8-1975

An atomic absorption method for determining micromolar quantities of primary aliphatic amines in the presence of secondary and tertiary aliphatic amines

Nathalie Harwood Perkins

Recommended Citation

Perkins, Nathalie Harwood, "An atomic absorption method for determining micromolar quantities of primary aliphatic amines in the presence of secondary and tertiary aliphatic amines" (1975). *Master's Theses.* Paper 814.

AN ATOMIC ABSORPTION METHOD FOR DETERMINING MICROMOLAR QUANTITIES OF PRIMARY ALIPHATIC AMINES IN THE PRESENCE OF SECONDARY AND TERTIARY ALIPHATIC AMINES.

by

Nathalie Harwood Perkins

Thesis

Submitted to the Graduate Faculty
of the
University of Richmond
in Candidacy
for the Degree of
Master of Science in Chemistry

August 1975

Approved by:
W. Allan Powell
R. W. Topham
Stuart C. Clough
W. H. Myers
Thomas Gillespie Jr.
Jackson J. Taylor
Wm. E. Trout Jr.
Addison E. Campbell

ABSTRACT

A method for the determination of primary aliphatic amines in the presence of secondary and tertiary amines is described. The primary amine is reacted with a complexing reagent containing cupric chloride, salicylaldehyde and triethanolamine. The copper complex formed is extracted into 10% hexanol in toluene. The amount of copper in the toluene layer is determined by atomic absorption spectroscopy. This is a measure of the primary amine in the sample. The method can be successfully applied to both monoamines and diamines as well as an amino alcohol. Data for the analysis of several amine mixtures are given. The average standard deviation is ± 0.05% at the 2% level and below. Ammonia, if present, interferes, but a correction can be made. Secondary and tertiary amines do not interfere even when present at the 98% level.

DEDICATION

To my mother, Nathalie Hubbard Harwood, who shared with me a fascination for chemistry and to my friend and teacher, Dr. J. Stanton Pierce, this thesis is respectfully dedicated.

ACKNOWLEDGEMENTS

I wish to express my appreciation to Dr. W. Allan Powell for his guidance and encouragement throughout this project. I also wish to thank the members of the department of chemistry for their interest and support, particularly Dr. William H. Myers, who graciously shared his laboratory space with me. My appreciation and thanks are expressed to the management of Froehling and Robertson, Inc. for the use of their facilities and instrumentation. Finally my thanks are extended to Pauline F. Pones for her help in proof reading and typing this thesis; to Robert Parker for his assistance with some of the experimentation, and to my son, Robert Colby Perkins, Jr. for his patience.

TABLE OF CONTENTS

INTRODUCTION

An organic compound is most often determined by the reaction of its functional group. One class of organic compounds which lends itself to this type of analysis is the amines. However, it is frequently difficult to find a method which will determine one type of amine in the presence of another. The problem is further complicated if the amine to be determined is there as a contaminant rather than as a major component of the mixture.

In 1956 Critchfield and Johnson (3) proposed a new method for the determination of primary aliphatic amines. This procedure is based on the reaction of the amine with salicylaldehyde to form an imine which complexes with copper in the presence of triethanolamine. This complex is separated from its aqueous reaction mixture by extraction with 1-hexanol. The copper present in the hexanol layer is then determined colorimetrically by reaction with bis-(2-hydroxyethyl)-dithiocarbamic acid.

This method has some major advantages. It is specific for primary aliphatic amines even in trace amounts. Also, since within certain limits the ratio of copper to amine in the complex is constant, one curve of copper concentration (absorbance of the colored complex) versus the concentration of amine will apply for all amines determined. But one disadvantage is the number of manipulations necessary before the actual determination of the copper. Not only must the complex be formed and extracted, but also an additional complex must be formed before the copper concentration is determined. In addition, the second complex is not specific for copper.

Since the work of Walsh (27) in 1955, the use of atomic absorption spectroscopy has made the determination of a metal, such as copper, easier and more specific. Atomic absorption spectroscopy would offer an alternative method for the determination of copper in the above method, which would eliminate the formation of a second complex and thereby possibly improve the 5% accuracy claimed for it.

This thesis gives the results of the adaptation and modification of the method of Critchfield and Johnson for atomic absorption spectroscopy.

HISTORICAL

The reaction of an aldehyde with a primary amine to form an imine and water has been well known for many years. As early as 1869, Schiff (21) reported the ability of certain imines to form metal chelates. Both of these reactions have been used extensively as a means for qualitative and quantitative analysis of primary amines. The major interference noted for these reactions has been due to the presence of ammonia which undergoes similar reactions.

Duke (5) has proposed a qualitative test for primary amines based on the formation of an insoluble metallo-organic complex when a primary amine is reacted with salicylaldehyde in the presence of nickel (II) ion. In order to eliminate ammonia interference, he substituted the 5-nitro derivative of salicylaldehyde for the parent molecule. The test reagent consisted of an aqueous solution of triethanolamine, 5-nitro-salicylaldehyde and nickel (II) chloride. Precipitation occurred immediately with a primary amine while several hours were required for reaction with ammonia. The test proved to be sensitive for concentrations greater than 0.02 M; below this concentration, the precipitate ceased to be easily observable. As proposed, the test was specific for primary amines even in the presence of ammonia, secondary amines or tertiary amines.

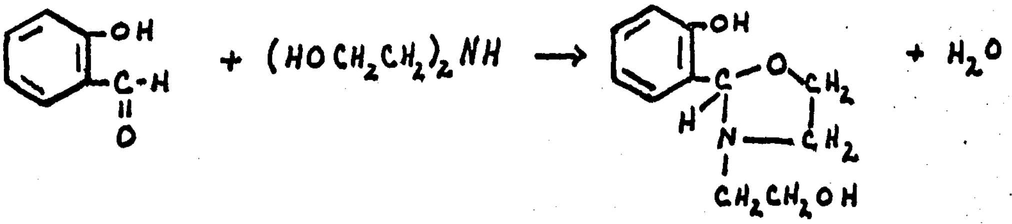
Prior to the work of Duke; Hawkins, Smith and Mitchell (7) had proposed a quantitative procedure for primary amines based on their reaction with aldehydes. In their procedure, benzaldehyde was allowed to react with the amine in a pyridine medium. The water produced was subsequently titrated with Karl Fisher reagent. The precision and accuracy of the method were reported as within 0.2 % in most cases. No indication was made of any attempt to deal with ammonia interference.

However, they found no appreciable interference from aliphatic and aromatic secondary amines and tertiary amines.

Wagner, Brown and Peters (26) found the preceding method unsatisfactory due to the compensation for or the elimination of water in the reagents. In addition, benzaldehyde was found to react with some secondary amines producing erroneous results. By their method, the total amine present was determined by potentiometric titration. Then the primary amine was allowed to react with salicylaldehyde to form the imine, thereby eliminating the problem with benzaldehyde. Since the imine formed was a very weak base, the secondary and tertiary amines could be titrated together and the primary amine determined by difference. The precision and accuracy of the method were found to be 0.7 %.

Ammonia interference was eliminated in the foregoing method by precipitation with cobalt nitrite. Secondary amino alcohols were found to react with salicylaldehyde but the addition product was easily hydrolyzed on addition of acid and therefore did not cause an error when mixtures of primary and secondary amino alcohols were analyzed.

The proposed reaction was :



A third method was proposed by Johnson and Funk (9). The amine mixture and excess salicylaldehyde were reacted in a pyridine medium.

The unreacted salicylaldehyde was titrated with sodium methylate using either phenolphthalein or thymolphthalein indicator. Again ammonia was a non-correctable source of error due to its non-stoichiometric reaction with salicylaldehyde. Amino alcohols also gave non-stoichiometric results, partly due to the reaction of the secondary amino alcohols with salicylaldehyde as noted above. The accuracy and precision of this method were not well defined but appeared to be in the range of 0.5 %.

Critchfield and Johnson (3) developed a method based on a modification of the qualitative test proposed by Duke. They found the previous method discussed to be unsatisfactory, either because of the toxic materials involved or because of the limited range of amines detected. A colorimetric method was proposed in which the amine was reacted with salicylaldehyde in the presence of copper (II) ion. The complex formed was extracted into 1-hexanol where the copper was determined by its reaction with bis-(2-hydroxyethyl)-dithiocarbamic acid to produce a complex which could be measured colorimetrically at 430 mμ.

Certain major advantages over previous methods were noted. Within certain limits, the copper-amine ratio remained constant necessitating only one calibration curve. The amino alcohols, while not having the same copper-amine ratio, did give quantitative results. The extraction step eliminated any interference from possible secondary or tertiary amine products. .

The disadvantages were the number of manipulations necessary before the colorimetric determination, the non-specific behavior of bis-(2-hydroxyethyl)-dithiocarbamic acid towards metals, and the unusually large blanks obtained. Ammonia did not react in a quantitative manner and therefore was a source of error. There was a 5 % relative accuracy for those amines which reacted quantitatively.

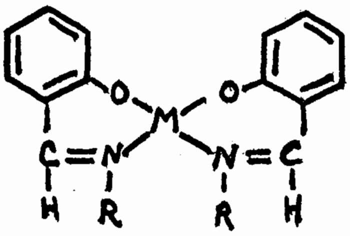
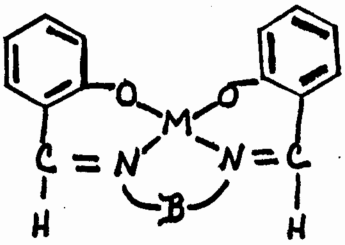
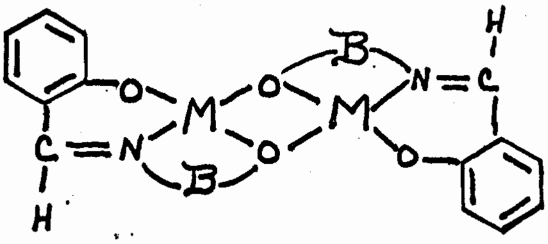
The varied responses of primary amines to the method of Critchfield and Johnson were explained in a review of the metal complexes of Schiff bases compiled by Holm, Everett and Chakravorty (8). Three general structures for the metal complexes were documented. These structures gave two metal-amine ratios, 1:2 and 1:1 (Table I). Structure "A" would be, typical of the alkyl amines while structure "B" would be expected for primary diamines and structure "C" for amino alcohols.

Also given in this review was a proposed mechanism for the complex formation. This mechanism followed the procedure proposed by Schiff and modified first by Duke and then by Critchfield and Johnson (Table II). The salicylaldehyde metal complex was formed first, then the primary amine was added to form the final product. The nucleophilic attack was rapid, while the dehydration of the carbonolamine intermediate was the rate determining step.

Two other important structural features were noted. The bridging chains noted in structures "B" and "C" of Table I had to be at least two carbons long. Also the larger the alkyl group in structure "A" became, the more distorted the complex became. The normal configuration was planar. Branching in the α position to the nitrogen was particularly distorting. This last supports the inability of Critchfield and Johnson to get quantitative results for primary amines of this type.

