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DEPARTMENT OF MINES AND TECHNICAL SURVEYS
MINES BRANCH

2 THE COLORIMETRIC DETERMINATION OF COPPER
WITH 2,2-DIQUINOLYL IN MINERALS AND ORES

by
R. J. GUEST
RADIOACTIVITY DIVISION



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Abstract

A colorimetric procedure for the determination of copper with 2,2-diquinolyl (cuproine) is described. The method is based upon the fact that cuproine forms an intensely coloured purple complex with cuprous ions, the colour of the complex bearing a linear relationship to the copper present. The reagent is specific for monovalent copper. Ions which are themselves coloured do not interfere as the copper-cuproine complex is extracted with amyl alcohol from a weakly acid solution. The effect of pH and shaking time on the extraction was found to be important. Optimum conditions for complete extraction of the complex are indicated. The method, being very rapid and simple in execution, is especially suited for routine work.

THE COLORIMETRIC DETERMINATION OF COPPER WITH 2,2-DIQUINOLYL IN
MINERALS AND ORES

INTRODUCTION

Classical procedures for the determination of copper are usually time consuming and laborious. The analysis of large amounts of copper is often carried out by electroplating the copper after preliminary separations have been made. Volumetric procedures usually require one or more preliminary separations. Standard separations, such as the sulphide separation, are not always complete. Traces of copper can not be detected accurately by either gravimetric or volumetric means.

For detecting small amounts of copper several colorimetric methods have been proposed. The most frequently used of these procedures is the colorimetric determination of copper with diphenyl-dithiocarbamate. This procedure is subject to interference from a number of commonly occurring ions(1). Another well known method utilizes the blue colour given by ammonia with cupric salts. This method is not very sensitive.

Dithizone forms a coloured dithizonate with copper, but many elements interfere. Some investigators have used special techniques to overcome the lack of specificity of dithizone and have applied the reagent to routine determinations of copper (2, 3, 4). A method which has been applied in this laboratory (5) is based on the work of Bendix and Grabenstetter (6). In this procedure the pH is carefully regulated to eliminate as many interferences as possible and such remaining contaminants as bismuth, tin and mercury are

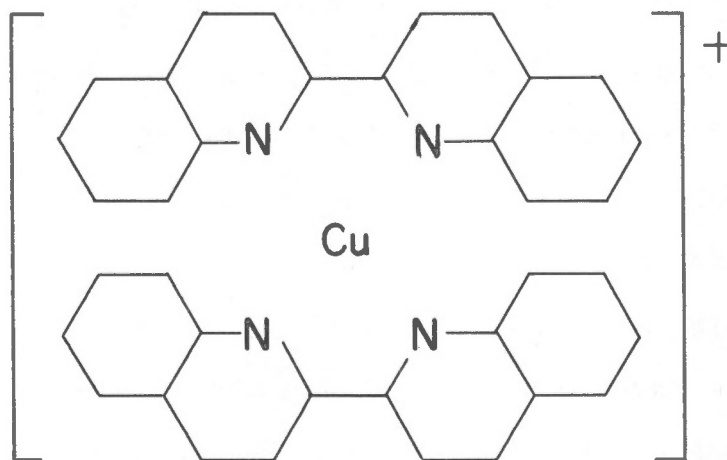
removed by extraction with potassium iodide. Excess dithizone is then removed by shaking the sample with dilute ammonia and the copper determined as the coloured dithizonate. While this procedure has proven quite satisfactory it is subject to a number of possible errors. The sensitivity of the method is so great that scrupulous care must be taken to use clean glassware and purified reagents. Determination of amounts of copper greater than 1 per cent requires great care by the analyst as the dilution factor becomes very high. The presence of small amounts of common oxidizing agents can not be tolerated.

Breckenridge, Lewis and Quick (7) showed that monovalent copper forms a purple complex with 2,2-diquinolyl (cuproine) in alcoholic or acetic acid media. Hoste (8, 9) investigated the specificity of this reaction and stated that the reagent is completely specific for monovalent copper. The effect of coloured ions can be eliminated by extracting the copper-cuproine complex by an organic solvent immiscible with water. Cuproine has been used for the determination of copper in tap water, alloy steel and vegetable matter (10, 11).

Cuproine is reputed to be 100 times more sensitive to copper than the colorimetric ammonia procedure, 10 times more sensitive than the method with diethyldithiocarbamate and 4 times less sensitive than the dithizone method (9). As this reagent appeared to offer advantages over other colorimetric reagents for copper an investigation was carried out into its possible use for determining copper in minerals and ores.

