of metal ions. These solutions are suitable for colorimetric analysis if they do not decompose or fade too rapidly, and also follow Beer's Law. This law as given by Willard, Merritt, and Dean²⁰ states that the intensity of a ray of monochromatic light decreases exponentially as the concentration of the absorbing material increases. Presented symbolically this takes the form of equation (1),

$$\log \frac{I_0}{I} = K'c \quad (1)$$

where I_0 is the incident light intensity, I is the intensity of the transmitted light, K' is a constant depending on the wavelength of the light and the nature of the medium, and c is the concentration. If the wavelength and medium are not varied then $\log \frac{I_0}{I}$ will be a function of the concentration only. This enables the measurement of concentration of the unknown solution by determining the percentage of light transmitted as compared to a known plot of concentration versus transmittancy.

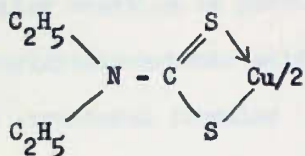
Study of the Copper Compound Formed

In the use of organic reagents for inorganic analysis, according to Yoe and Sarver,²¹ it is usually found that when an inorganic ion undergoes a direct union with an organic molecule, it replaces an acidic hydrogen to form a true salt. However, it sometimes forms, almost simultaneously, an additional coordinate bond giving rise to a ring or chelate structure which has a small degree of dissociation, a low solubility in water, and a high solubility in organic solvents. It is these properties which make some of the organic reagents extremely valuable for analytical purposes. The most stable chelate rings are those composed of five or six atoms, or in more rare instances, four or seven atoms. Either of the bonds may be normal (coordinate) in nature, although one is usually electrovalent in nature.

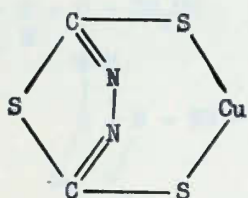
In order to obtain a coordinate bond, one of the bonding atoms must possess an unshared electron pair in its structure while the other must have room for an additional electron in its valence orbital. Through consideration of these factors it is often possible to predict whether or not an untried compound will have desirable analytical properties.

A further study of the literature reveals several structural formulas²² which have been proposed for the copper salts of organic reagents which owe their reactivity to sulfur groups. Several examples of these are shown below:

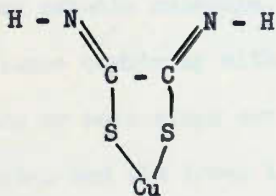
Diethyldithiocarbamic acid



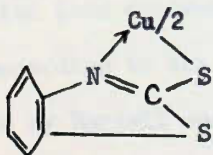
2,5-Dimercapto-1,3,4,-thiodiazole



Dithiooxamide



Mecaptobenzothiazole

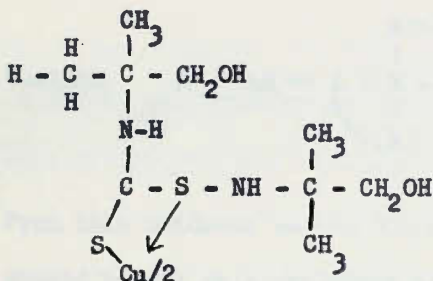


It can be observed that these compounds form copper salts by breaking one of the sulfur double bonds and replacing a hydrogen from

the second sulfur.

If a similar reaction is postulated for the salt of 1-methyl-(1-methylol)-ethyldithiocarbamic acid, the resulting copper salt could have one of the structural formulas

A.

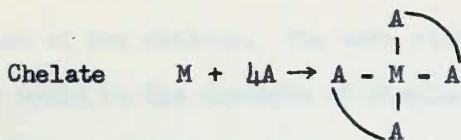
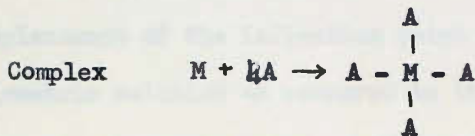


B.



Each of these shows a single copper atom attached at two points to the same organic molecule. In Martell and Calvin,⁷ it is stated that if a substance combining with a metal contains two or more donor groups so that one or more rings are formed, the resulting structure is said to be a chelate, and the donor is called a chelating agent. In the majority of cases the metal is united to the rest of the compound by two bonds; however, a full consideration of this class of substances requires their classification into unidentate, bidentate, terdentate, and quadridentate compounds according to the number of points of union involved. Mention is also made by Martell and Calvin⁸ of the donor atoms which combine with the metals. These are restricted to the strongly non-metallic elements of Groups V and VI in the periodic table. Of these the common examples are nitrogen, oxygen, and sulfur.

An illustration of the basic difference⁹ between a chelate and a complex is presented below:



From this evidence we can observe that the salt under investigation should behave as a chelating agent.

There are a number of methods for proving the existence of a chelate structure. Unfortunately the majority of these lend themselves to a variety of interpretations and in some cases apply to simple complexes as well.

The only direct proof so far developed⁹ for the existence of chelate rings is provided by x-ray crystal analysis. The other methods all rely on inference from observed phenomena rather than direct demonstration.

It was believed that a potentiometric titration⁴ would be most interesting to use in the attempt to determine whether the colored reaction product was a chelate. This titration involved the neutralization of a chelate-forming acid with sodium hydroxide to obtain a normal inflection point. Then, to test for presence of a

chelate formation, stoichiometric amounts of cupric sulfate were reacted with the acid (N,N'-dialkylethylene-diaminediacetic acid) and the resulting solution again titrated with sodium hydroxide. The displacement of the inflection point in the titration of the stoichiometric solution as compared to the normal neutralization titration is due to the presence of a chelate compound. This shift in inflection point was caused by the release of H ions during the formation of the chelate. The more stable the chelate formed, the greater would be the distance of displacement of the inflection point.

This method was used to study the reagent under consideration. A change in procedure was necessary since the one per cent solution of the amine salt was strongly basic. Hydrochloric acid was the titrant used in the attempt to determine the normal inflection point. The titration was unsuccessful as the reagent solution exhibited buffer characteristics caused by the presence of the two amine groups in the molecule. This made it obvious that further work along this line would be unavailing.

It was then considered that if a solution of known concentration of the acid salt solution were titrated against a definite quantity of copper ion, an inflection point would be obtained from which the number of molecules of the reagent combining with a copper atom could be determined. This would operate on the theory of a precipitation titration, with the change of potential in the solution being followed with the platinum electrode. This procedure was carried out and a weak inflection point obtained. Computations involving the use of Avogadro's number to determine the ratio of copper atoms to reagent

molecules at the inflection point failed to give conclusive evidence of the formation of a cupric chelate.

The data were used to determine the stability constants of the cupric chelate at this point.

Initial Concentration	0.001 M
Final Concentration	0.0005 M
Initial Volume	10 ml.
Final Volume	20 ml.

The initial concentration of the cupric ion was 0.001 M. The initial concentration of the ligand was 0.001 M. The initial concentration of the cupric chelate was 0.0005 M. The initial concentration of the cupric ion was 0.001 M. The initial concentration of the ligand was 0.001 M. The initial concentration of the cupric chelate was 0.0005 M.

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EXPERIMENTAL

Formation and Purification

The amine used was 2-amino-2-methyl-1-propanol. Characteristics of this amine¹¹ are:

Mol. Wt.	89.14
Index Refraction	1.449 ²⁰
Density	0.934 g./ml.
Boiling Point	165°C.

The initial attempt used 19.09 ml. of the amine dissolved in 25 ml. of 95 per cent ethanol. This solution was placed in a 125 ml. Erlenmeyer flask and cooled in an ice bath. To this, 6.03 ml. of carbon disulfide was added dropwise. No reaction was evident at this low temperature and the mixture was left standing in the hood overnight. There was no visible reaction after 24 hours; however after the reaction mixture had stood for 15 days at room temperature small quantities of yellow solid formed in the flask. This solid was present in a heavy, viscous yellow fluid.

The second preparation used the same quantities of amine and carbon disulfide. The amine was dissolved in 50 ml. of 95 per cent ethanol. This solution, in a 125 ml. Erlenmeyer flask, was left at room temperature of 28° C. and the carbon disulfide added dropwise. There was an immediate reaction as demonstrated by the heating of the flask. This soon went to completion and after the flask had cooled the solution was poured into a large evaporation dish and allowed to stand overnight in the hood. After 24 hours a good yield of yellow crystals was obtained.