Another method for determining secondary and tertiary amines in mixtures was proposed by Critchfield and Johnson (4). This titration method was carried out in a chloroform medium using bromcresol green indicator. The primary amines were converted to the imines with salicylaldehyde. This type of blocking with an aldehyde was also used by Silverstein (22)

Table I

Structure	Ratio (Metal:amine)
 "A"	1:2
 "B"	1:1
 "C"	1:1

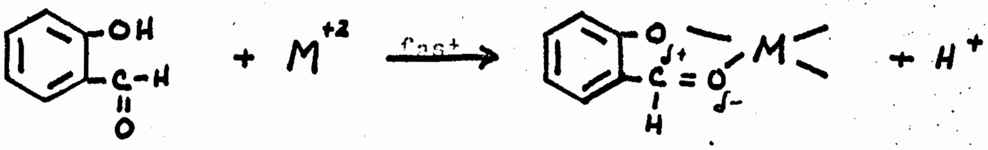
M = Metal

R = alkyl group

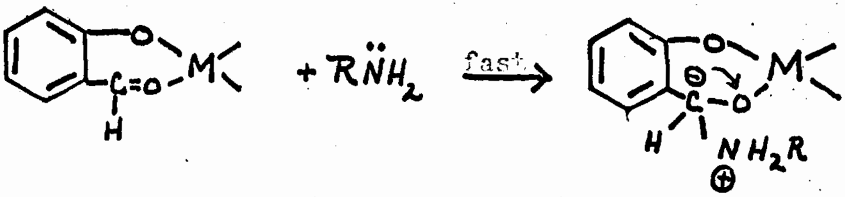
B = bridging chain

Table II

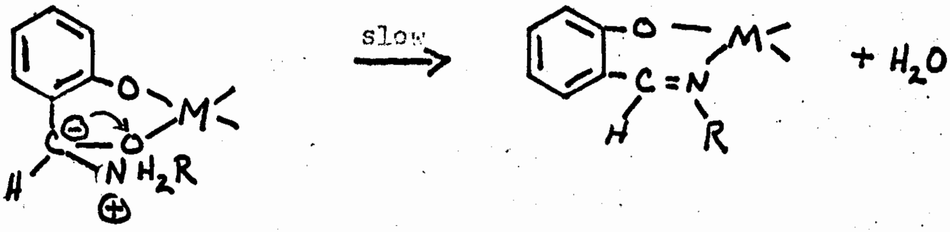
Step 1:



Step 2:



Step 3:



in his colorimetric method for secondary amines and by Strepikheev, Zalikin and Chimishkyan (25) in their titration method for polyamines.

Recently, Korenman and Sotnikova (15) used the reaction of salicylaldehyde, copper (II) nitrate and a primary amine to determine both aromatic and aliphatic primary amines. They analyzed the colored complex, after extraction into amyl alcohol, at 420 nm.

In 1974, Mitsui and Fujimura (17) used a reagent similar to that used by Duke. They filtered the precipitate formed on reaction with a primary amine and then determined either the excess copper in the filtrate or decomposed the precipitate with nitric acid and determined the copper in it. In both cases they used atomic absorption spectroscopy to determine the copper.

No additional work on the detection of primary amines using the Schiff base formation, particularly the use of the imine-metal complexes, has been found.

EQUIPMENT

The first recorded observation of the phenomenon of atomic absorption was made by Woolaston (30) in 1802. He noted that the solar spectrum contained "dark lines" or wavelengths at which radiation was absorbed. In a series of papers beginning in 1860, Kirchoff and Bunsen (10-14) explored the possibility of using this phenomenon for analytical determinations. However, actual instrumentation was not proposed until Woodson's work in 1939. (29) It still remained an oddity until 1955 and the work of Walsh. (27) At about this same time Alkemade and Milatz (1,2) designed a basic atomic absorption spectrophotometer. Since then, the use of atomic absorption has grown rapidly to its current prominence as a fast, reliable means for the quantitative determination of metals.

The principle of atomic absorption spectroscopy is relatively simple. The energy required to excite an atom from its ground state to its first excited state is very specific and relatively insensitive to temperature fluctuations. If a beam of a given energy (wavelength) is passed through a fog of unbonded, unexcited and unionized atoms, and if the energy corresponds to the resonance line or excitation energy of any of the atoms present, absorption will occur in proportion to the number of those atoms present. (23)

The basic atomic absorption spectrophotometer consists of a radiation source focused so that its beam passes through a flame onto a detector. A schematic diagram is shown in Figure 1. (20) The sample is introduced through a nebulizer which converts the liquid sample to a fine mist. This mist is premixed with a specific proportion of fuel and oxidant in the spray chamber, then forced into the burner head where

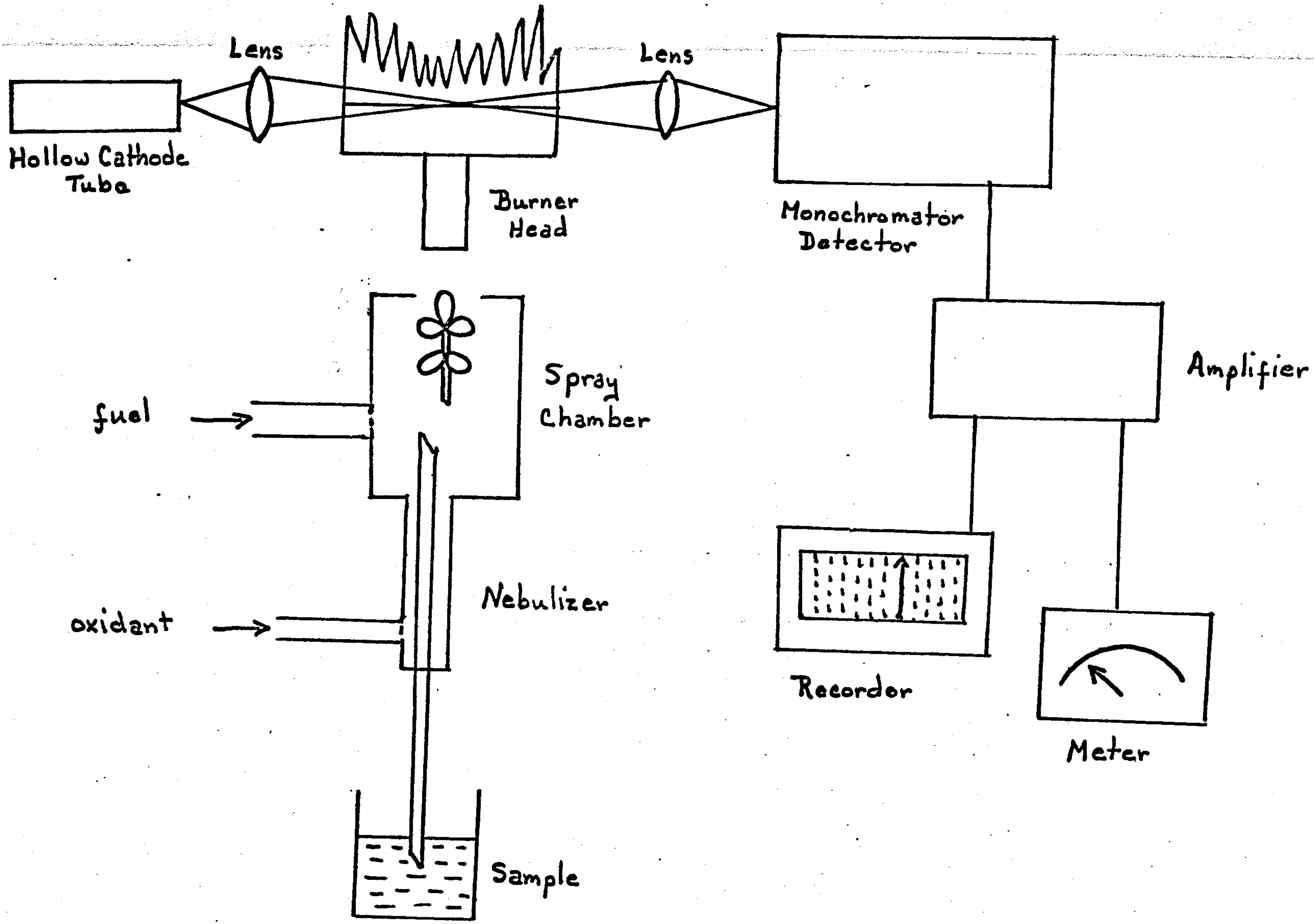

Hollow Cathode Tube
Lens
Burner Head
Lens
Monochromator Detector
Spray Chamber
fuel
Nebulizer
oxidant
Sample
Amplifier
Recorder
Meter

Figure 1. (20)

it is burned. The atomic vapor produced is suitable for analytical work.

A hollow cathode tube is generally used as the source of spectral energy. The fine line emission spectrum necessary is produced in a hollow cathode composed of the material whose spectrum is desired. However, the emission spectrum of the gas used to fill the tube is also produced. Therefore, care has to be taken that this spectrum does not interfere with that of the cathode. Argon and neon normally are used to fill the tube. The energy emitted passes through the silica window of the source and is focused via an optical system first on the flame and then on the monochromator. The monochromator is preset to "see" only the emission line of interest. The spectral band selected by the monochromator is converted into an electrical current by the photomultiplier. In the case of the double beam optics, the original spectral line is also "read" by the photomultiplier. The difference between the original and final intensity is the intensity absorbed by the atoms in the flame. The current produced is amplified and displayed either on a meter or recorder calibrated in absorbance units. (12)

The specific operating parameters for the Perkin-Elmer atomic absorption spectrophotometer Model 305 B are given in Appendix I. (19)

An atomic absorption spectrophotometer is designed for samples dissolved in an aqueous medium. Organic solvents may be used but they require some specific adjustments. The capillary tube of polyvinylchloride and some of the gaskets must be replaced with materials which will not decompose when exposed to organic solvents. The fuel-oxidant ratio must be adjusted to compensate for the flammability of the solvent. As nearly as possible the burning characteristics of the organic solvent should be like those of water. Ketones and alcohols are satisfactory but aromatics are not. The most commonly used organic solvent is methyl-isobutyl ketone. (18).

The three slot or Boling burner head is used for improved stability and sensitivity. Because it has a wider flame, the energy beam is enclosed within the flame. The outer flames sweep airborne contamination away from the inner flame thereby reducing flame noise. Since the flame is wide, the adjustment of the burner head becomes less critical (18,24).

The specific operating parameters for copper on the Perkin-Elmer atomic absorption spectrophotometer Model 305 B are given in Appendix II(18). The precautions indicated above may be unnecessary, since copper is probably the most easily detected element, having a linear response to high absorbance.

Heddings and Kaiser (16) have found the precision of atomic absorption spectrophotometric analysis of copper to be 0.4 %, while Weir and Kotluk (28) found it to be 0.51 %. These values are expressed as the percent coefficient of variation which is equal to 100 times the standard deviation divided by the mean value. The range of copper concentrations for which the values were determined was 10 to 20 parts per million. This range is well above the detection limit of copper. This precision is not as good as gravimetric or volumetric analysis, but it is acceptable in terms of a typical colorimetric analysis.

EXPERIMENTAL

The procedure developed by Critchfield and Johnson for the determination of primary aliphatic amines is given in full in Appendix III. In brief, the amine is reacted with an aqueous solution of salicylaldehyde, copper (II) ion and triethanolamine. The complex formed is extracted with 1-hexanol. A colorimetric determination is made on the reaction product of bis-(2-hydroxyethyl)-dithiocarbamic acid and the copper from the hexanol layer.

Critchfield and Johnson found it necessary to purify the triethanolamine used in the complexing reagent. In this work, triethanolamine with an actual lot analysis of 100.0 % was used. It was found unnecessary to further purify the triethanolamine.

I. <u>Development of Procedure</u>

In modifying the method to employ atomic absorption, which was the purpose of this work, the complexing reaction and solvent extraction were initially left unchanged. The aliquot of the hexanol layer was diluted to 50 milliliters with methyl isobutyl ketone and the copper determined by atomic absorption spectroscopy. A blank reading of 0.27 to 0.30 absorbance units was found. The reproducibility of identical samples was within 10%, relative.

It was reported by Critchfield and Johnson that the substitution of benzene for hexanol would eliminate the blank reading. For the present work, toluene was used instead of benzene. Benzene cannot be used for atomic absorption spectroscopy because it has such poor burning characteristics. The substitution of toluene for hexanol eliminated any extraction of copper into the blank; however, the relationship between copper and amine concentration was found to be non-linear near zero and reproducibility was erratic over the entire concentration range. Nonlinearity was also observed by Critchfield and Johnson when benzene was used as the extraction solvent.