THEORY

According to Hoste (9) monovalent copper forms intensely coloured complexes with compounds containing two pyridyl groups, a pyridyl and a quinolyl group or two quinolyl groups linked in 2,2 position. These complexes are insoluble in water, but soluble in organic solvents, and contain in solution two molecules of the organic reagent to one ion of copper. The same investigator examined several of these compounds and found that, of the compounds specific for copper, 2,2-diquinolyl most successfully fulfilled the requirements for a colorimetric reagent. The compound is readily available and forms with copper a complex which is sensitive and very stable in acid medium. The complex in solution may be represented as follows:



APPARATUS

Beckman spectrophotometer, Model "B"

Beckman pH meter

Fisher safety centrifuge

REAGENTS

Standard copper solution

Dissolve 1 gram of electrolytic copper foil in 15 ml of 1:1 nitric acid, add 8 ml of 18N (1:1) sulphuric acid and fume the solution to dryness. Take the soluble salts into solution with 5 ml of concentrated HCl plus 25 ml of distilled water and make the solution up to volume in a 500 ml volumetric flask with distilled water. This is the main copper solution and contains 2 mg copper per ml of solution. Place 2 ml of the main copper solution in a 1000 ml volumetric flask and make up to volume with distilled water. 1 ml of this solution contains 4 micrograms of copper.

10 per cent hydroxylamine hydrochloride solution

Dissolve 25 grams of hydroxylamine hydrochloride in distilled water and dilute to 250 ml. This solution should be made freshly each week.

10 per cent tartaric acid solution

Dissolve 50 grams of tartaric acid in distilled water and dilute to 500 ml.

0.02 per cent cuproine solution

Dissolve 100 mg of cuproine in 500 ml of n-amyl alcohol. Stir until complete solution has taken place.

1:1 ammonium hydroxide solution

Add 50 ml of concentrated ammonium hydroxide to 50 ml of distilled water.

1:1 hydrochloric acid solution

Add 50 ml of concentrated hydrochloric acid to 50 ml of distilled water.

1 per cent hydrochloric acid solution

Add 5 ml of concentrated hydrochloric acid to 495 ml of distilled water.

1:1 sulphuric acid solution

Add 50 ml of concentrated sulphuric acid to 50 ml of distilled water.

PROCEDURE FOR SOLID SAMPLES

Weigh out accurately one gram of the ore into a 250 ml beaker. Add 20 ml of 1:1 hydrochloric acid and boil the sample for 10 minutes. Add 5 ml of nitric acid (conc.) and 10 ml of 18N(1:1) sulphuric acid and take the sample to dryness on the hot plate. Take up the soluble salts in 5 ml of hydrochloric acid (conc.) and 50 ml of water. Bring the sample to a boil. Filter off the insoluble residue on Whatman #40 paper and wash the residue with 1 per cent hydrochloric acid solution. Make up the filtrate to an appropriate volume in a volumetric flask.

Place an appropriate aliquot in a 100 ml beaker (see note 1, below) and add 5 ml of 10 per cent hydroxylamine hydrochloride and 5 ml of 10 per cent tartaric acid solution. The same treatment is accorded a blank determination which should be carried along with each group of samples. By means of a pH meter, standardized at pH 4, adjust the pH of the solution to 5.0 - 5.5 with 1:1 ammonium hydroxide and 1:1 hydrochloric acid. Transfer the sample to a 60 ml separatory

funnel (see note 2) keeping the volume of sample plus washings at not greater than 40 ml. Add by pipette 10 ml of 0.02 per cent cuproine in a n-amyl alcohol. Shake the mixture for 2 minutes. Discard the aqueous layer. Draw off the organic layer into a 1.5 cm centrifuge tube and centrifuge the sample for 1 minute (see note 3). Read the sample against a reagent blank on the Beckman spectrophotometer, model "B", using a wave length of 545 millimicrons, no filter and 1 cm cells.

PROCEDURE FOR SOLUTION SAMPLES

For solution samples, take an appropriate aliquot, add 3-5 drops of concentrated hydrochloric acid and dilute to the required volume in a volumetric flask with distilled water. Place an appropriate aliquot in a 100 ml beaker, add 5 ml of 10 per cent hydroxylamine hydrochloride and continue as above for solid samples.

Notes

1. Care should be taken that all glassware used in the analysis is cleaned thoroughly before use.
2. It has been found helpful to apply silicone grease to the stopper and stopcock of each separatory funnel.
3. Centrifuging is necessary because of the cloudiness of the organic extract. If this cloudiness reappears on standing, the organic extract should be centrifuged a second time.