This same procedure was run again with 25 ml. of diethyl ether used as the amine solvent. A good yield of crystals was obtained; however, 48 hours were required for the evaporation. The reaction was again repeated with procedure identical to the above, using a different amine solvent. This preparation used 25 ml. of absolute ethanol and was found to give a good yield, fairly free from the viscous yellow fluid which accelerated decomposition when in contact with the crystals.

Purification

Ethyl ether, acetone, absolute ethanol, and petroleum ether were used in the first attempts to recrystallize the crude product. All these were unsuccessful. Recrystallization from boiling water gave a satisfactory yield of semi-transparent, rectangular crystals. These had an offensive odor and were rather soft.

Summary

The method of preparation and purification found to be most efficient was reaction of two molar quantities of the amine with one molar quantities of carbon disulfide. The amine is dissolved in absolute ethanol and left at room temperature. The carbon disulfide is added to this solution and the reaction allowed to go to completion. The reaction mixture is then poured into a large evaporation dish and allowed to stand in the hood until a yield of yellow crystals is evident. Purification of the crude product is best accomplished by repeated recrystallization from hot water.

Using the experimental apparatus pictured in Figure 1, the reaction was observed under more controlled conditions. At a constant temperature of 25° C. for the amine-alcohol solution, the temperature of the reaction mixture rose to 41° C. and then subsided. The gas traps contained 0.1 M. aqueous solution of lead nitrate to determine if hydrogen sulfide was produced in the reaction. No precipitation of lead sulfide was observed, however a gas did bubble through. This was probably air expanded by the heat of the reacting mixture.

Analysis

The method of freezing point depression¹⁵ was used in an attempt to find the molecular weight. Twelve determinations were run; however, the results were inconclusive. The experimental data are presented in Table I.

After failure of the freezing point method to yield the molecular weight, the procedure of comparing the calculated and experimental percentages of sulfur and nitrogen, was used.

The reagent samples for these determinations were recrystallized three times to attain maximum purity. After purification the samples were kept in the dark under refrigeration.

The Kjeldahl procedure as given in Fischer³ was used for the determination of nitrogen. Determinations were obtained of 10.97 and 11.07 per cent. These are compared with the calculated value of 11.10 per cent.

The Parr Bomb fusion method¹³ was used for the determination of sulfur. This gave sulfur determinations of 25.09 and 25.26 per cent. These are compared to the calculated percentage of 25.2 per cent.

Physical characteristics of the purified product are given in Table II.

Figure 1 Apparatus Used to Study Reaction

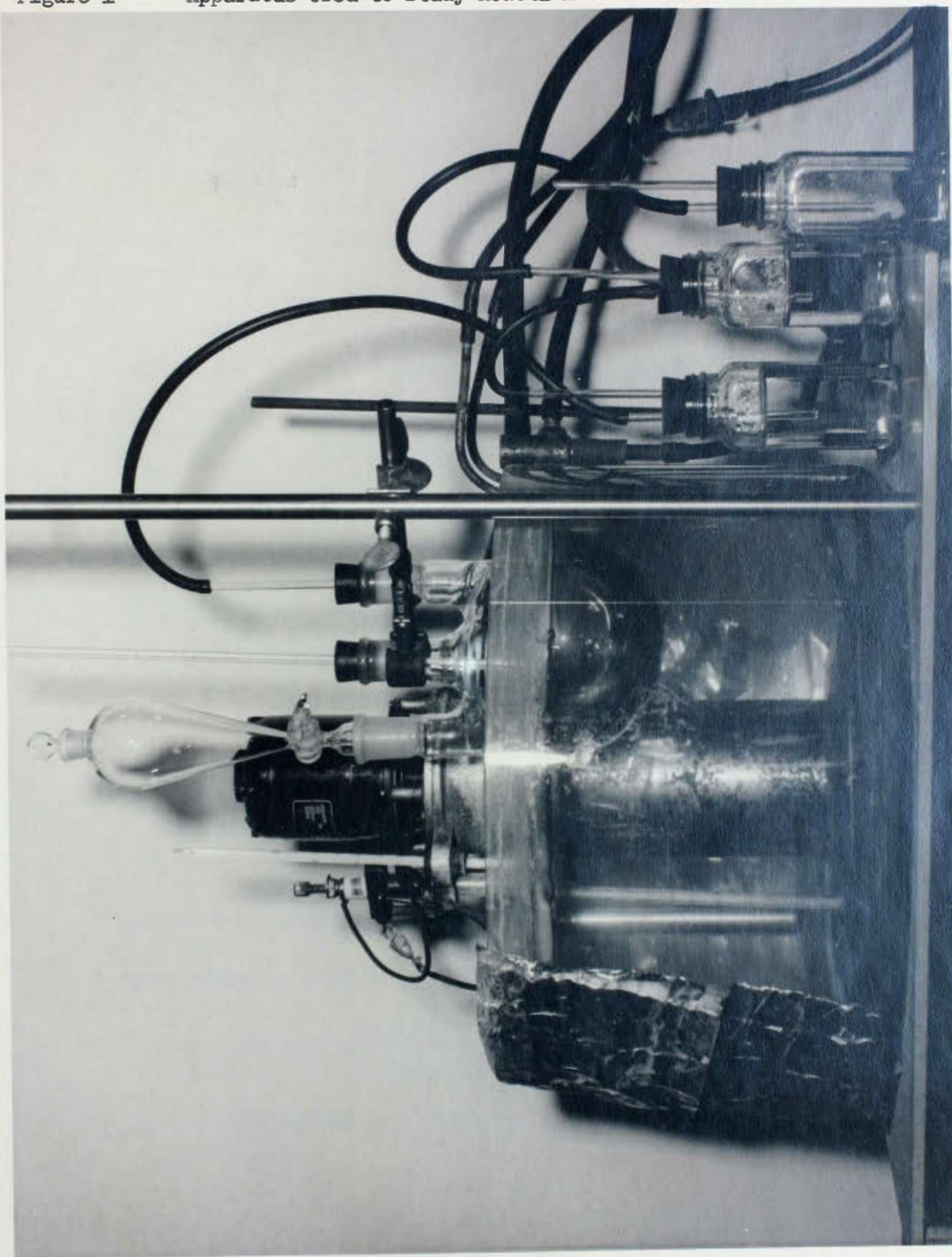


TABLE I

RESULTS OF ATTEMPT TO DETERMINE MOLECULAR
WEIGHT BY FREEZING POINT DEPRESSION

Determination Number	Δt ° C.	W (g.)	Molecular Weight
1.	.011	.0124	83.85
2.	.020	.0242	90.02
3.	.012	.0225	139.50
4.	.023	.0455	147.18
5.	.039	.0688	131.25
6.	.095	.1581	123.81
7.	.044	.0635	107.37
8.	.051	.0793	115.68
9.	.072	.1110	121.51
10.	.105	.1232	78.63
11.	.071	.1230	135.10

Above computed from the formula:

$$M.W. = \frac{(1.86) (1000) (W)}{(\Delta t) (25)}$$

$$K_f \text{ for water} = 1.86$$

TABLE II
SOME PHYSICAL CHARACTERISTICS OF THE AMINE SALT OF
1-METHYL-(1-METHYLOL)-ETHYLDITHIOCARBAMIC ACID

Top view of purified crystals

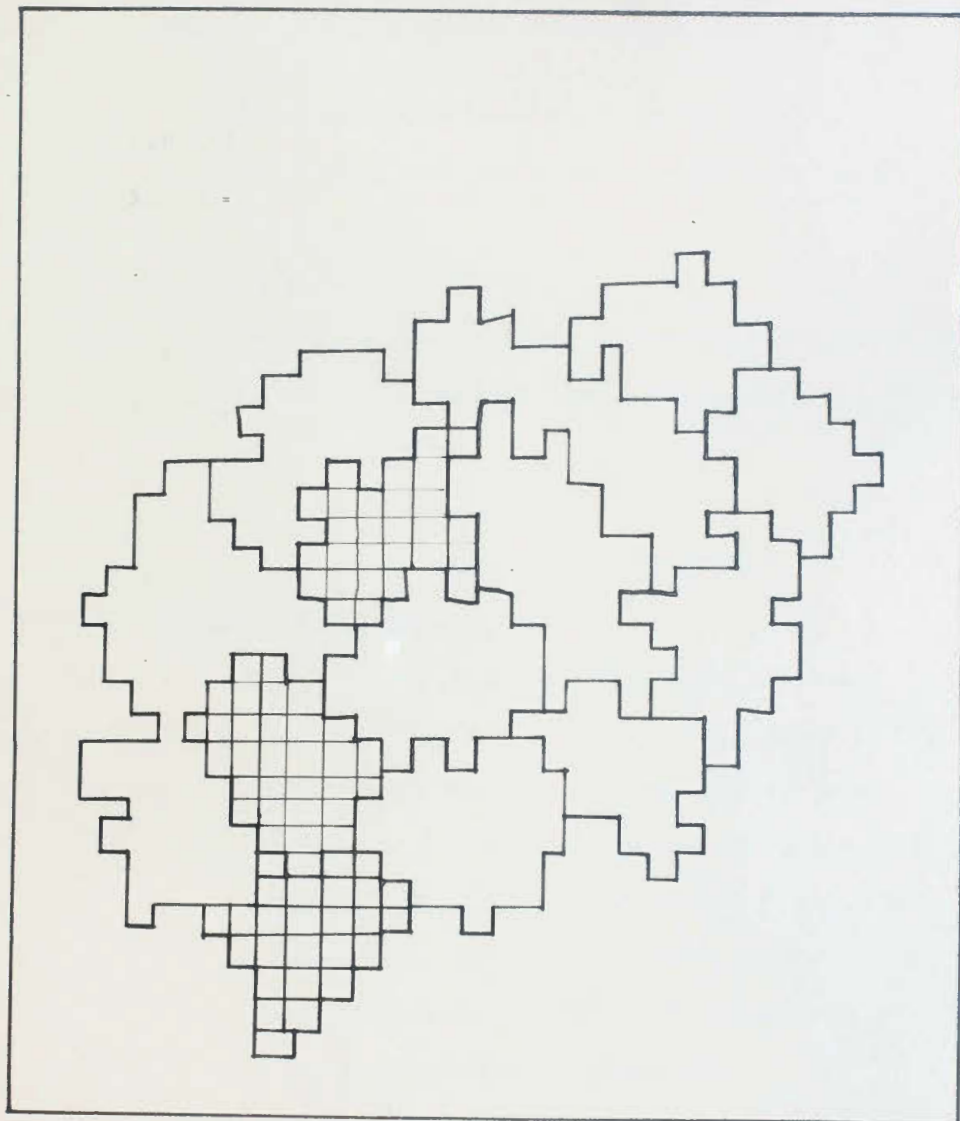


TABLE II (Continued)

SOME PHYSICAL CHARACTERISTICS OF THE AMINE SALT OF
1-METHYL-(1-METHYLOL)-ETHYLDITHIOCARBAMIC ACID

State:	Rectangular, semitransparent crystals
Oder:	Offensive, combination of amine-hydrogen sulfide
Color:	Light yellow
M. P.	Decomposes, 97-98° C.
Stability:	Decomposes upon standing at room temperature. If kept in dark under refrigeration, the crystals are stable for over six months.
Formula: (Probable)	$\text{CH}_3 - \text{C} - \text{CH}_2\text{NH} - \text{CH}_2\text{OH}$ $\text{S} = \text{C} - \text{S} - \text{NH} - \text{CCH}_3\text{CH}_2\text{OHCH}_3$
Molecular Weight:	253 g./mole
Solubility:	Sol. in ether, acetone, 95% ethanol, and water
Combustion Data:	The application of heat to a small sample of the solid caused white fumes of acrid odor to be produced. A green tint was evident in the melting crystal. The crystals burned with a yellow flame, but no soot. After combustion a small amount of dark residue was observed. This was neutral to litmus and soluble in dilute HCl.

Analytical Application

Formation and Extraction. A one per cent aqueous solution of the amine salt of 1-methyl-(1-methylol)-ethylthiocarbamic acid was used in all the following work. A standard copper solution of 0.01 per cent was prepared by dissolving 0.1964 g. of clear, uneffloresced crystals of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in water, adding enough HCl to make the final acidity about 0.1 N. and diluting to 500 ml. This gives a copper concentration of 100 ppm. (parts per million) from which weaker solutions can be prepared by dilution with 0.1 N. HCl.

The instrument used was the Coleman Jr. Spectrophotometer, Model 6-A with 50 ml. cuvettes.

Ten ml. of a standard 2 ppm. copper solution was placed in a separatory funnel. The addition of one ml. of the one per cent reagent solution resulted in a distinct yellow color. This was clear and homogeneous, and if stable would have been suitable for colorimetric determinations. However the color faded too rapidly to be directly useful. In an effort to stabilize the color, the procedure was repeated with one ml. of a 0.1 M. solution of ammonium citrate added to the solution before the reagent. It was hoped that this would cause increased complexing and inhibit fading but it resulted in a cloudy solution which was useless for colorimetric measurements.

Concentrated ammonium hydroxide was next used in an attempt to deter color fading. Unfortunately the addition to the colored solution of 2 ml. in 0.5 ml. portions only increased the fading rate.

It became evident that a solvent extraction would be necessary to

get the colored copper thiocarbamate out of solution. Carbon tetrachloride was the first solvent used. In this procedure 10 ml of the 2 ppm. copper solution was placed in a separatory funnel and one ml. of reagent solution added. After the color reaction, 10 ml. of carbon tetrachloride was added and the mixture shaken vigorously for 30 seconds. At the end of this time, the copper thiocarbamate had formed a brownish oil in the solvent layer. This caused the carbon tetra chloride to be discarded as a possibility for solvent extraction.

Amyl acetate was the next solvent investigated. Using the same method employed for carbon tetrachloride it gave a very good, clear, homogenous yellow color. However when tested on a blank composed of 10 ml. of the reagent solution it gave an identical yellow coloration and was deemed unsatisfactory.

Further extractant study used 10 ml. of a 2 ppm. copper solution placed in a separatory funnel, with one ml. of the reagent solution. To this was added one ml. of a solution of gum tragacanth and 10 ml. of isoamyl alcohol. The colored compound was successfully extracted and fading was reduced but not to the degree necessary to make an accurate determination possible.

Ethanol and methanol were next tried as extractants. Using 5 ml. of the alcohol with 5 ml. of the reagent solution combined in a separatory funnel and shaking vigorously for 30 seconds, the methanol was observed to react with the reagent solution giving off heat and a gas, while ethanol developed a yellow color during the shaking process.

Neither was a suitable solvent.

Next, 5 ml. of a 3 ppm. copper solution was placed in a separatory funnel and 5 ml. of ethylene glycol monobutyl ether (butyl cellosolve) added. One ml. of the reagent solution was dropped into the mixture. This system was shaken thoroughly for 30 seconds. The copper thiocarbamate was successfully extracted; however, the color faded badly and the solvent layer failed to clear up but increased in opacity. Butyl cellosolve was rejected as an extractant.

Ethyl ether was the next reagent used in the search for a satisfactory solvent. Ten ml. of a 3 ppm. copper solution was placed in a clean separatory funnel, with 15 ml. of ethyl ether, and one ml. of the reagent solution added. This mixture was shaken for 30 seconds. After the layers had separated, the ether portion was observed to have extracted the copper thiocarbamate. The solution was clear and homogeneous, fading was inhibited, and the extractant seemed suitable for colorimetric determinations. A blank was run using 10 ml. of the reagent and 15 ml. of diethyl ether. The mixture was shaken vigorously in a separatory funnel for 30 seconds and no color was imparted to the ether by the reagent.

On the basis of this series of investigations, diethyl ether was selected to use as the solvent in the extraction process.

Spectral Absorption. The next step in the development of an analytical procedure was to determine the wavelength at which the colored compound would absorb the maximum amount of light. To accomplish this, 10 ml. of a 3 ppm. copper solution were placed in a clean, dry separatory funnel. Fifteen ml. of ether and one ml. of

the reagent solution were added. The mixture was shaken for 30 seconds and allowed to separate. The bottom water layer was released from the funnel and the delivery stem thoroughly dried. Next the colored layer was delivered into a clean cuvette. Another cuvette was filled with ether to serve as a blank.

The spectrophotometer had a range of 400 to 700 microns. The absorption curve was run in 10 micron increments. First the blank was inserted and the instrument adjusted by means of the galvanometer to give 100 per cent transmittancy at the selected wavelength setting. The blank was then removed, and the colored sample inserted. The per cent transmittancy at that wavelength was then entered on a graph. From the resulting curve, the wavelength of maximum absorbancy can be observed from a low point on the curve. From the data shown in Table III a curve was plotted, Figure 2, which indicates that the wavelength most suitable for this procedure is 440 microns.