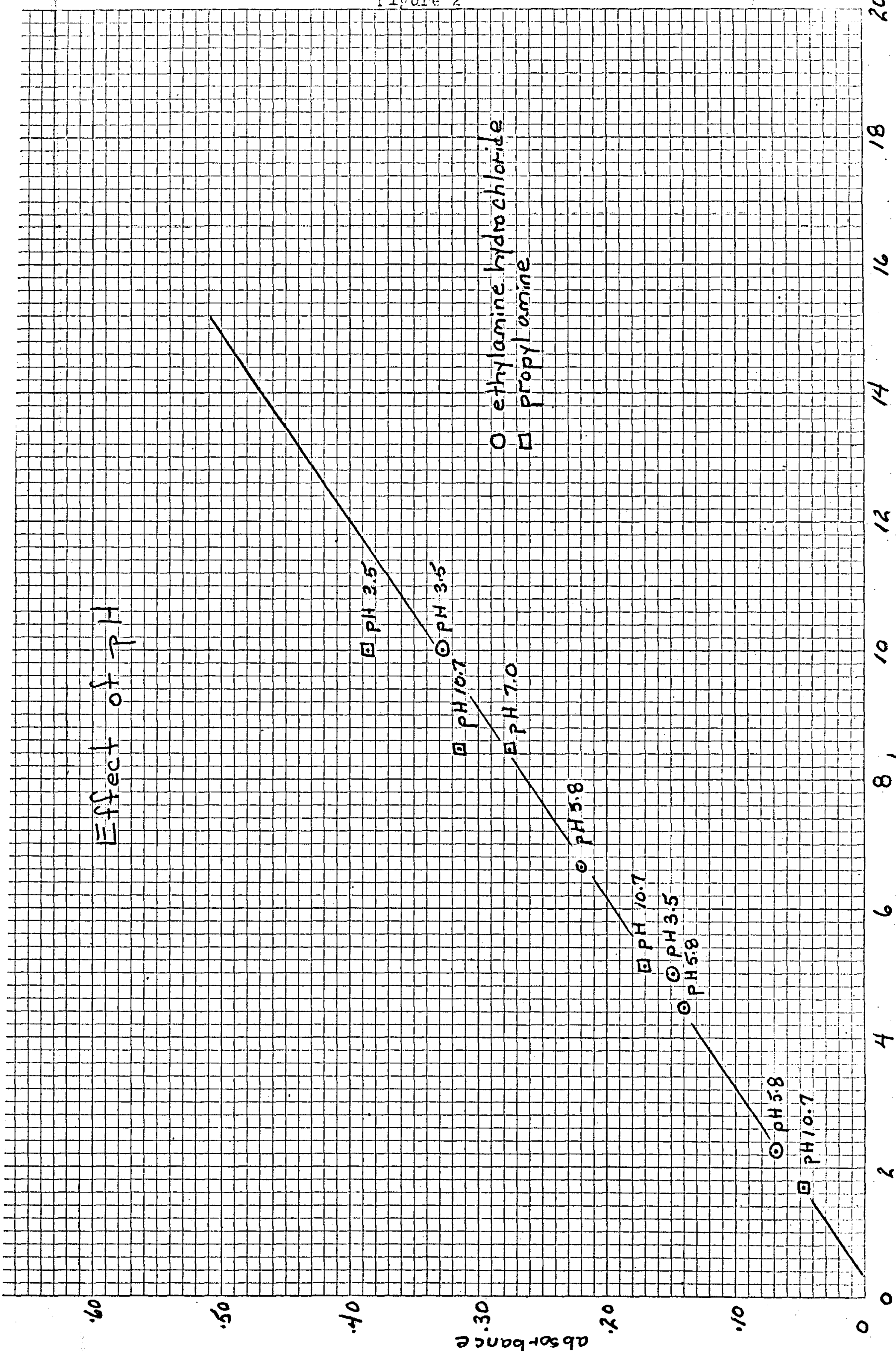
An attempt was made to decrease the solubility of the complex in the reaction mixture by acidification. The reaction and extraction proved to be independent of pH (Figure 2). A multistep extraction using a separatory funnel improved the extraction but made reproducibility worse, since emulsions frequently failed to separate.

Mechanical shaking improved both the extraction and the reproducibility. The reaction vessel was changed from a 25 milliliter cylinder to a 50 milliliter volumetric flask to improve mixing. Shaking time was found to be optimum at 10 minutes. However, the reproducibility of identical samples was still not as good as that obtained by a hexanol extraction.

Several mixtures of hexanol and toluene were used in an attempt to improve the solubility of the complex. A 1:1 mixture gave an appreciable absorbance reading for the blank; therefore, smaller percentages of hexanol were tried. A mixture of 5% hexanol in toluene gave no reagent blank but showed no improvement in reproducibility. However, a 10% mixture of hexanol in toluene gave the reproducibility of the pure hexanol extraction without any reagent blank. In fact, the reproducibility actually improved to 5%. This mixture was used for all subsequent determinations.

The use of a toluene-hexanol mixture did not eliminate the nonlinear behavior of the method as the amine concentration approached zero. A minimum of approximately one micromole of primary amine was required to reach the range of linear behavior.

Figure 2


Effect of pH
○ ethylamine hydrochloride
□ propyl amine
pH 3.5
pH 3.5
pH 10.7
pH 7.0
pH 5.8
pH 10.7
pH 3.5
pH 5.8
pH 5.8
pH 10.7
absorbance
micromoles amine
0
.10
.20
.30
.40
.50
.60
0
2
4
6
8
10
12
14
16
18
20

The maximum amount of amine which may be determined is influenced by three factors: (1) the concentration of copper in the reagent, (2) the marked deterioration of the reproducibility of the extraction of the complex for quantities greater than 10 micromoles of amine, and (3) the loss of linear response for copper by the instrument above 0.6 absorbance units. (Figure 3). Of these, number two is the limiting factor.

In the development of the complexing reagent by Critchfield and Johnson, a study was made to determine the optimum copper concentration for the reagent. A similar study was made using the proposed procedure (Figure 4). The concentration of copper used by Critchfield and Johnson was found to be satisfactory in this work. However, it became apparent that at least 0.05 grams more $CuCl_2 \cdot 2\,H_2O$ could be added to the complexing reagent without the formation of an insoluble precipitate between copper and salicylaldehyde. An attempt to use this data to calculate a copper amine ratio for the complex formed failed to give any results which could be explained.

Critchfield and Johnson indicated that the complexing reagent was stable for at least a month. It was found, however, that if the reagent was prepared fresh daily the erratic results sometimes obtained for the higher molecular weight amines ceased.

II. Procedure

The new procedure with the noted modifications is as follows: Prepare standards and unknowns in the same manner. Use at least three standards between one and ten micromoles of amine. To each 50 milliliter volumetric flask, add two milliliters of complexing reagent. This reagent contains 15 milliliters of triethanolamine, 0.5 milliliters

Figure 3

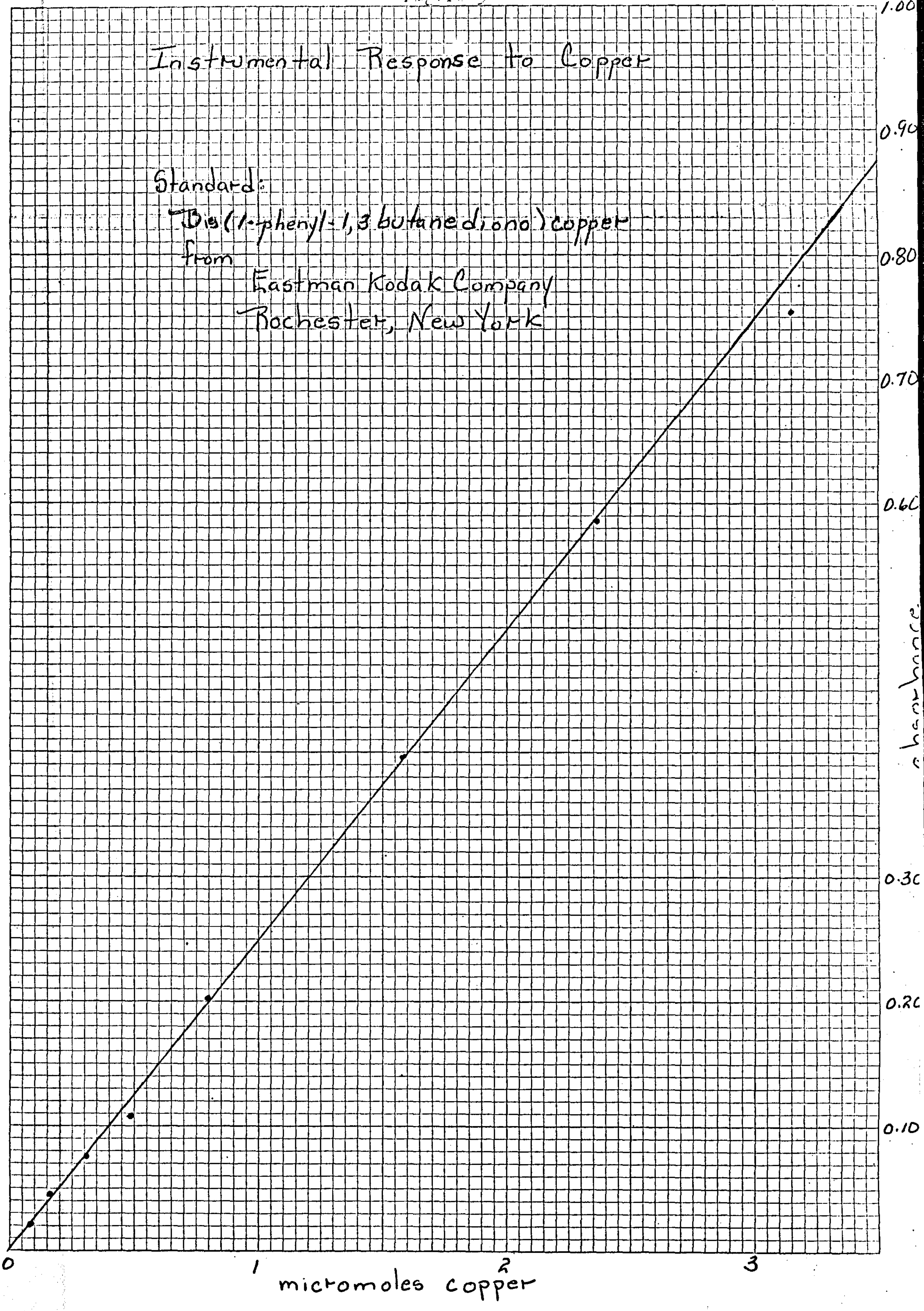
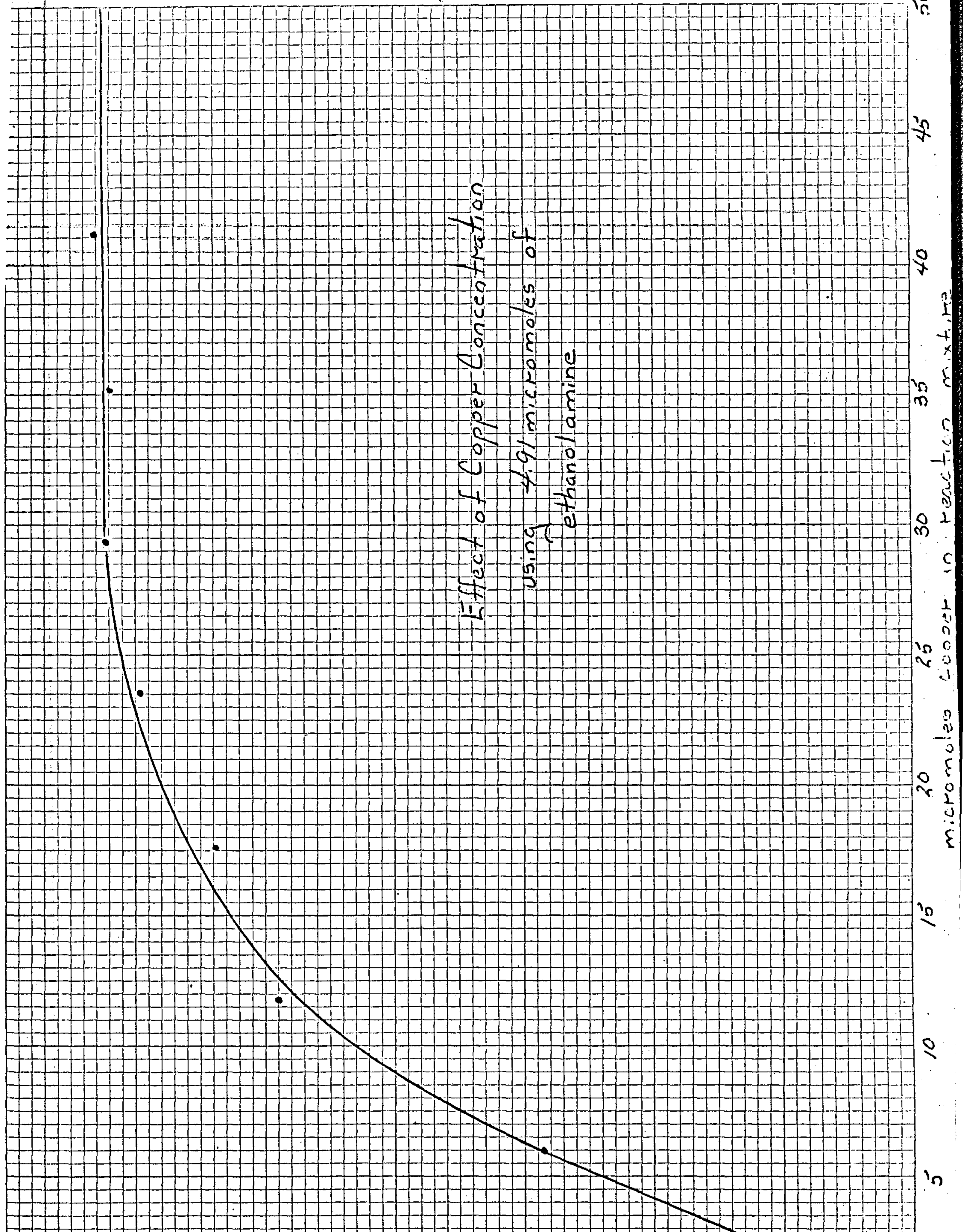