EXPERIMENTAL

A series of aliquots of the standard copper solution covering the range 4 micrograms to 60 micrograms of copper was taken. The samples were placed in 100 ml beakers and diluted to about 20 ml with distilled water. 5 ml of 10 per cent hydroxylamine hydrochloride solution and 5 ml of 10 per cent tartaric acid solution were added. The pH of the solutions was adjusted to approximately 3.5, as according to the literature (9), extraction of the copper-cuproine complex is complete at a pH of over 3.0. This source also recommended the use of hydroxylamine hydrochloride as a reducing agent for the copper, and tartaric acid for complexing such elements as iron. 5 ml and 10 ml aliquots of a 0.2 per cent solution of cuproine in n-amyl alcohol were added to separatory funnels containing the samples and the mixtures shaken for varying amounts of time up to 10 minutes.

It was found that at a pH of 3.5 extraction of the complex varied with the shaking time. Extraction of small amounts of copper (10 micrograms) appeared to level out after 6-8 minutes shaking time, but this did not hold true for larger amounts of copper (20 micrograms) even after 10 minutes shaking. As erratic results were obtained by following the general recommendations found in the literature it was necessary to conduct a thorough investigation of the procedure.

Optimum pH and shaking time

Tests showed that a pH of between 4.4 and 7.5 is required for complete extraction of the copper-cuproine complex in 30 seconds. As can be seen from Figure 1, extraction of the complex falls off sharply after pH 7.5, possibly due to the formation of a copper-ammonia

complex. At these pH levels the copper-ammonia complex apparently forms more readily than the copper-cuproine complex. A shaking time of 30 seconds is satisfactory for amounts of copper up to at least 175 micrograms as long as the pH is kept within the required limits (Figure 1). It is shown in Figure 2 that extraction of the copper varies with shaking time if the pH falls below optimum levels. Extraction of 10 micrograms of copper, for example, was not complete after 8 minutes shaking at pH 3.5 even though the extraction curve levelled out in this period of time. When the pH of the solution was raised to 5.0, extraction was complete in 30 seconds or less.

Effect of hydroxylamine hydrochloride

Tests indicated that hydroxylamine hydrochloride solutions up to at least a week old could be successfully used. Addition of the hydroxylamine hydrochloride in solid form did not change results. Boiling the sample for 1 - 2 minutes after addition of the reducing agent did not alter the copper values. A standard amount of 5 ml of 10 per cent hydroxylamine hydrochloride is added in the procedure, but possibly a smaller amount than this would be adequate.

Absorption spectrum

The absorption spectrum of the copper-cuproine complex was plotted and the absorption was found to reach a maximum at 547 millimicrons and a minimum at 430 millimicrons. See Figure 3.

Stability

The colour of the copper-cuproine complex was found to be stable for periods of at least one week.

Optimum molecular proportion of copper-cuproine

The molecular proportion of copper-cuproine should be 1 of copper to at least 2 of cuproine. No change in absorption readings was noted by increasing the ratio of cuproine to copper by more than 2 to 1.

Calibration curve

A calibration curve was drawn up covering a range from 4 - 140 micrograms of copper in 10 ml of 0.02 per cent cuproine in n-amyl alcohol and using a wave length of 545 millimicrons.

Figure 4 shows a portion of the calibration curve.

APPLICATION OF METHOD

Synthetic samples

The reported specificity of cuproine for monovalent copper was investigated by adding a number of ions commonly found in minerals and ores to synthetic copper solutions. Results of these tests are found in Table 1.

None of the ions tested interfered in the copper determination. The extraction procedure eliminated the effect of any ions which are themselves coloured. If ions which form insoluble chlorides are present, the precipitated chlorides can be filtered off before the extraction is carried out. This modification was carried out successfully in cases where large amounts of such ions as mercury or silver were present. Small amounts of these ions caused no trouble. The presence of moderate amounts of common oxidizing agents does not affect results.

Bureau of Standards samples and ore samples

A series of Bureau of Standards samples and ore samples was analyzed for copper. The samples were taken into solutions by standard acid treatment, with any insoluble material being fused with sodium peroxide and added to the main solution. The results of these tests are shown in Table 2. Uranium oxide (U_3O_8) was added to three of the samples, but in no case was the copper value affected.

RESULTS AND DISCUSSION

Copper values by the cuproine method compare very favourably with Bureau of Standards values and with results obtained on ore samples by the dithizone method. Reproducibility of results was excellent on all samples analyzed.