Quantitative Determinations. With the wavelength of maximum absorbancy known, the reagent was tested for Beer's Law sensitivity. The procedure for this phase of the investigation consisted of introducing 10 ml. of the copper solution of the desired concentration into a separatory funnel, adding 15 ml. of ether, and finally one ml. of the reagent solution. This mixture was shaken vigorously for 30 seconds, the water layer removed from the funnel, the bottom delivery tube dried thoroughly, and the colored solution delivered into the cuvette. A blank was inserted into the instrument which was

TABLE III

SPECTRAL ABSORPTION DATA

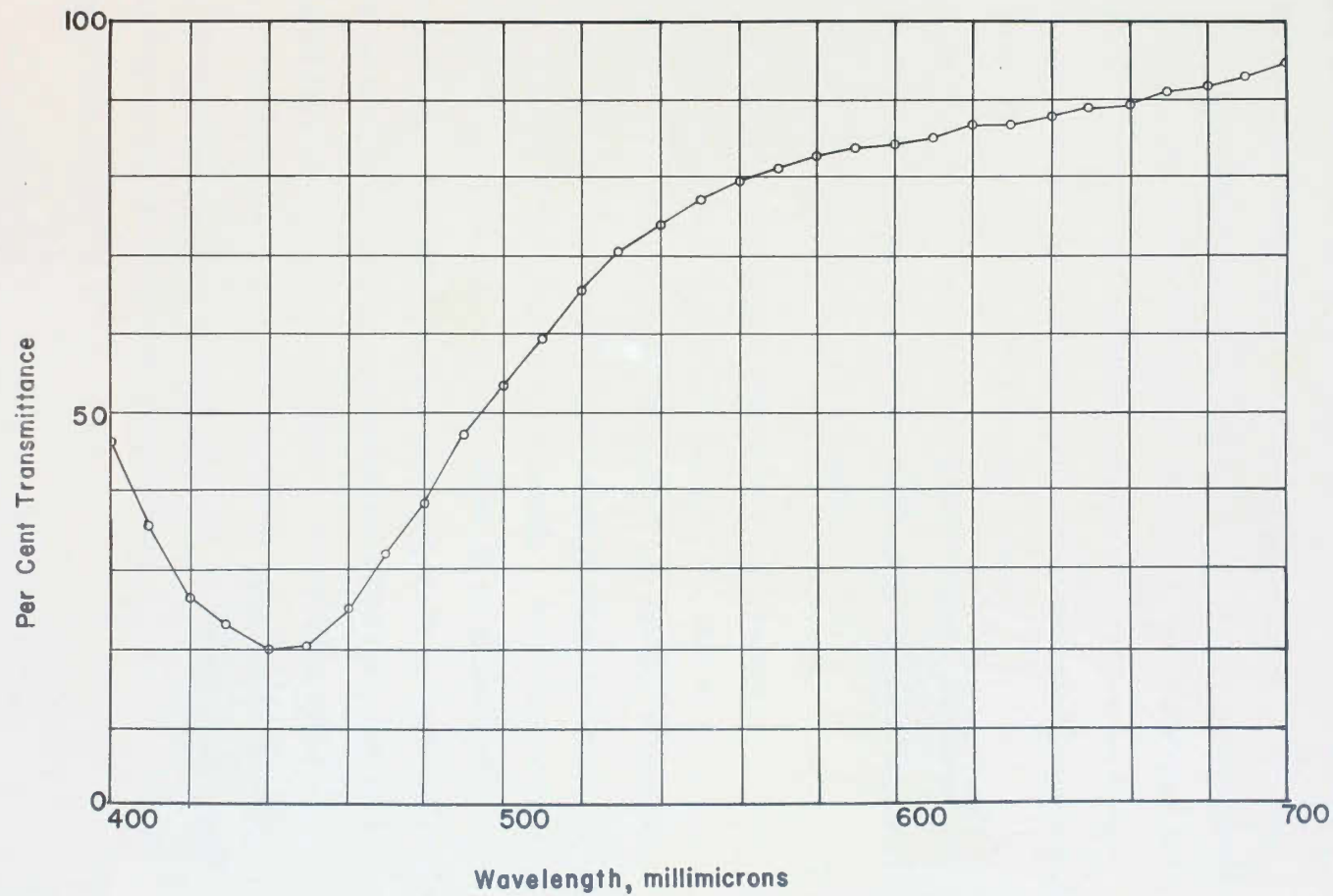
Wavelength	Per Cent Transmittancy
400	46.8
410	36.3
420	27.5
430	22.6
440	20.0
450	21.0
460	25.0
470	31.5
480	38.8
490	47.0
500	53.5
510	59.6
520	65.4
530	70.5
540	73.9
550	77.3
560	79.9
570	80.9
580	83.0
590	84.0
600	84.1
610	84.9
620	87.0
630	86.9
640	87.9
650	89.0
660	89.9
670	91.1
680	92.1
690	93.0
700	95.0

Figure 2

Spectral Absorption

Concentration: 3 ppm. copper

Extractant: ether



adjusted to read 100 per cent transmittancy at 440 microns. The colored solution was inserted into the spectrophotometer and the per cent transmittancy observed. Table IV gives the results of three such procedures done at different times. Reference to Figures 3, 4, and 5 shows a line of constant slope obtained by plotting the percentage transmittancy against concentration. From this it is evident that the transmission increases as the concentration decreases therefore the determination follows Beer's Law.

By the procedure given above, sensitivity can be determined accurately. An increase in the amount of copper solution used would increase the sensitivity of the procedure.

Fading Determinations. Since fading of the complex is detrimental to the effectiveness of the determinations, the role of pH in this respect was next investigated. Several of the schemes of analysis using the dithiocarbamates adjust the pH with indicators while the copper solution is in the separatory funnel. From this fact it was believed necessary to determine the effect of pH adjusted by the use of indicators. The procedure used two drops of the selected indicator added to the copper solution, then adjusted pH to end point through addition of dilute ammonium hydroxide or hydrochlorid acid.

The indicators used were thymol blue, methyl orange, methyl red, bromothymol blue, phenolphthalein, and alizarin yellow. After adjusting the pH the analytical procedure was carried out, and the color fading determined by noting the increase in per cent transmittancy

TABLE IV

BEER'S LAW SENSITIVITY

DETERMINATION NUMBER	CONCENTRATION (PPM.)	PER CENT TRANSMITTANCY
I.	5	10.4
	4	14.0
	3	21.0
	2	34.1
	1	57.1
	0.5	78.1
II.	4	12.2
	3	18.5
	2	30.4
	1	49.9
	0.5	69.3
III.	4	11.6
	3	18.4
	2	30.1
	1	51.4
	0.5	69.9