Instrumental Response to Copper
Standard:
Bis(1-phenyl-1,3 butanediono)copper
from
Eastman Kodak Company
Rochester, New York
1.00
0.90
0.80
0.70
0.60
0.30
0.20
0.10
absorbance
0
1
2
3
micromoles copper

Figure 4



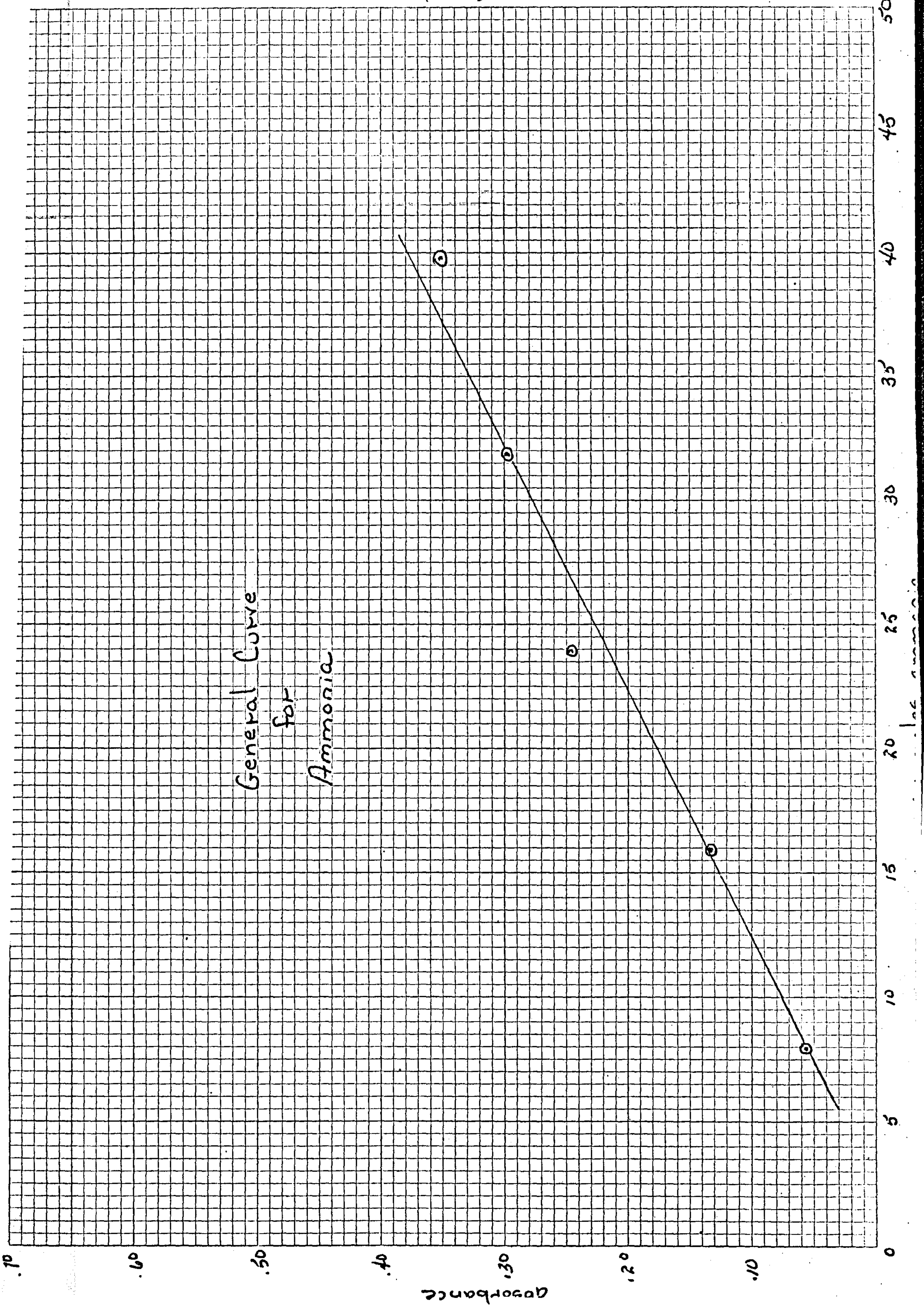
Effect of Copper Concentration using 4.91 micromoles of ethanolamine of salicylaldehyde and 0.25 grams of $CuCl_2 \cdot 2 H_2O$ diluted to 100 milliliters with distilled water. Add known amounts of amine to three flasks. Reserve one flask as a blank. For each unknown add 5 milliliters of a water solution made by dissolving or diluting the sample to an approximate concentration of 0.05 milligrams per milliliter for the primary amine. Add enough water to bring the volume of all flasks to 10 milliliters. Stopper and mix. Allow to react for one hour at room temperature. (The reaction time used was based on the maximum determined by Critchfield and Johnson. See Appendix III.) After one hour, add exactly 15 milliliters of 10% hexanol in toluene to each flask. Stopper and shake for 10 minutes on a mechanical shaker. Allow the layers to separate. Carefully withdraw 5 milliliters of the organic layer. Transfer this aliquot to a 50 milliliter volumetric flask and dilute to volume with methyl isobutyl ketone. Run standards and unknowns for copper using atomic absorption spectroscopy. Read the micromoles of amine in the unknown from a plot of the absorbance of copper versus the micromoles of amine in the standards.

III. Interferences

An important interference noted for the method was ammonia. Its behavior was similar to that of the primary amines. Sixteen micromoles of ammonia gave about the same absorbance as four micromoles of monofunctional primary amine. This relationship was found to hold throughout the range of the monofunctional primary amines used. This indicates that, contrary to the findings of Critchfield and Johnson, ammonia interference could be dealt with by separate assay and correction techniques. The general curve for ammonia is shown in Figure 5.

Secondary and tertiary amines show no reaction under the conditions of the procedure and therefore constitute no interference.

Figure 5


General Curve
for
Ammonia
absorbance
.70
.60
.50
.40
.30
.20
.10
0
5
10
15
20
25
30
35
40
45
50

IV. Standard Curves

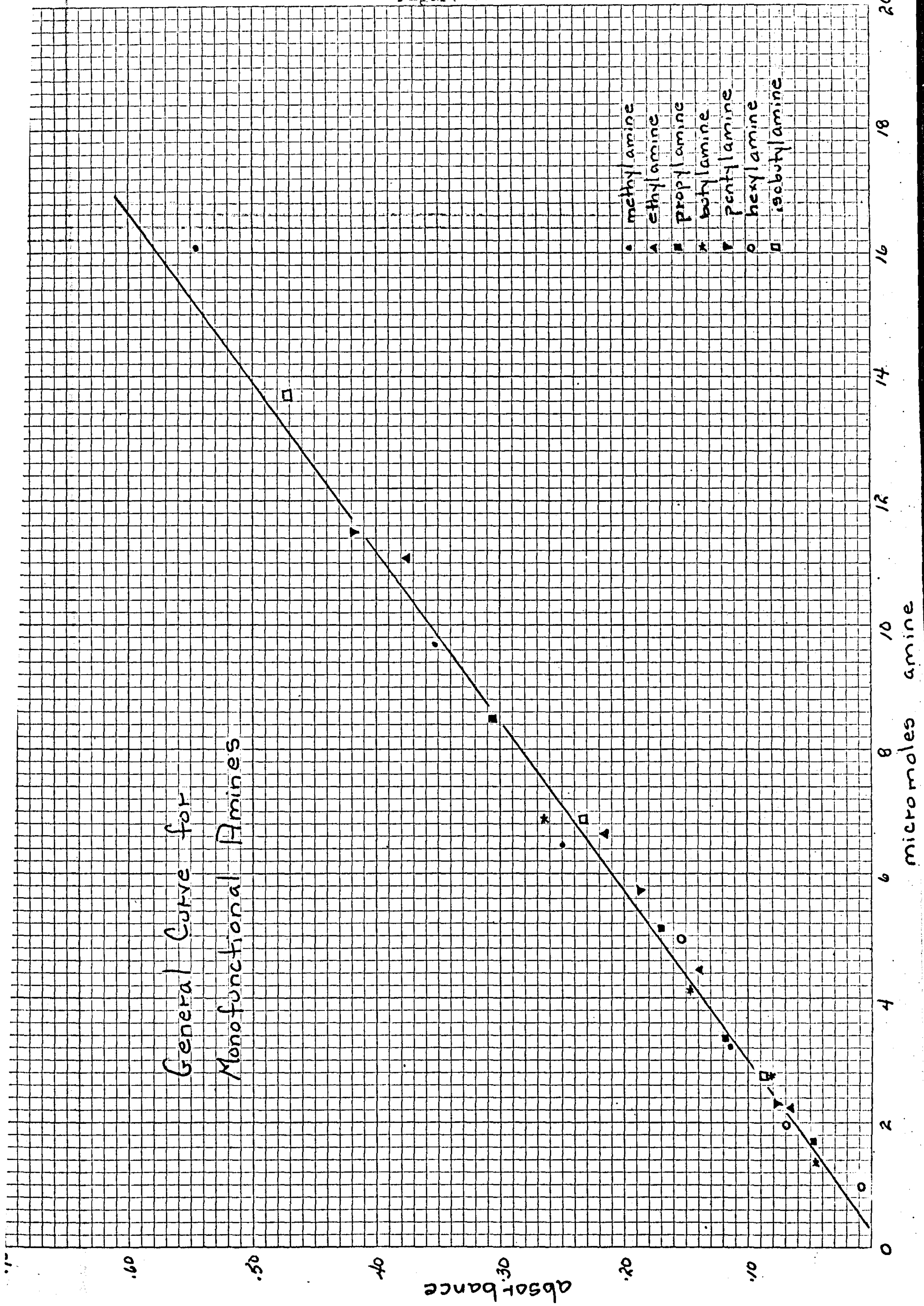
As also found by Critchfield and Johnson, monofunctional aliphatic primary amines gave the same general curve, indicating a constant copper to amine ratio. Actually a first approximation of the primary amine present can be made using any of the simple primary amines as standards. The general curve is shown in Figure 6 and the data from which it was plotted is given in Table III. One difference from the findings of Critchfield and Johnson was noted--methylamine fell on the general curve. Isopropylamine did not form an extractable complex, which agreed with their findings.