Hoste (9) states that cuproine is a specific reagent for monovalent copper. Work carried out in Mines Branch laboratories substantiates this claim. The extraction procedure was found to be essential for many of the samples analyzed. Under the conditions of the procedure, such ions as titanium and iron when present in large quantities give definite colours. As only the copper-cuproine complex is extracted by the amyl alcohol, the colouration of these contaminants is without effect. The substitution of iso-amyl alcohol for n-amyl alcohol gave a small increase in the colour intensity. Brief tests indicated that the two amyl alcohols acted much the same in such matters as extraction rate and optimum pH conditions. As a plentiful supply of n-amyl alcohol was available, this compound has been used for all work described.

It has been found essential that the pH of the sample solution be kept between 4.4 and 7.5 for complete extraction of copper. These findings do not agree with Hoste (9) who indicates that complete extraction of copper is obtained with 30 seconds shaking at a pH greater than 3.0. For analysis of all samples it has been found satisfactory to adjust the pH of the sample to 5.0 - 5.5. Shaking time variance of 30 seconds to 120 seconds had no effect on results if optimum pH values were maintained.

No trouble has been caused by precipitation of such ions as iron and aluminum at pH values as high as 7.5 providing tartaric acid is present. If large quantities of ions which form insoluble chlorides are present, it is necessary to remove the insoluble compounds by filtration.

TABLE 1

The effect of other ions on the determination of copper by 2,2-diquinolyl

| Test | Contaminant Added Micrograms | Copper Present Micrograms | Copper Found Micrograms |
|------|---|------------------------------|----------------------------|
| 1 | 5,000 TiO ₂ | 30.1 | 29.9 |
| 2 | 4,000 Bi | 30.1 | 29.9 |
| 3 | 5,000 Co | 30.1 | 31.0 |
| 4 | 20,000 NiCl ₂ | 30.1 | 29.8 |
| 5 | 2,000 V | 30.1 | 29.7 |
| 6 | 13,000 Na | 30.1 | 30.2 |
| 7 | 15,000 Fe | 12.0 | 12.1 |
| 8 | 50,000 Fe | 0.0 | 0.7 |
| 9 | 12,000 U ₃ O ₈ | 12.0 | 12.1 |
| 10 | 5,000 U ₃ O ₈ | 0.0 | none detected |
| 11 | 3,000 As † 3,000 P ₂ O ₅ | 30.1 | 30.7 |
| 12 | 3,000 As † 3,000 P ₂ O ₅ | 0.0 | none detected |
| 13 | 170 SnCl ₂ | 30.1 | 29.8 |
| 14 | 1 x 10 ⁶ SO ₄ ⁻² | 30.1 | 30.2 |
| 15 | 1 x 10 ⁶ NO ₃ | 30.1 | 30.2 |
| 16 | 40,000 common oxidizing agent | 30.1 | 30.2 |

TABLE 2

Comparative Analyses on Typical Samples

| Sample | Type of Sample | Main Contaminants Present Per Cent | Copper Present (B. of S. value) Per Cent Cu. | Copper Found (cuproine) Per Cent Cu. |
|-------------------------|-----------------|--|--|--------------------------------------|
| Bureau of Standards 11e | Steel | Mn - 0.5 | A 0.105 | 0.107 |
| | | Si - 0.3 Fe - ††† U ₃ O ₈ added to B equivalent to 5 per cent U ₃ O ₈ | B 0.105 | 0.106 |
| Bureau of Standards 63b | Phosphor-bronze | Sn - 9.8 Pb - 9.4 Zn - 0.7 Sb - 0.5 Fe - 0.5 P - 0.4 Ni - 0.3 | 78.0 | 77.0 |
| Bureau of Standards 69 | Bauxite | Al ₂ O ₃ - 55.1 Fe ₂ O ₃ - 5.7 TiO ₂ - 3.1 SiO ₂ - 6.3 MnO - 0.6 | 0.03 (as CuO) | 0.02 (as CuO) |
| Bureau of Standards 85a | Aluminum Alloy | Mg - 1.6 Mn - 0.7 Ni - 0.4 Cr - 0.2 Al - ††† | 2.48 | 2.47 |
| Bureau of Standards 94a | Zinc-base Alloy | Al - 3.9 | A 1.08 | 1.09 |
| | | Zn - ††† U ₃ O ₈ added to B equivalent to 10 per cent U ₃ O ₈ | B 1.08 | 1.08 |
| Bureau of Standards 98 | Plastic Clay | SiO ₂ - 59.1 Al ₂ O ₃ - 25.5 Fe ₂ O ₃ - 2.0 TiO ₂ - 1.4 K ₂ O - 3.2 Na ₂ O - 0.3 MgO - 0.7 | 0.009 (as CuO) | 0.009 (as CuO) |