Figure 3
Beer's Law Sensitivity

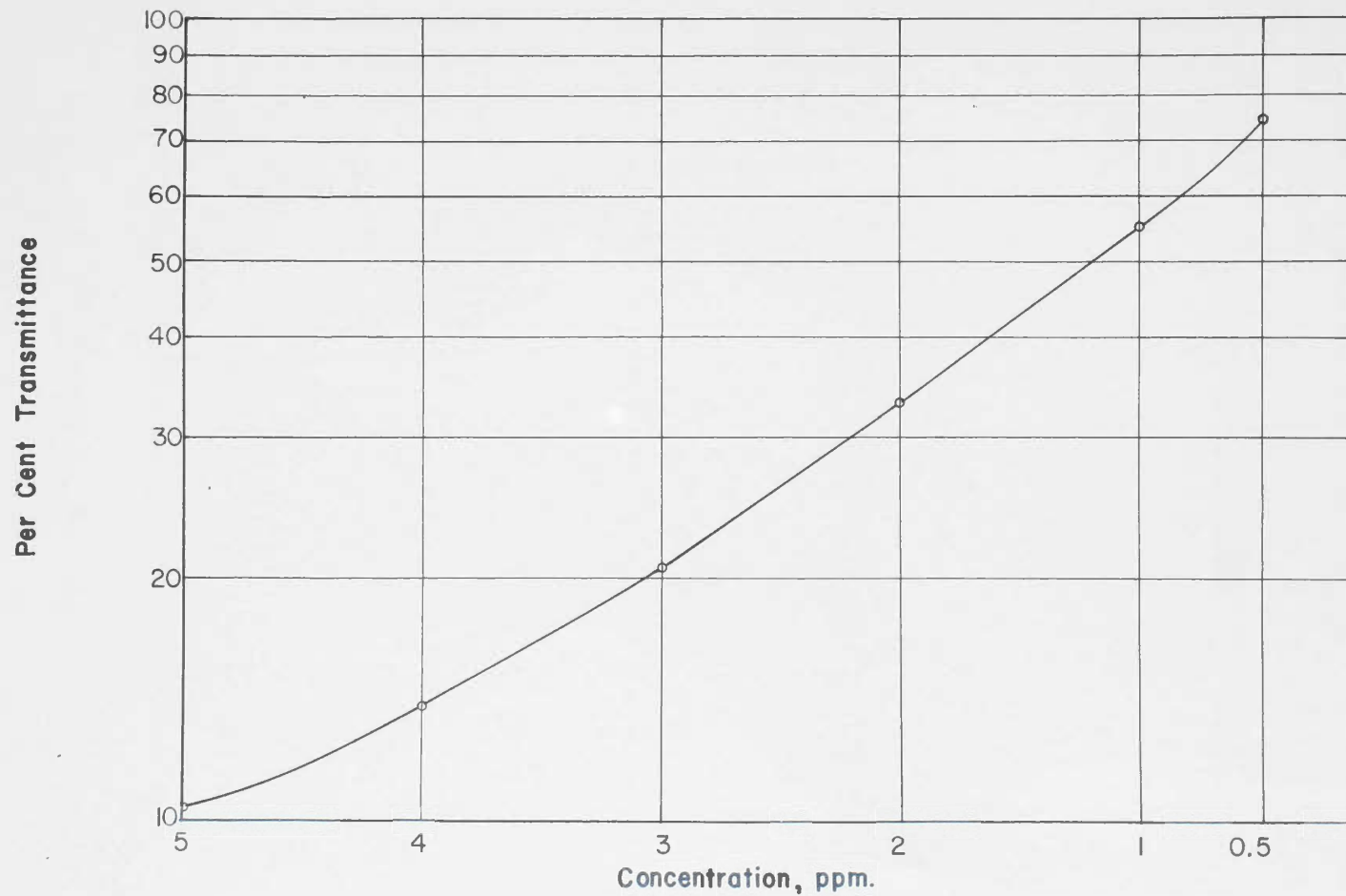


Figure 4
Beer's Law Sensitivity

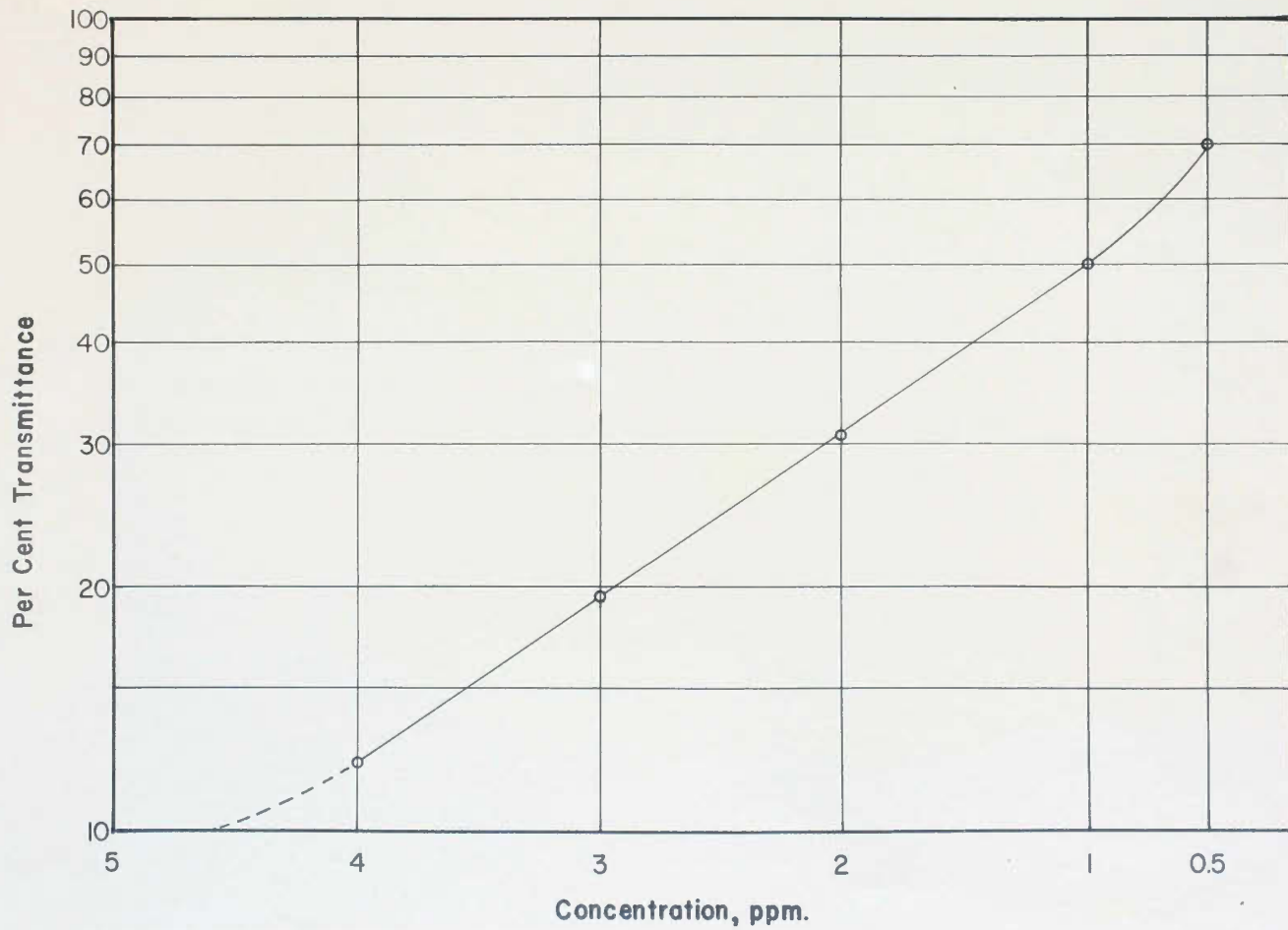
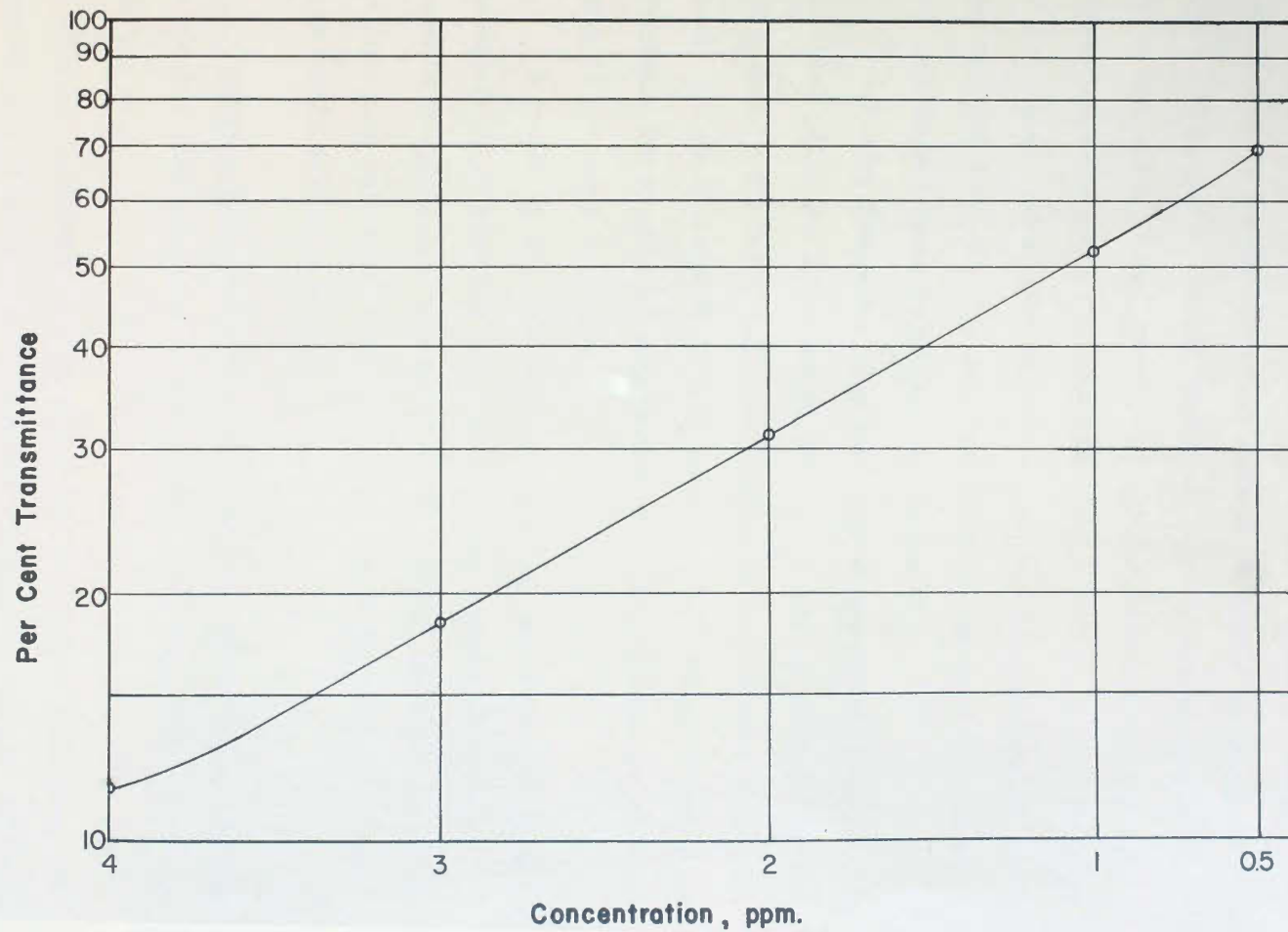