The general behavior noted above did not extend to the primary amines containing more than one primary amine group or to the amino-alcohols. Each compound responded in a linear manner throughout the range but the slopes were quite dissimilar. The results for several bifunctional amines are shown in Figures 7-9. Contrary to the findings of Critchfield and Johnson, aminoethyl ethanolamine did not form an extractable complex.

V. Analysis of Mixtures

Since the purpose of the proposed procedure and that of Critchfield and Johnson is to have a method specific for primary aliphatic amines even in the presence of secondary and tertiary amines, a number of synthetic mixtures of primary, secondary and tertiary amines were prepared for analysis. When the method developed in this work was applied to these mixtures, both accurate and precise results were obtained. In some cases the experimental results were slightly below the calculated results. This was expected as the calculations were based on 100% purity, whereas the actual material varied from 96 to 99% purity.

Figure 6



General Curve for Monofunctional Amines

Table III.

Data for Monofunctional Primary Aliphatic Amines

Amine	Micromoles	Absorbance Units
Methylamine	3.22	0.115
	6.44	0.250
	9.66	0.352
	16.10	0.546
Ethylamine	2.22	0.067
	4.44	0.139
	6.65	0.217
	11.09	0.374
Propylamine	1.69	0.048
	3.38	0.118
	5.08	0.170
	8.46	0.306
Butylamine	1.37	0.047
	2.74	0.081
	4.10	0.147
	6.85	0.264
Pentylamine	2.29	0.078
	5.73	0.187
	11.47	0.419
Hexylamine	0.99	0.039
	1.98	0.070
	4.94	0.153
Isobutylamine	2.74	0.086
	6.84	0.233
	13.67	0.471

Figure 7

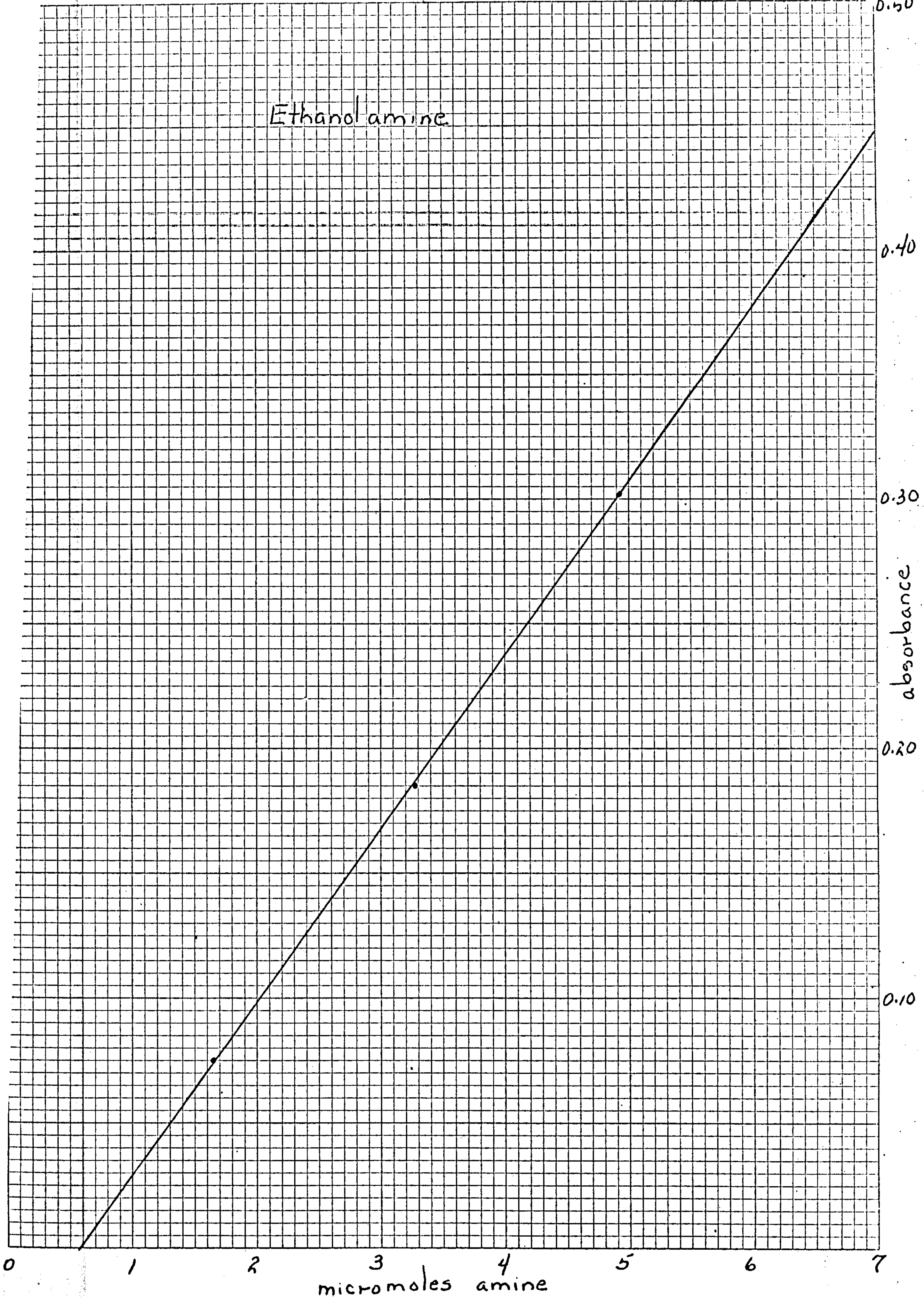

Ethanolamine
0.50
0.40
0.30
0.20
0.10
absorbance
0
1
2
3
4
5
6
7
micromoles amine

Figure 8

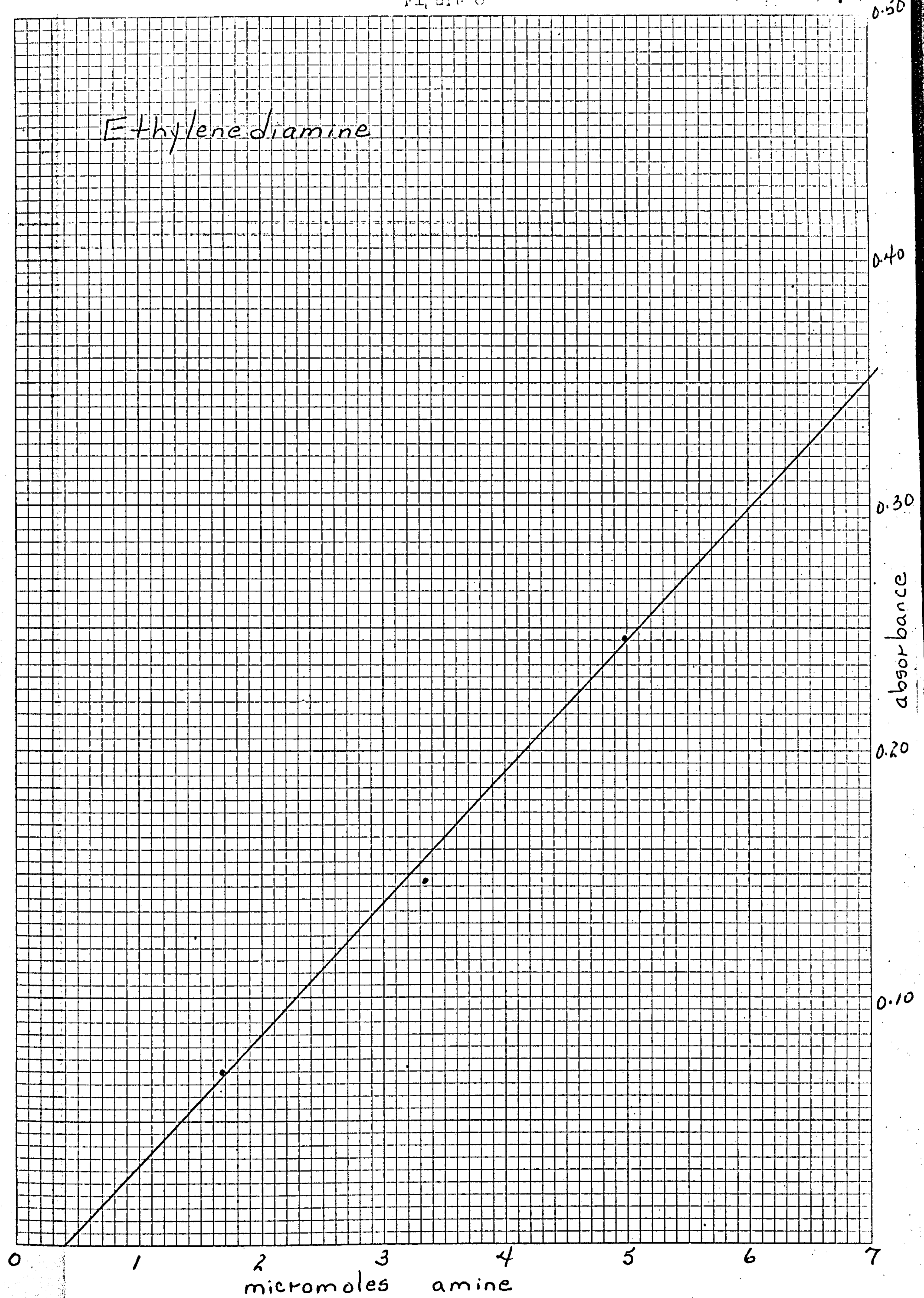
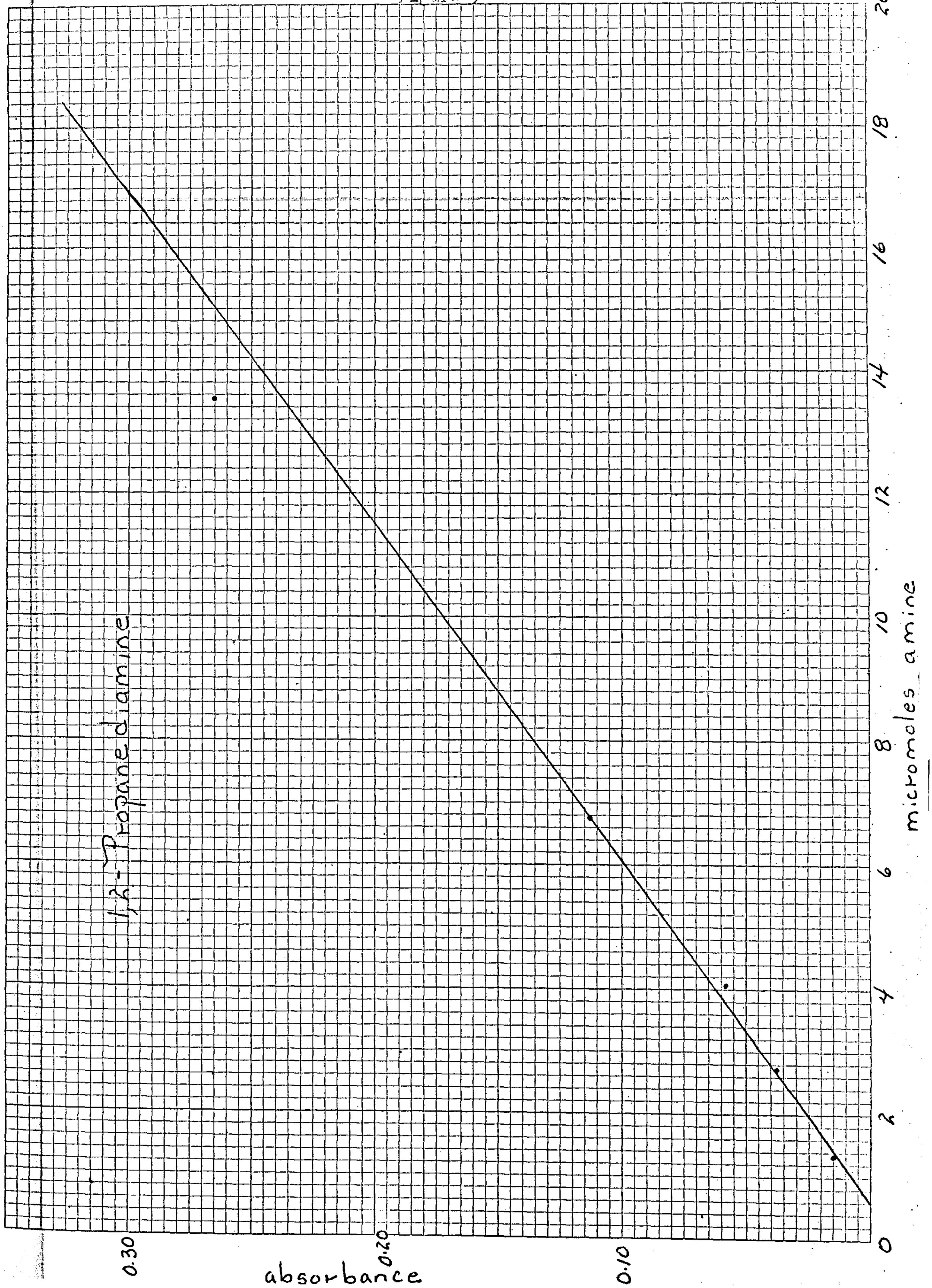

Ethylenediamine
0.50
0.40
0.30
0.20
0.10
absorbance
0
1
2
3
4
5
6
7
micromoles amine

Figure 9


1,2- Propanediamine
micromoles amine
0
2
4
6
8
10
12
14
16
18
20
absorbance
0.30
0.20
0.10

The low results could also be caused by a difference in percent recovery of the complex when extracted from the mixture and when extracted from the standards. The results are given in Table IV and Table V.