| Sample | Type of Sample | Main Contaminants Present Per Cent | Copper Present (B. of S. value) Per Cent Cu. | Copper Found (cuproine) Per Cent Cu. |
|-------------------------|----------------|--|--|--------------------------------------|
| Bureau of Standards 108 | Spelter | Pb - 0.1 Cd - 0.1 Zn - $\dagger\dagger\dagger$ | 0.0004 | None detected |
| Bureau of Standards 115 | Cast Iron | Ni - 15.9 Si - 1.6 Cr - 2.2 Mn - 1.0 | 6.44 | 6.36 |
| R3002 | Precipitate | ---- | g/l Copper Value (Dithizone Method) 0.07 | 0.08 |
| R4129 | Solution | U ₃ O ₈ added to B equivalent to 120 g/l U ₃ O ₈ | A 0.25 B 0.25 | 0.25 0.25 |

SUMMARY AND CONCLUSIONS

A rapid, accurate method for determining copper colorimetrically has been described. The method is based upon the coloured complex formed by cuproine and monovalent copper. This complex can be extracted by amyl alcohol from a weakly acid solution. A study of the various factors involved has been made and suitable operating conditions are indicated. The procedure is suitable for samples containing between 0.001 per cent and 10.0 per cent copper. Material containing larger amounts of copper can be successfully analyzed. The technique required is simple and results are reproducible under routine conditions. After sample dissolution, a trained analyst can complete a single determination in less than 15 minutes.

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EFFECT OF pH ON EXTRACTION OF COPPER-CUPROINE
COMPLEX WITH N-AMYL ALCOHOL