Figure 5
Beer's Low Sensitivity



after the lapse of measured time intervals.

The result of this study as presented in Table V showed thymol blue to be unsatisfactory because it caused an extremely rapid fading curve. Methyl Orange was usable, however the fading curve was fairly steep. Methyl Red reacted with the reagent and proved unsatisfactory. Bromothymol blue is usable, giving a curve of low slope. Phenolphthalein also gave satisfactory results having the smallest slope for the four and one-half hour testing period. The results are shown graphically in Figure 6.

A Fisher Titrimeter with the glass electrode was used to find the exact pH of the solutions at the fading points. Samples of pH 3.00, 4.05, 5.20, 6.65, 8.01, and 10.00 were used in this fading check. Dilute HCl and NH_4OH were used to adjust the pH of the copper solution. The results of this series of investigations are given in Table VI and shown in Figure 7.

A review of the data obtained from the use of indicators and the solutions of known pH indicates that the optimum pH for this scheme of analysis lies between 4 and 8. It must also be noted that the fading is not greatly affected by pH unless the copper solution is extremely acidic or basic.

Reaction with Metals other than Copper. The reagent solution was reacted with solutions of metal ions, other than copper to determine the presence of a color-forming reaction. The procedure used 5 ml. of a 1.0 M. solution of the metal ion in a 6 inch test tube, and added two ml. of the reagent solution. The reagent reacted with many

TABLE V

FADING DETERMINATION

INDICATOR	TIME (Min.)	INCREASE IN % TRANSMITTANCY
Thymol Blue	30	14
Bromthymol Blue	30	0.8
	60	5.0
	120	10.1
	180	14.5
	240	16.9
	270	18.0
Methyl Orange	30	4.1
Phenolphthalein	30	2
	60	5
	120	8
	180	10.6
	240	12.2
	270	13
Alizarin Yellow	30	8.0
	60	13.4
	120	20.0
	180	24.4
	240	27.9

Figure 6
Effect of indicator on fading

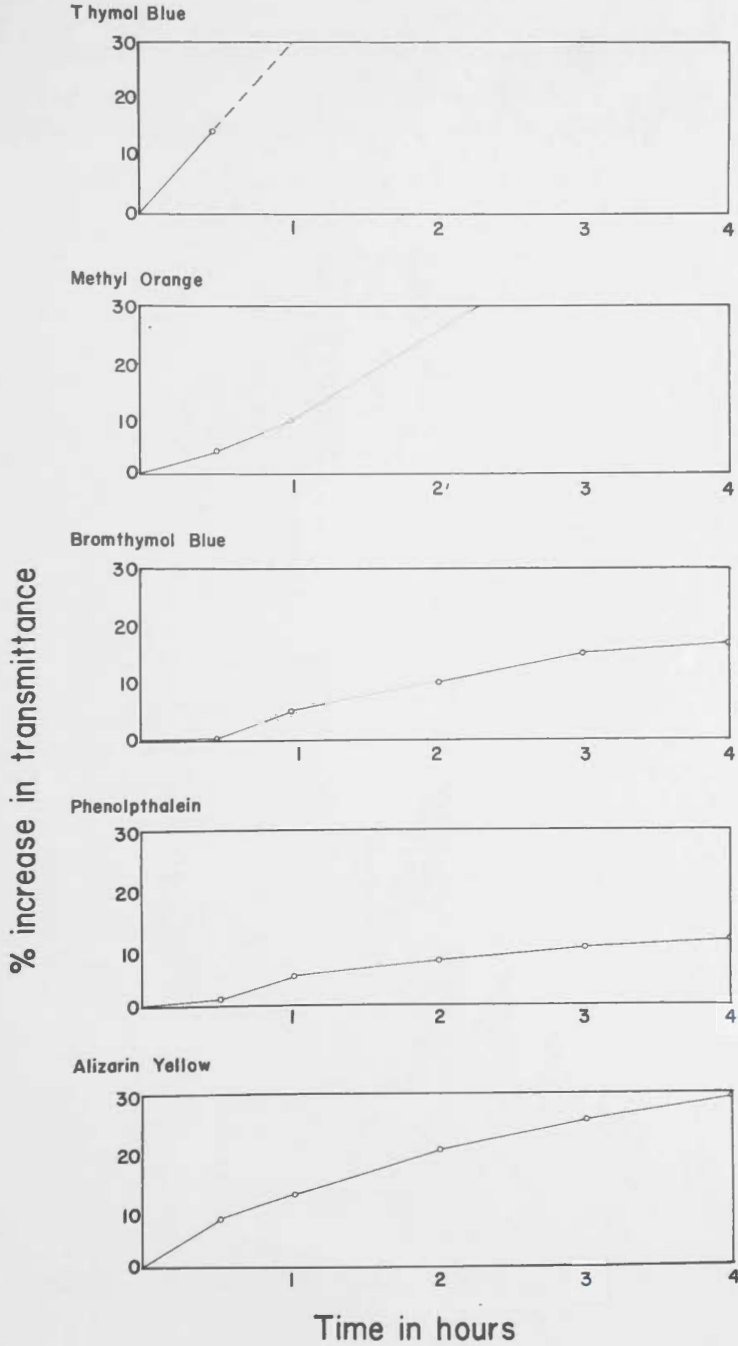


TABLE VI

pH EFFECT ON FADING

pH	TIME (Min.)	INCREASE IN PER CENT TRANSMITTANCY
3.00	30	1.9
	45	3.8
	75	5.8
	135	9.9
	195	15.9
	255	22.8
4.05	15	1.0
	45	2.5
	105	6.5
	165	12.1
	225	18.4
5.20	15	0.1
	30	0.6
	45	1.5
	60	2.2
	120	7.6
	180	13.5
	270	20.6
6.65	15	1.4
	30	3.4
	60	5.0
	120	9.9
	180	14.0
	240	19.0
8.01	30	0.2
	60	1.6
	120	4.5
	180	9.5
	240	14.4
10.00	30	0.2
	60	1.3
	120	5.3
	180	10.3
	240	14.6