It should be noted that blanks for each mixture were determined and corrections made.

Table IV.

Ethylamine Mixtures

Ethylamine in Diethylamine

Percent Ethylamine Prepared	Percent Ethylamine Found	
0.39	0.37	
	0.41	Average = 0.39 %
	0.40	Standard Deviation = ± 0.02
	0.41	% Coefficient of Variation = 5.1%
	0.36	
0.78	0.72	
	0.76	Average = 0.78 %
	0.82	Standard Deviation = ± 0.04
	0.74	% Coefficient of Variation = 5.1%
	0.79	
	0.82	
1.17	1.17	
	1.13	Average = 1.16 %
	1.16	Standard Deviation = ± 0.02
	1.18	% Coefficient of Variation = 1.7%
	1.17	

Ethylamine in Diethylamine and Triethylamine

0.44	0.37	
	0.44	Average = 0.42 %
	0.43	Standard Deviation = ± 0.04
	0.46	% Coefficient of Variation = 9.5%
1.31	1.23	
	1.27	Average = 1.26 %
	1.30	Standard Deviation = ± 0.03
	1.25	% Coefficient of Variation = 2.4%
2.14	2.03	
	2.06	Average = 2.08 %
	2.07	Standard Deviation = ± 0.06
	2.16	% Coefficient of Variation = 2.9%

Table V.

Ethanolamine Mixtures

Ethanolamine in Diethanolamine

Percent Ethanolamine Prepared	Percent Ethylamine Found	
0.46	0.44	
	0.45	Average = 0.43 %
	0.43	Standard Deviation = ± 0.02
	0.40	% Coefficient of Variation = 4.6%
0.74	0.64	
	0.65	Average = 0.67 %
	0.64	Standard Deviation = ± 0.06
	0.76	% Coefficient of Variation = 8.9%
0.93	0.84	
	0.81	Average = 0.88 %
	0.95	Standard Deviation = ± 0.07
	0.93	% Coefficient of Variation = 7.9%

DISCUSSION

As shown by the experimental results, the proposed method is specific for primary aliphatic amines, even when they occur as a minor component of an amine mixture. It is a simple straight-forward method requiring approximately three hours of laboratory time to complete a determination. The major interference comes from ammonia, which frequently exists in amine mixtures. However, corrections may be made for this interference if the amount of ammonia present is known. The precision is good as indicated by an average standard deviation of ± 0.04 % for values of primary amine 2% or below. In most cases the theoretical value is within one standard deviation of the average value obtained. Exceptions are believed to be the result of impurities in the material, which were not taken into account.

The proposed method gave linear standard curves for all primary amines used with two exceptions. Isopropylamine did not form an extractable complex. This was attributed to lack of complex formation due to the steric hindrance which branching on the α carbon is known to cause. Aminotheyl ethanolamine also did not form an extractable complex. The polarity of the secondary amine group present in this molecule possibly made the complex formed more soluble in the aqueous phase than in the extraction solvent.

Generally, these results represent an improvement over the method of Critchfield and Johnson. While the accuracy shows little improvement, the applicability is wider and the interferences fewer. Amines containing more than one primary amine group can be successfully determined by the proposed method. Corrections can be made for ammonia if it occurs in a mixture. And only metals which form a similar complex, such as nickel, would affect the results of the metal analysis.

The alkylamines from methylamine through hexylamine were found to give a standard curve with the same slope and the same y-intercept. The exception of methylamine found by Critchfield and Johnson did not occur in the proposed method. However, the bifunctional amines did give curves with different slopes, indicating a different copper to amine ratio. This was confirmed in the review of Schiff bases compiled by Holm, Everett and Chakravorty (8) and previously cited. Their work indicated that while a bifunctional amine may form a complex with a 1:2 metal to amine ratio, it may also form one with a 1:1 ratio.

The individual behavior noted for each bifunctional amine determined probably indicates an equilibrium mixture of the two complexes unique to that amine. This is further supported by the loss of linear behavior noted for ethanolamine when an unexpected rise or drop in room temperature occurs during the reaction time. A similar behavior is not observed for the monofunctional amines. Another possible explanation, however, is the decrease of excess copper from six fold to three fold when bifunctional amines are determined.

Whether the amine was present as the free base or as a hydrochloride salt had no effect on the results of the analysis. The presence of a large excess of triethanolamine, which acts as a proton acceptor, in the complexing reagent would explain this behavior. Its presence also would explain the fact that adjustment of the samples to neutral or acidic pH did not effect the complex formation.

SUMMARY

The proposed method represents a significant modification of the method of Critchfield and Johnson for primary aliphatic amines. Without a loss of accuracy, the proposed method widens the scope and decreases the interferences from those of the previous method.

The substitution of atomic absorption spectroscopy for colorimetry makes the analysis specific for copper and thereby minimizes trace metal interference. It also eliminates the need for any reaction except the original complex formation. This represents a decrease in glassware, time and operator error.

Changing the type of extraction solvent results in a wider applicability of the method. Not only can amines previously found to respond to the method of Critchfield and Johnson be determined, but also at least one more diamine as well as the major interference of the method, ammonia. This represents an improvement, probably directly related to the elimination of the extraction of copper by the solvent when no amine is present.

Precision and accuracy are good for this type of analysis. Both are comparable to and in some cases better than that found by Critchfield and Johnson. The lack of any great improvement here indicates that the extraction efficiency is the limiting factor.

BIBLIOGRAPHY

1. Alkemade, C.T.J. and Milatz, J.M.W., *Appl. Sci. Res. Sec. B* *4*, 289(1955).

2. Alkemade, C.T.J. and Milatz, J.M.W., *J. Opt. Soc. Am.*, *45*, 583 (1955).

3. Critchfield, F.E. and Johnson, J.B., *Anal. Chem.*, *28*, 436(1956).

4. Critchfield, F.E. and Johnson, J.B., *Anal. Chem.*, *29*, 957(1957).

5. Duke, F.R., *Ind. Eng. Chem. Anal. Ed.*, *17*, 196(1945).

6. *Handbook of Chemistry and Physics*, 48th Ed., Robert C. Weast, ed., Chemical Rubber Company, Cleveland, 1962.

7. Hawkins, W., Smith, D.M. and Mitchell, J., Jr., *J. Am. Chem. Soc.*, *66*, 1662(1944).

8. Holm, R.H., Everett, G.W., Jr. and Chakravorty, A., "Metal Complexes of Schiff Bases and β-Ketoamines", *Progress in Inorganic Chemistry*, *7*, pp. 83-214, Interscience Publishers, New York, 1966.

9. Johnson, J.B. and Funk, G.L., *Anal. Chem.*, *28*, 1977(1956).

10. Kirchoff, G., *Phil. Mag.*, *20*, 1(1860).

11. Kirchoff, G. and Bunsen, R., *Phil. Mag.*, *20*, 89(1860).

12. Kirchoff, G. and Bunsen, R., *Phil. Mag.*, *22*, 329(1861).

13. Kirchoff, G. and Bunsen, R., *Pogg. Ann.*, *110*, 161(1860).

14. Kirchoff, G. and Bunsen, R., *Pogg. Ann.*, *113*, 337(1861).

15. Korenman, Ya. I. and Sotnikova, N.G., *Zh. Anal. Khim.*, *28*, 2063(1973).

16. Meddings, B. and Kaiser, H., *Atomic Absorption Newsletter*, *6*, 24(1967).

17. Mitsui, Toshiyuki and Fujimura, Yoshikazu, *Bunseki Kagaku*, *23*, 1309(1974).

18. Perkin-Elmer, Inc., *Analytical Methods for Atomic Absorption Spectrophotometry*, Norwalk, Conn., March 1973.

19. Perkin-Elmer, Inc., *Instructions, Model 305B, Atomic Absorption Spectrophotometer*, Norwalk, Conn., 1973.

20. Price, W.J., *Analytical Atomic Absorption Spectrometry*, Heyden and Son, Ltd., London, 1972.

21. Schiff, Hugo, *Justus Liebigs Annalen der Chemie*, *150*, 193(1869).

22. Silverstein, R.M., *Am. Chem. Soc. Div. Water Waste Chem.*, Preprints March 1962, pp. 15-21.

23. Slavin, W., *Atomic Absorption Spectroscopy*, Interscience Publishers, New York, 1968. (Vol. 25 of *Chemical Analysis*, P.J. Elving and I.M. Kolthoff, editors.)

24. Sprague, S. and Slavin, W., *Atomic Absorption Newsletter*, *4*, 293(1965).

25. Strepikheev, Y. A., Zalikin, A.A., and Chimishkyan, A.L., *Zh. Analit. Khim.*, *18*, 1262(1963).

26. Wagner, C.C., Brown, R.H. and Peters, E.D., *J. Am. Chem. Soc.*, *69*, 2609(1947).

27. Walsh, A., *Spectrochim. Acta.*, *7*, 108(1955).

28. Weir, D.R. and Koflik, R.P., *Atomic Absorption Newsletter*, *6*, 24(1967).

29. Woodson, T.T., *Rev. Sci. Instr.*, *10*, 308(1939).

30. Woolaston, W.H., *Phil. Trans. Roy. Soc. London Ser. A92*, 365(1802).

APPENDIX I (19)

Perkin-Elmer Model 305 B Technical Data

Photometer--Double-beam system with a single detector shared by both beams; source light modulated, flame light unmodulated.

Monochromator--High-dispersion Czerny-Turner grating system; UV dispersion about 0.65 nm per mm; VIS dispersion about 1.3 nm per mm. Monochromator focal length 400 mm. UV grating ruled 2800 lines/mm, blazed at 210.0 nm; VIS grating ruled 1440 lines/mm, blazed at 600.0 nm. Wavelength range from 188 to 900 nm. Wavelength as read on the WAVELENGTH Counter is accurate to ± 1 nm. The counter reads directly in nanometers (1 nanometer is equal to 10A) with RANGE Control at UV; reading must be multiplied by 2 with RANGE Control at VIS.