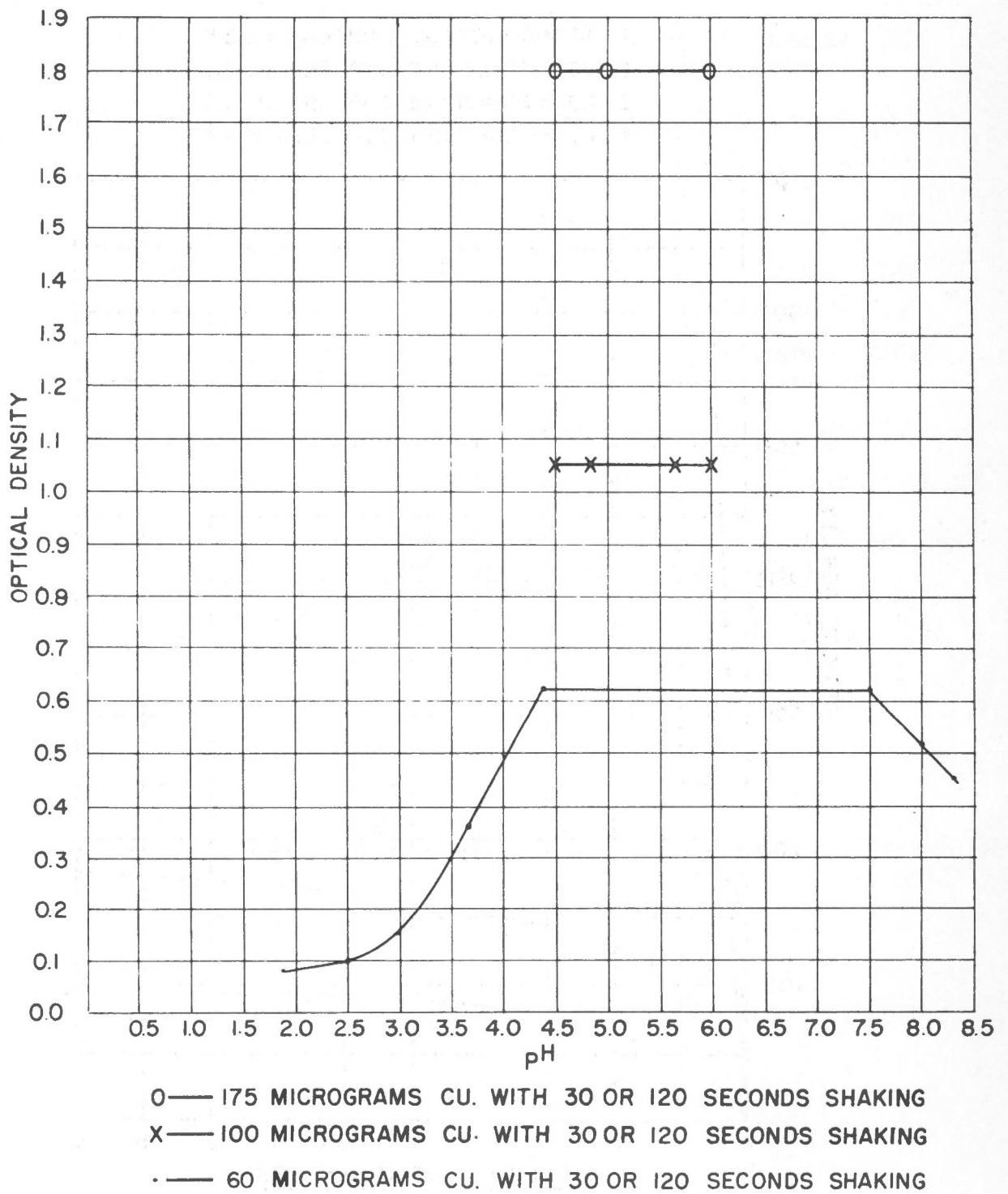


FIGURE I

EFFECTS OF SHAKING TIME ON EXTRACTION OF
COPPER-CUPROINE COMPLEX WITH N-AMYL ALCOHOL

1. 10 MICROGRAMS COPPER, pH 3.5
2. 20 MICROGRAMS COPPER, pH 3.5
3. 20 MICROGRAMS COPPER, pH 5.0
4. 60 MICROGRAMS COPPER, pH 4.5