Figure 7
Effect of pH on Fading

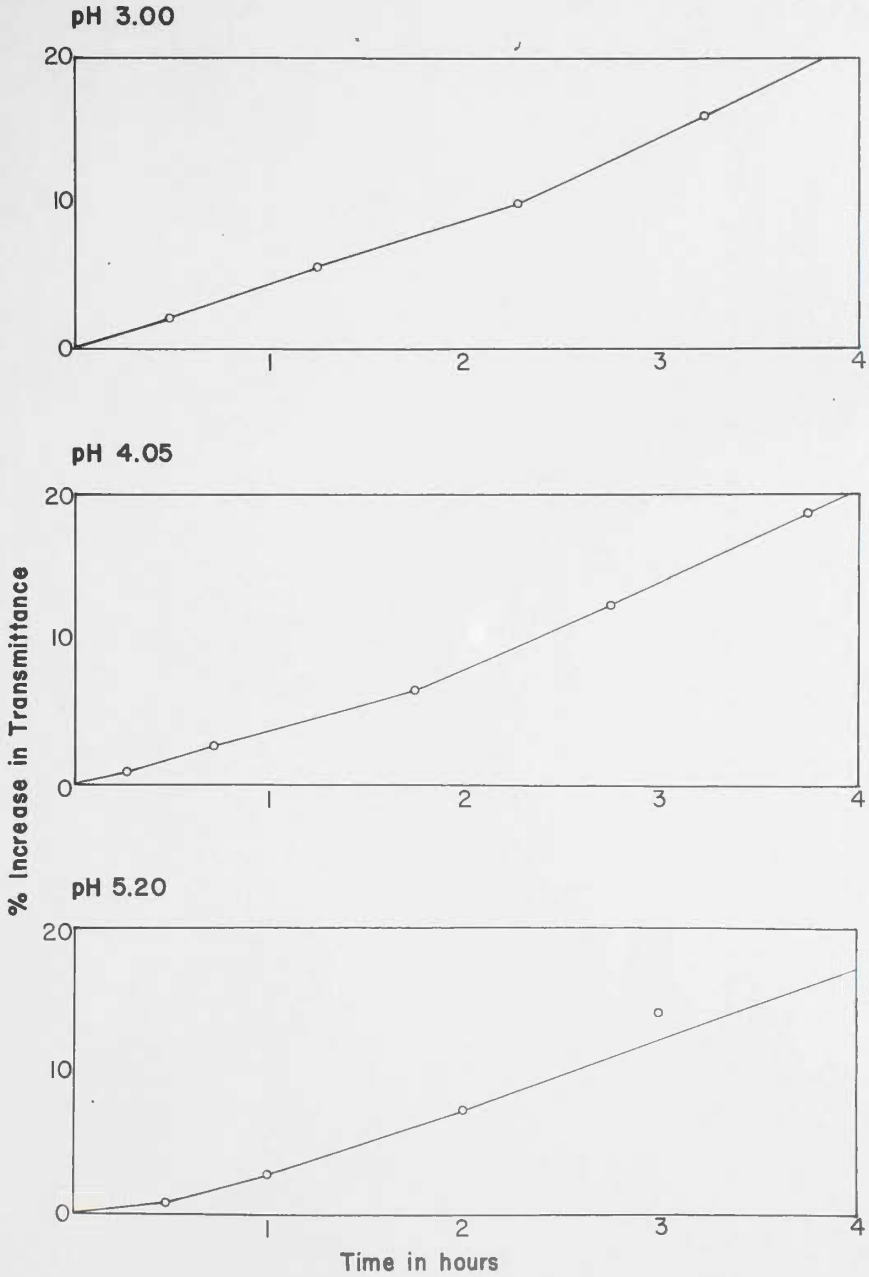
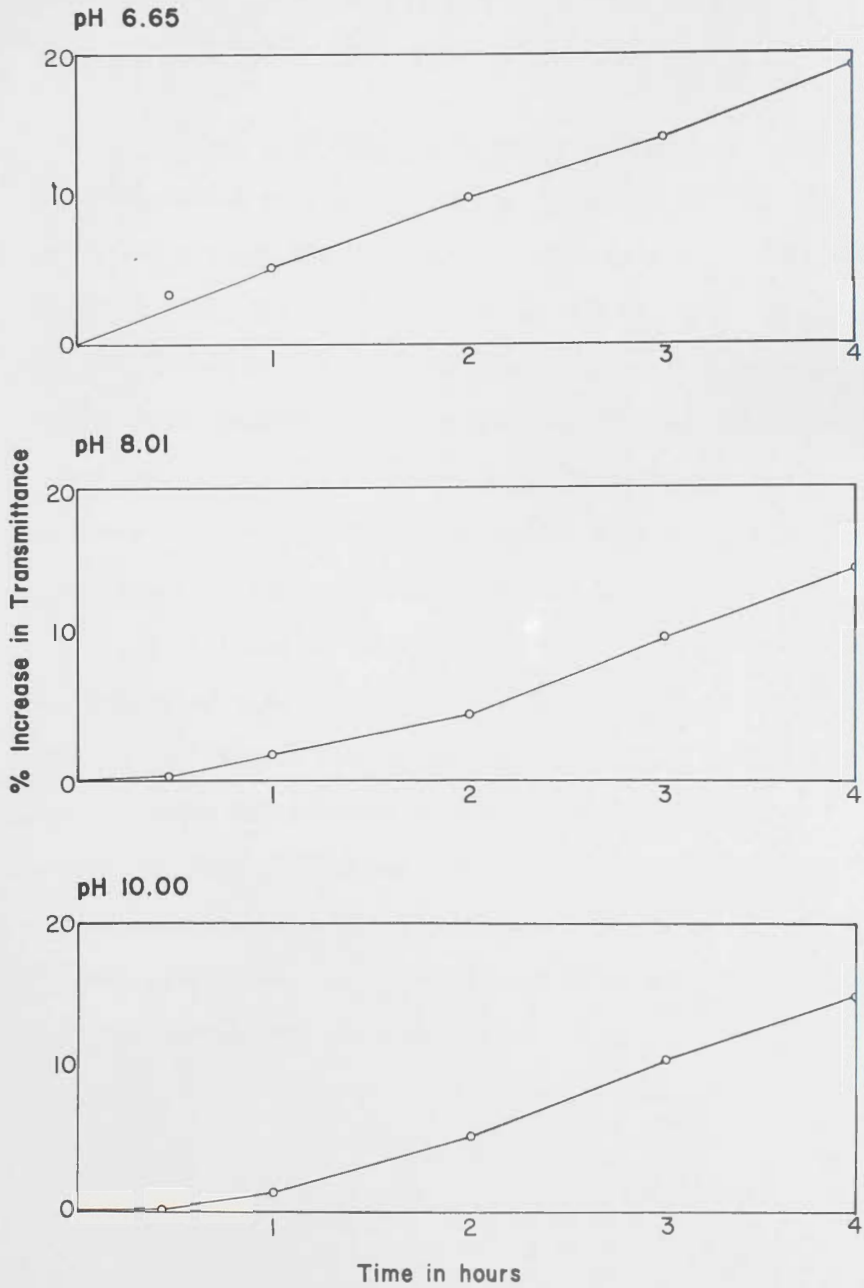


Figure 7-A
Effect of pH on Fading



of the ions to produce colored precipitates as shown in Table VII. From these color reactions it seems probable that the reagent could be used effectively in the analysis of ions other than copper.

Study of Properties of Colored Compound. An aqueous solution of 0.004 M. acid salt was prepared. Forty ml. of this solution was placed in a clean 250 ml. beaker. Against this solution was titrated 0.1028 N HCl. The Fisher Titrimeter with the glass electrode was used to follow this titration. The initial pH of this solution was 8.98. This failed to decrease upon the addition of the acid and after adding 39.1 ml. of the acid and stirring for one hour, the pH had increased to 9.1. Since the buffer effect would prevent the effecting of a valid inflection point, the procedure was abandoned.

As outlined in the theory section, a precipitation titration was attempted next. For this procedure, 30 ml. of a 0.0016 M. solution of the reagent was titrated with 0.0016 M. CuSO_4 . The E.M.F. of the titration was followed with the platinum electrode. From the results of these titrations as given in Table VII, the inflection points occurred at ratios of approximately 10.5 molecules of reagent to each atom of copper. This did not allow positive assignment of the structure of the chelate.