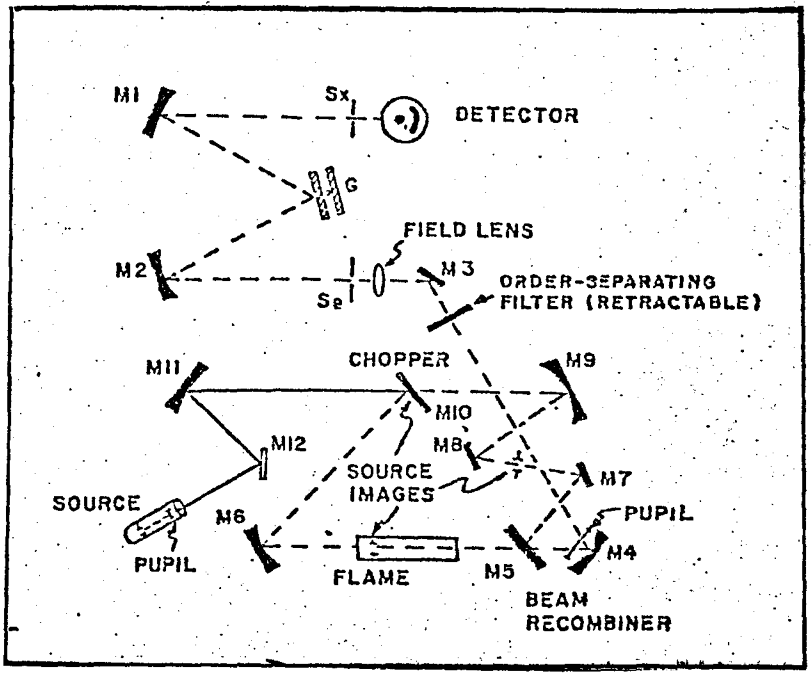
Slit Openings--0.03, 0.1, 0.3, 1.0, 3.0, 10.0 (mm).

Minimum Spectral Band Width--UV--about 0.02 nm; VIS--about 0.04 nm.

Readout--Direct readout in concentration units. Scale expansion in concentration variable up to 100X.

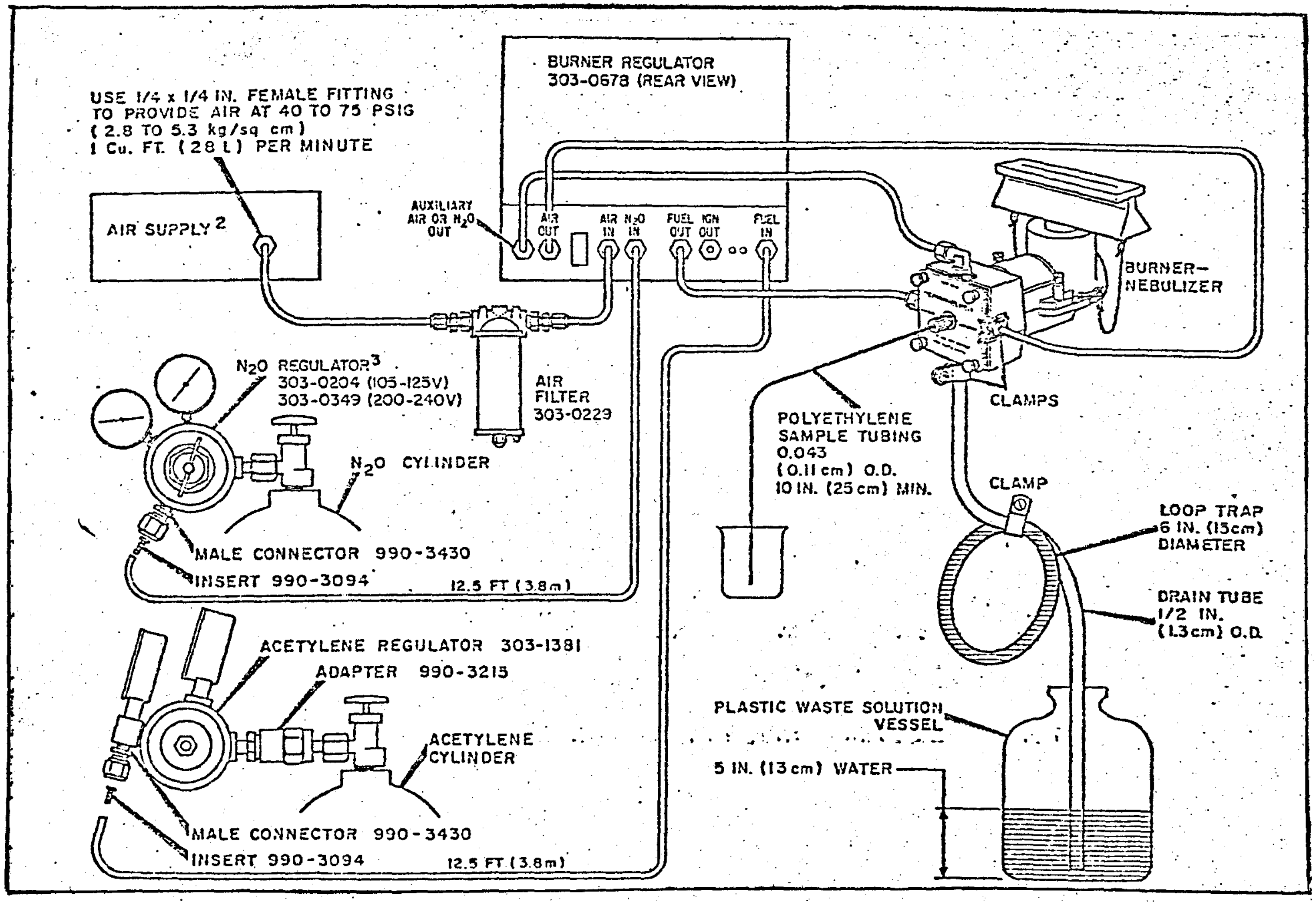
Source Current--adjustable to 50 ma.

Power Requirements--105-125 V or 200-250 V, 50 or 60 Hz, 250 W.



Optical Diagram

APPENDIX I (Cont'd.)



Plumbing Diagram

APPENDIX II

Operating Data for Copper (18)

Operating Parameters	Perkin-Elmer Instrument Settings
Instrument	503, 403, 306, 305 (A,B), 303
Wavelength-324.7 nm	325 - UV
Slit Setting	4 (0.7 nm)
Light Source	Hollow Cathode Lamp
Flame Type	Air-acetylene Flame Oxidizing (lean, blue)

Lamps

With multi-element lamps containing nickel or iron, a 0.2 nm spectral slit width should be used with the copper 324.7 nm line.

(The lamp used in this project contained iron as well as copper and therefore the above correction was made.)

APPENDIX III

Method of Critchfield and Johnson (3)

Reagents. Cupric chloride dihydrate.
1-Hexanol, Carbide and Carbon Chemicals Co.
Salicylaldehyde, reagent grade.

TRIETHANOLAMINE, Carbide and Carbon Chemicals Co. Distill 98% material under 1- to 2- mm. pressure, using a column 6 inches long and 30 mm. in diameter packed with 2-mm. glass beads and heated by means of resistance wire. Use a 3-liter, round-bottomed flask fitted with a thermometer well. Stir the contents of the flask by means of a magnetic stirrer, and do not allow the kettle temperature to exceed 185°C. during the distillation. An absorbance of 0.65 ± 0.02 for 0.372 mg. of ethanolamine should be obtained by the procedure described below, when this material is used to prepare the copper-salicylaldehyde reagent.

COPPER-SALICYLALDEHYDE REAGENT. Into a 100-ml. glass-stoppered graduated cylinder measure 15.0 ml. of redistilled triethanolamine, 0.5 ml. of salicylaldehyde, and 0.25 gram of cupric chloride dihydrate. Dilute to 100 ml. with distilled water and mix the contents. This reagent is stable for at least a month; however, the reagent blank increases with age.

BIS(2-HYDROXYETHYL)DITHIOCARBAMIC ACID REAGENT. Prepare a 2% by volume solution of carbon disulfide in methanol and a 5% by volume solution of diethanolamine in methanol. Prepare the reagent fresh daily by mixing equal volumes of the two components.

Calibration Curve. Prepare a dilution of the pure compound in distilled water so that a 5-ml. aliquot contains not more than the maximum sample size given in Table I. To each of five 25-ml. glass-stoppered graduated cylinders add 2 ml. of copper-salicylaldehyde reagent by means of a pipet. Transfer 1.0-, 2.0-, 3.0-, and 5.0-ml aliquots of the above dilution to respective 25-ml. graduated cylinders, reserving one as the blank. Measure the absorbance of each standard at 430 mμ, using 1-cm. cells and a suitable spectrophotometer.

Procedure. Add 2.0 ml. of copper-salicylaldehyde reagent from a transfer pipet to each of two 25-ml. glass-stoppered graduated cylinders. Reserve one of the cylinders as a blank, and into the other measure an amount of sample calculated to contain not more than the maximum amount of primary amine listed in Table I. The sample must not contain more than 0.01 mg. of ammonia or 0.5 gram of secondary and tertiary amine. For samples of less than 0.1 gram use an aliquot of a suitable aqueous dilution. Dilute the contents of each graduate to the 10-ml. mark with distilled water, stopper, and mix thoroughly. Allow the sample to react under the conditions specified in Table I.

After the reaction is complete, add sufficient 1-hexanol to bring the total volume of liquid to 25 ml. Stopper the cylinders, shake vigorously 15 or 20 times, and allow the layers to separate. Add 5 ml. of bis(2-hydroxyethyl)dithiocarbamic acid reagent to each of two additional 25-ml. glass-stoppered graduated cylinders. In this step it is important that the graduated cylinders and stoppers be clean and void of any metallic ions that react with this reagent. Pipet 5.0 ml. of the hexanol layer from the graduated cylinders in which the reaction was performed to the graduates containing the dithiocarbamic acid reagent. Add the hexanol dropwise to prevent the material from clinging to the walls of the pipet. Dilute the contents of each cylinder to the 25-ml. mark with methanol, stopper, and mix the contents. Measure the absorbance of the sample vs. the blank at 430 mμ, using 1-cm. cells. Read the concentration of primary amine from the calibration curve.

TABLE I. REACTION CONDITIONS FOR DETERMINATION OF PRIMARY AMINES BY COPPER-SALICYLALDEHYDE METHOD

Compound	Primary Amine, Mg., Maximum	Time, Minutes[a]
Aminoethylethanolamine	1.10	30 to 60
N-Aminoethylmorpholine	0.85	15 to 60
Amylamine	1.20	15 to 45
Butylamine	0.70	15 to 60
Ethanolamine	0.50	15 to 60
Ethylamine	0.53	15 to 60
2-Ethylhexylamine	1.40[b]	15 to 60
Hexylamine	1.10	15 to 60
Isoamylamine	1.10	15 to 45
Isobutanolamine	0.60	60 to 120
Isobutylamine	0.90	15 to 60
Isopropanolamine	0.60	15 to 60
Methylamine	0.30	15 to 60
Propylamine	0.73	15 to 60
Propylenediamine	0.42	10 to 20[c]

[a] Reaction time at 20° to 30° C. unless otherwise specified.

[b] Make dilutions using a 10% solution of methanol.

[c] Perform reaction at 98° ± 2° C. Use 50-ml. glass-stoppered graduated cylinders; do not stopper during reaction.

APPENDIX IV.

Data for a Sample Run

Run #33

Lamp: P.E. # 303-6110 (hollow cathode)
Element: Copper
Wavelength: 324.7 nm
Slitwidth: 3(0.2 nm)
UV or VIS: Ultraviolet
Fuel Setting: 5.0
Oxidant Setting: 10.5
Fuel: Acetylene
Oxidant: Air
Burner Head: Boling, three slot
No scale expansion

Run Identification: Ethylamine Mixtures

Sample #	Composition
0	Blank
1	Standard (2.22 µm)
2	Standard (4.44 µm)
3	Standard (6.65 µm)
4	Blank, Secondary mixture
5	0.39% mixture
6	0.78% mixture
7	1.17% mixture
8	Blank, Secondary and Tertiary mixture
9	0.85% mixture
10	1.71% mixture
11	2.18% mixture

Sample Preparation:

Dilute one milliliter of sample to 100 milliliters. Use a 2 milliliter aliquot for reaction.

Standard Preparation:

Use 1, 2 and 3 milliliters of a 100 ppm water standard of ethylamine.