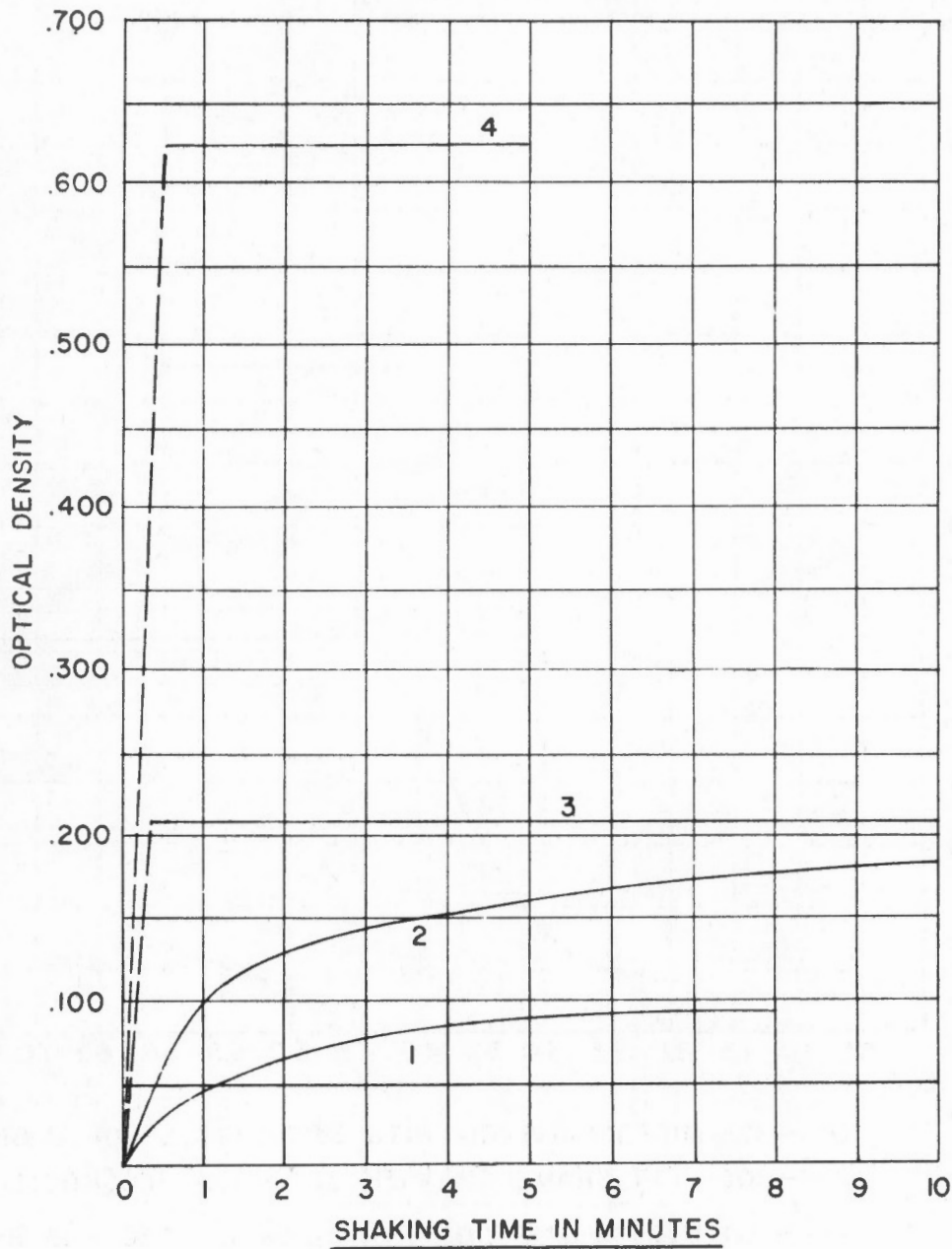


FIGURE 2

60 MICROGRAMS OF COPPER WITH 10 ML. 0.02% CUPROINE IN N-AMYL ALCOHOL

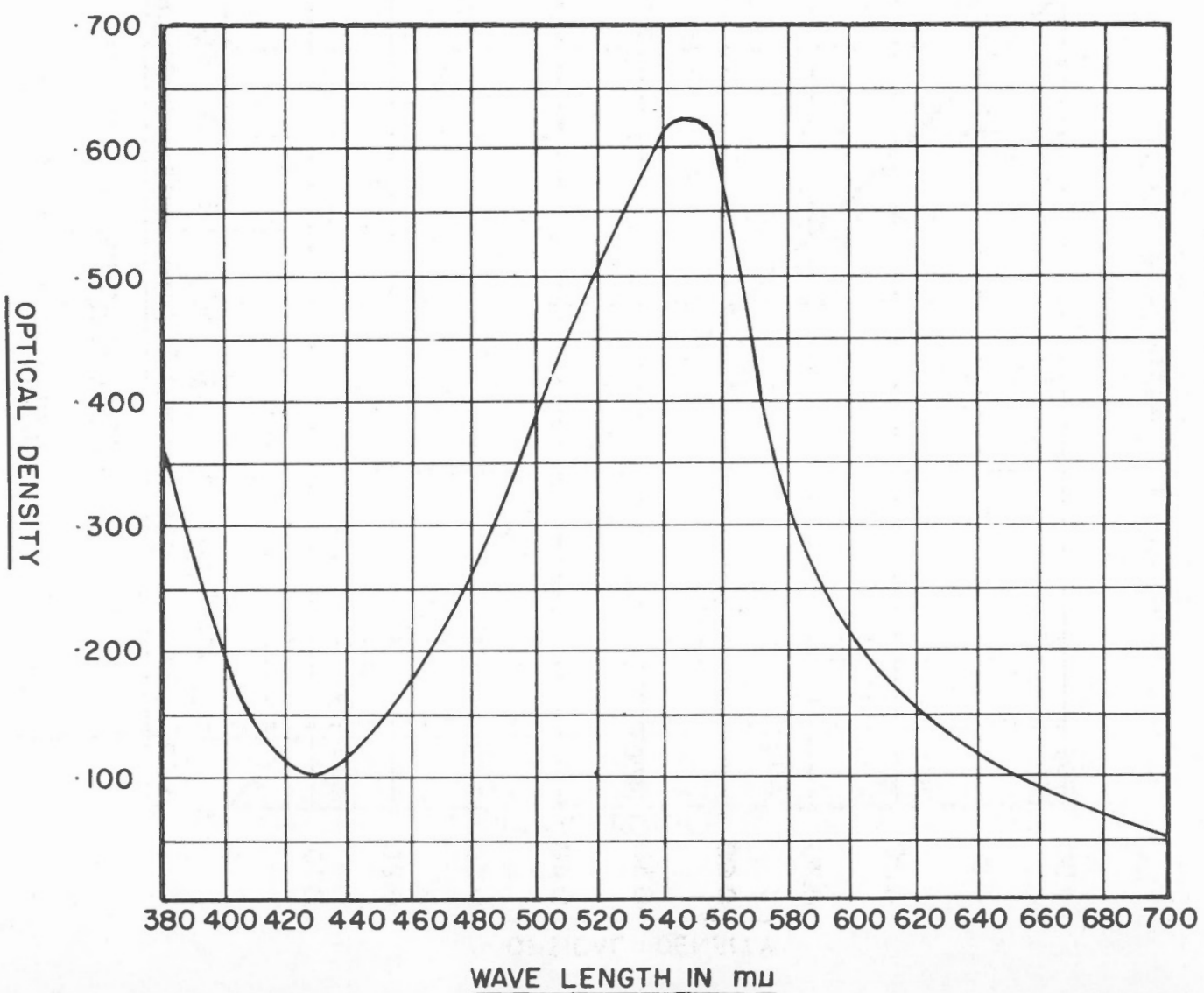


FIGURE 3
OPTICAL DENSITY

ABSORPTION SPECTRUM OF COPPER-CUPROINE COMPLEX

BECKMAN SPECTROPHOTOMETER-MODEL "B"