TABLE VII

COLOR REACTIONS WITH METAL IONS

Test Ion	Precipitate color
Bismuth	bright yellow
Cobalt	black
Nickel	greenish-yellow
Mercury	black
Manganese	no reaction
Iron III	white
Calcium	no reaction
Strontium	no reaction
Lead	brown
Magnesium	no reaction
Aluminum	yellowish-white
Barium	no reaction
Chromium	light gray
Tin II	bright yellow
Zinc	white

TABLE VIII

PRECIPITATION TITRATIONS

Titration I		Titration II	
Ml. Reagent	E.M.F.	Ml. Reagent	E.M.F.
00.00	0.160	00.00	0.161
00.07	0.190	00.10	0.202
00.15	0.202	00.20	0.216
00.20	0.208	00.30	0.220
00.25	0.209	03.00	0.244
00.31	0.210	09.00	0.270
00.39	0.210	11.39	0.293
00.45	0.212	12.37	0.340
03.00	0.239	12.49	0.360
07.00	0.256	12.60	0.379
12.00	0.256	12.70	0.392
12.50	0.325	13.00	0.423
12.65	0.344	13.50	0.456
12.69	0.357	14.00	0.475
12.80	0.371	14.50	0.490
12.91	0.385	15.00	0.499
13.00	0.394	15.50	0.506
13.14	0.405	16.00	0.511
13.50	0.439	17.00	0.524
14.00	0.462	18.00	0.530
14.50	0.471		
15.00	0.484		
16.00	0.502		
17.00	0.519		
18.00	0.529		
19.00	0.533		
20.00	0.539		

Figure 8

Precipitation Titration II

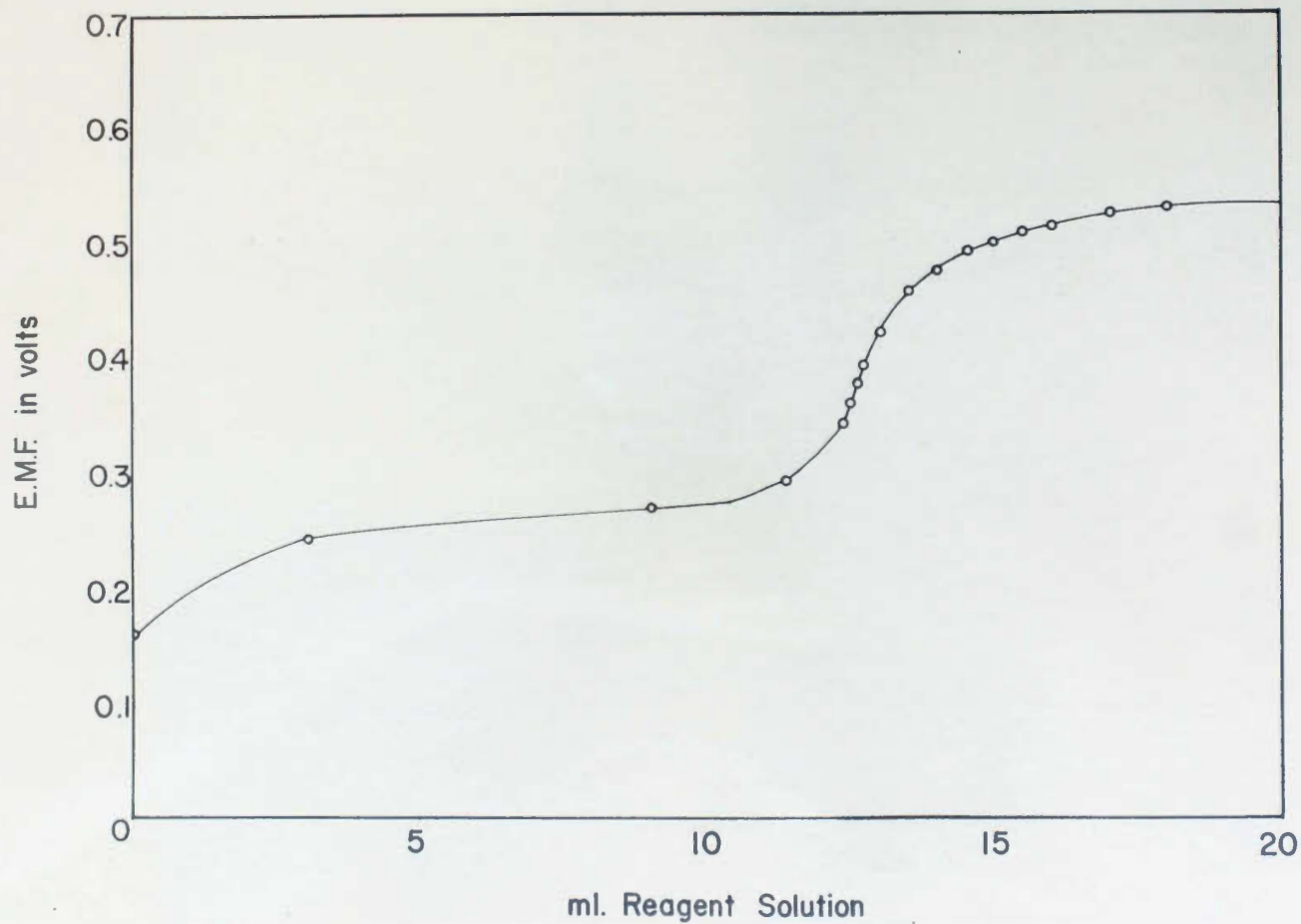
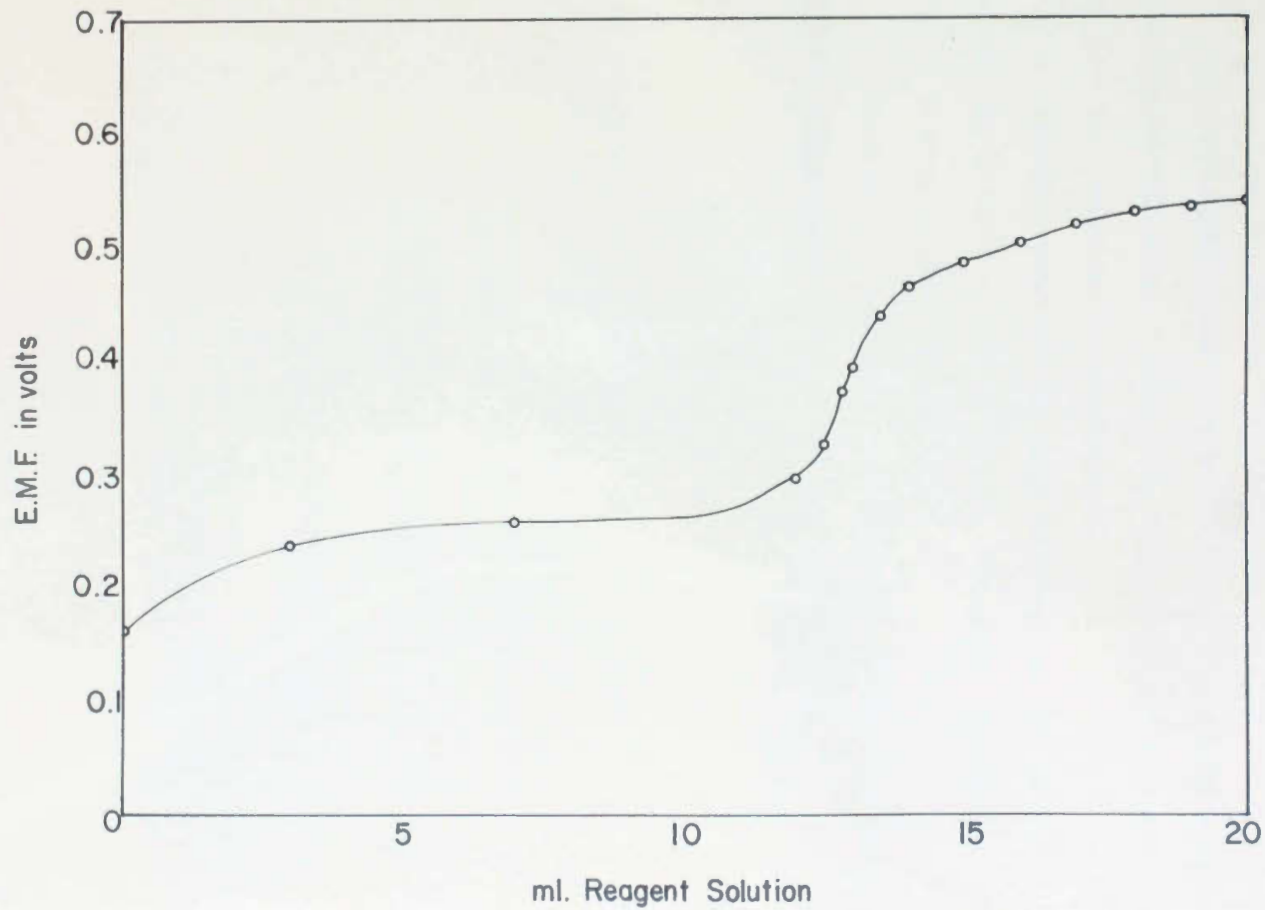


Figure 9

Precipitation Titration I



CONCLUSION

The preparation of the amine salt of 1-methyl-(1-methylol)-ethylthiocarbamic acid, is described. Physical characteristics which have been investigated are reported.

An analytical procedure has been developed for the colorimetric determination of trace amounts of copper. The method as described is sensitive to concentrations of one ppm.

The role of this acid salt as a chelating agent in the formation of colored precipitates of metals has been investigated.

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