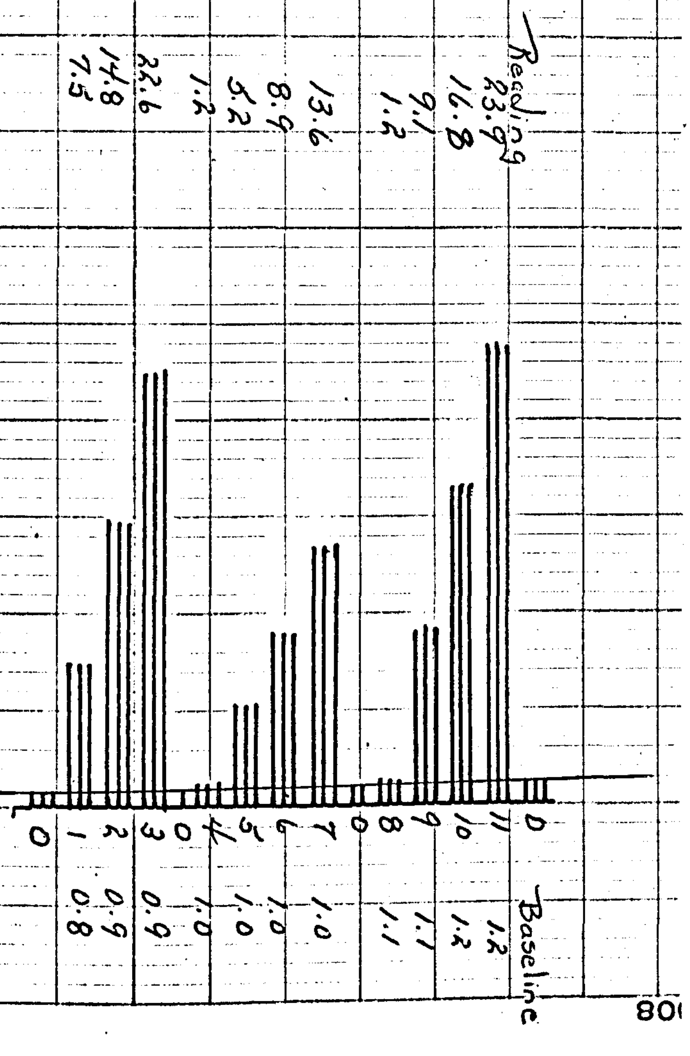
Data for Graph:

Sample #	Absorbance	Sample #	Absorbance
1	0.067	7	0.126
2	0.139	8	0.001
3	0.215	9	0.080
4	0.002	10	0.156
5	0.042	11	0.227
6	0.079		

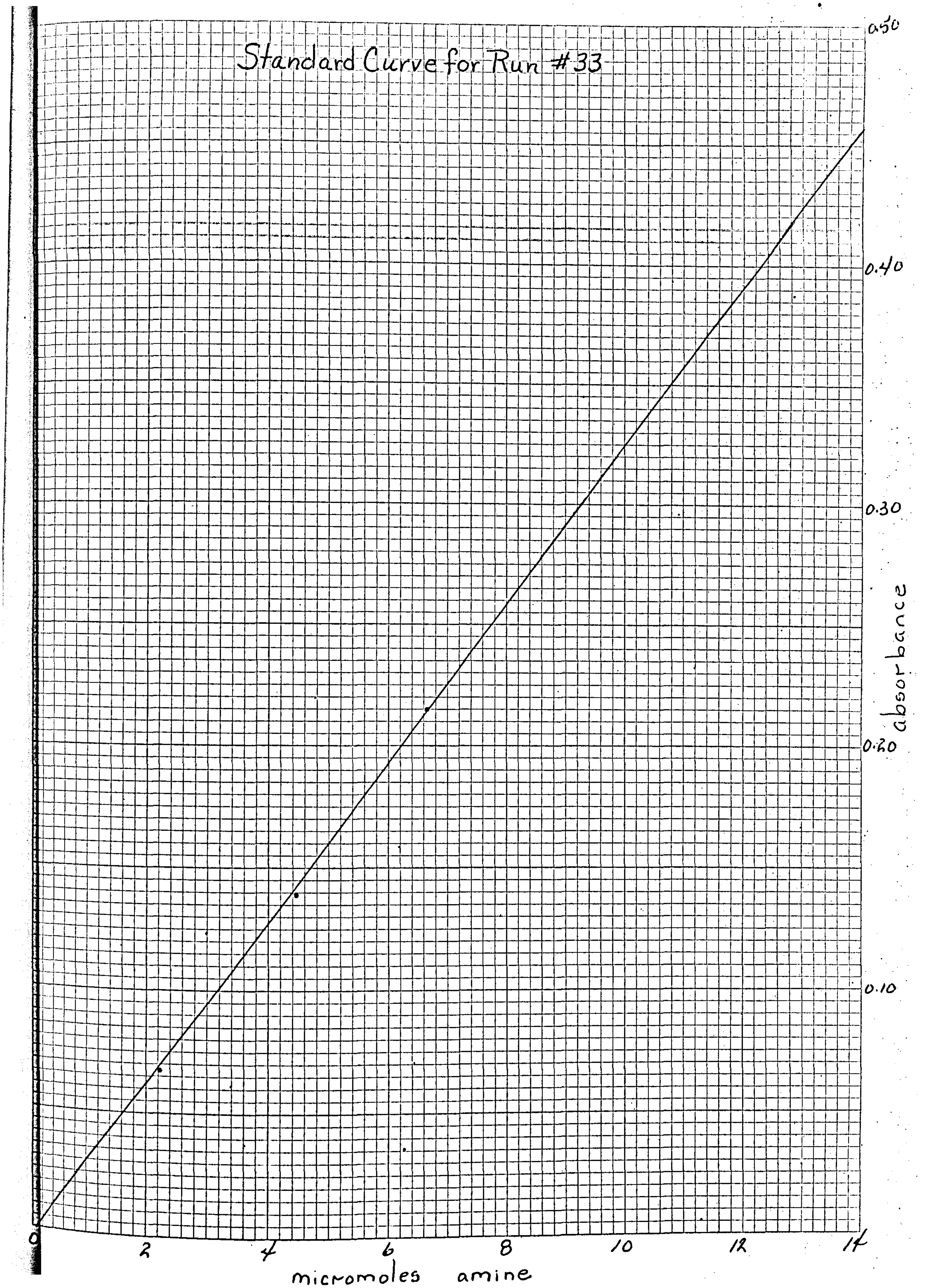
Strip Chart from Recorder

10 second (peak height) readings

Scale: −.10 to .90 absorbance units



80


Standard Curve for Run #33
0.50
0.40
0.30
0.20
0.10
absorbance
0
2
4
6
8
10
12
14
micromoles amine

Data from Graph:

Sample #	Micromoles as Read	Micromoles as Corrected	Micrograms
4	0.16		
5	1.38	1.16	52.30
6	2.60	2.44	110.02
7	3.95	3.79	170.89
8	0.15		
9	2.55	2.40	108.22
10	4.85	4.70	211.92
11	7.05	6.90	311.12

Calculations:

Sample #	Total Micrograms	Percent	% Found - % Added
5	15520	0.34	- 0.05
6	15640	0.70	- 0.08
7	15740	1.08	- 0.09
9	16000	0.68	- 0.17
10	16120	1.31	- 0.40
11	16720	1.86	- 0.32

APPENDIX V.

Reagents

Source	Reagent	Physical Data(6)
Aldrich Chemical Co., Inc. Milwaukee, Wisconsin	Isopropylamine	M.W. = 59.11 amu Density = 0.889 g/ml
E&A, Allied Chemical Co. Morristown, New Jersey	Copper(II)chloride dihydrate	M.W. = 170.49 amu
J.T. Baker Chemical Co. Phillipsburg, New Jersey	Triethanolamine (100.0%)	M.W. = 149.19 amu Density = 1.1242 g/ml
"	Methylisobutylketone	
"	1-Hexanol	
"	Butylamine	M.W. = 73.14 amu Density = 0.741 g/ml
"	Ethylenediamine (100.5%)	M.W. = 60.11 amu Density = 0.899 g/ml
"	Diethylamine	
"	Triethylamine	
Eastman Kodak Co. Rochester, New York	Salicylaldehyde	M.W. = 122.12 amu Density = 1.1669 g/ml
"	Methylamine hydrochloride	M.W. = 31.06 amu
"	Ethylamine hydrochloride	M.W. = 45.09 amu
"	Propylamine	M.W. = 59.11 Density = 0.717 g/ml
"	Isobutylamine	M.W. = 73.14 amu Density = 0.736 g/ml
"	Pentylamine	M.W. = 87.17 amu Density = 0.755 g/ml
"	Hexylamine	M.W. = 101.19 amu Density = 0.766 g/ml
"	1,2-Propanediamine (90%)	M.W. = 74.13 amu Density = 0.858 g/ml

APPENDIX VI.

Mixtures

Series #1: Ethylamine in Diethylamine

Reagents:	Ethylamine • HCl	55.28 % amine
	Diethylamine	0.7056 g/ml
	Water, distilled	1.000 g/ml

#1

Ethylamine •HCl	1.000 g
Diethylamine	49.392 g
Water	20.000 g
	70.392 g

$$\% \text{ Primary Amine} = \frac{0.5528(1.000)}{70.392} \times 100$$

$$= 0.78 \%$$

#2

Ethylamine .HCl	1.500 g
Diethylamine	49.568 g
Water	20.000 g

% Primary Amine = 1.17 %

#3

Ethylamine • HCl	0.500 g
Diethylamine	49.921 g
Water	20.000 g

% Primary Amine = 0.39 %

Series #2: Ethylamine in Diethylamine and Triethylamine

Reagents:	Ethylamine • HCl	55.28 % amine
	Diethylamine	0.698 g/ml
	Triethylamine	0.7275 g/ml
	Water, distilled	1.000 g/ml

#1

Ethylamine • HCl	0.1500 g
Diethylamine	6.2820 g
Triethylamine	7.2750 g
Water	5.0000 g
	18.7070 g

% Primary Amine = 0.44 %

#2

Ethylamine • HCl	0.4500 g
Diethylamine	6.2820 g
Triethylamine	7.2750 g
Water	5.0000 g
	19.0070 g

% Primary Amine = 1.31 %

APPENDIX VI. (Cont'd.)

#3

Ethylamine • HCl	0.7500 g
Diethylamine	6.2820 g
Triethylamine	7.2750 g
Water	5.0000 g
	19.3070 g

% Primary Amine = 2.4 %

Series #3: Ethanolamine in Diethanolamine

Reagents:	Ethanolamine	1.0180 g/ml
	Diethanolamine	1.0966 g/ml

#1

Ethanolamine	1.1080 g
Diethanolamine	108.5674 g
	109.5854 g

$$\% \text{ Primary Amine} = \frac{1.0180 \text{ g}}{109.5854 \text{ g}} \times 100$$

$$= 0.93 \%$$

#2

Ethanolamine	0.8144 g
Diethanolamine	108.7867 g
	109.6011 g

% Primary Amine = 0.74 %

#3

Ethanolamine	0.5090 g
Diethanolamine	109.1157 g
	109.6247 g

% Primary Amine = 0.46 %

AUTOBIOGRAPHY

I, Nathalie Harwood Perkins, was born in Richmond, Virginia on November 9, 1940. I graduated from St. Catherine's School in June 1959 where I had received a Future Scientist of America award in 1954 and science award given by the school in 1959. In June 1963, I graduated from Westhampton College of the University of Richmond with a B.S. degree in chemistry. While attending college I was elected to Gamma Sigma Epsilon and Sigma Pi Sigma honorary chemistry and physics societies. From 1963 to 1970 I was employed as a chemist, wife and mother. In January 1971 I returned to the University of Richmond as a part-time graduate student in chemistry. While studying I have been employed full-time as a chemist by Froehling and Robertson, Inc. in Richmond, Virginia.

The preceding thesis is being submitted in partial fulfillment of the requirements for the Master of Science degree in chemistry.