WAVE LENGTH - 545 mu

NO FILTER- 1 CM CELLS

READ AGAINST REAGENT BLANK

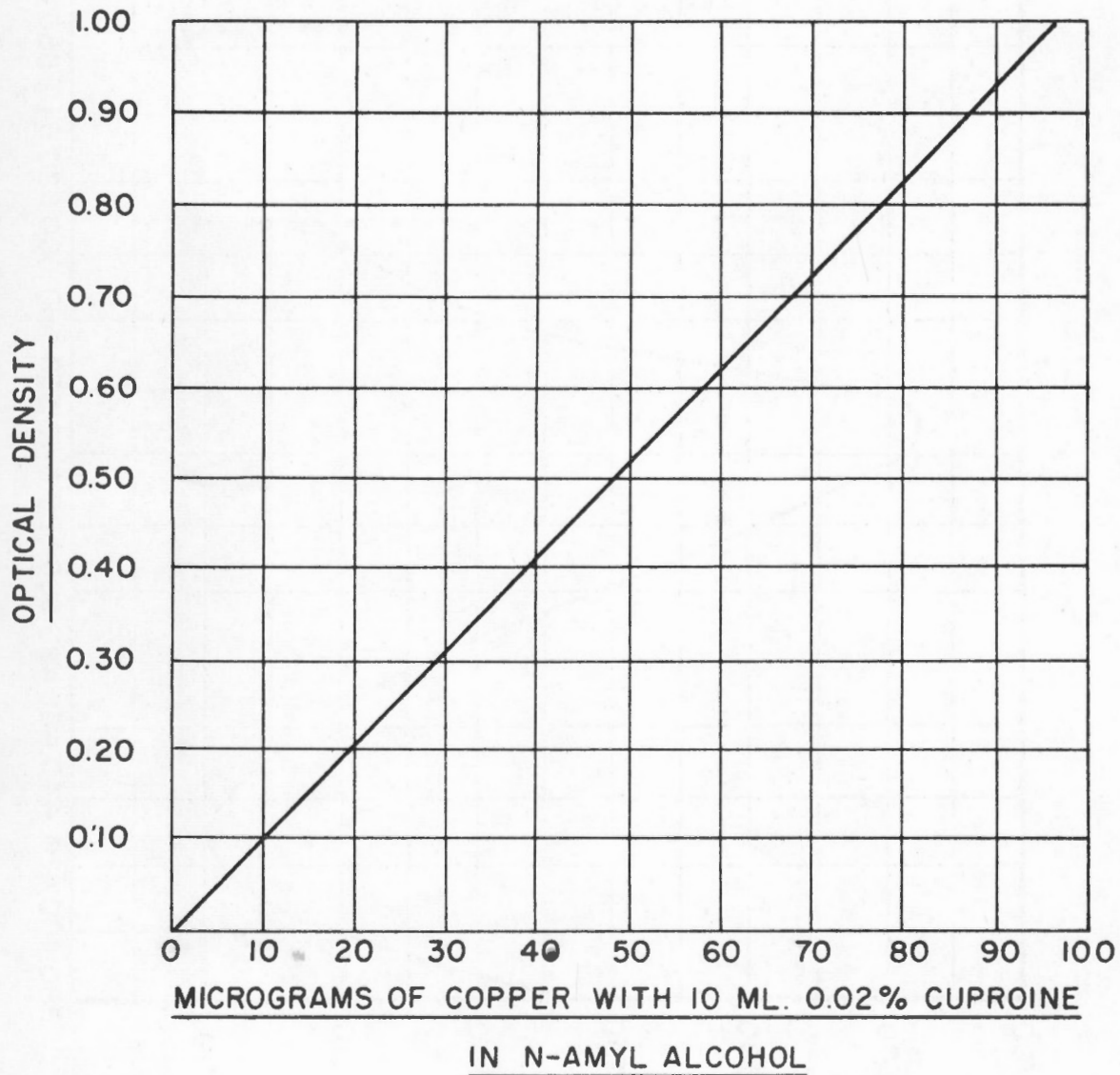


FIGURE 4

