

SPECTROPHOTOMETRIC DETERMINATION  
OF COPPER IN ORES WITH 2,2'-BIPYRIDYL

by

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A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of  
the requirements for the  
degree of

MASTER OF SCIENCE

June 1951

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Date thesis is presented August 18, 1950

Typed by Miriam Schubert

### ACKNOWLEDGEMENT

The writer wishes to acknowledge the generous and valuable assistance of Dr. J. P. Mehlig in the experimental work and the organization of this thesis.

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# SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN ORES WITH 2,2'-BIPYRIDYL

## INTRODUCTION

The belief that spectrophotometric methods are limited to micro quantities has been widely accepted. In 1945 Mellon (15, p.86), in referring to absorption spectrophotometry, pointed out the need for further study of existing and new color systems to determine the upper concentration limit for reliable work with modern instruments.) Previously the emphasis was placed on the lower concentration limit. Various spectrophotometric methods of analysis have been developed in recent years which make use of the extinction coefficient of the colored system at a definite wave length, or of a curve relating extinction or transmittancy at a definite wave length to concentration. It is frequently found that the upper limit of concentration that can be determined accurately is surprisingly high.

Most methods of determining copper involve precipitation or titrimetry; however, in recent years it has become possible, through the use of the spectrophotometer, to apply colorimetric procedures to quantitative analysis with an accuracy comparable to that of the more common methods.

Blau (1, pp.647-698) described the properties of 2,2'-bipyridyl, along with its method of preparation. Tartarini (18, pp.599-600) in discussing new color reactions involving cuprous salts reported that 2,2'-bipyridyl forms a cupric complex which can be reduced with hydroxylamine in ammoniacal solution to give a highly colored cuprous compound. 2,2'-bipyridyl has been applied to the spectrophotometric determination of iron (13, pp.52-55; 17, pp.862-864).

Moss and Mellon (16, p.116) in their study of the 1,10-phenanthroline-cuprous system stated that 2,2'-bipyridyl was not as sensitive as 1,10-phenanthroline in the formation of colored cuprous complexes.

The work described herein was carried out for the purpose of developing a spectrophotometric method for the determination of copper in ores, based upon the separation of iron by ammonia, and measurement of light transmitted by the 2,2'-bipyridyl-cuprous color system at a wave length of 430 mμ. In addition, the effect of diverse ions, concentration and order of addition of reagents, solvents, and stability of the system were also studied. Optimum conditions were established under which the colored complex could be used for the spectrophotometric determination of copper in ores.

## THEORETICAL CONSIDERATIONS

All colorimetric quantitative analysis is based upon the fundamental Beer-Lambert equation

$$I = I_0 \times 10^{-elc}$$

in which  $I$  represents the intensity of light of a given wave length transmitted by a color system;  $I_0$  is the intensity of light entering the system;  $e$  is the molecular extinction coefficient, which is the absorption due to a single molecule;  $l$  is the length of the absorbing medium through which the light passes expressed in centimeters; and  $c$  is the concentration of the solute expressed in moles per liter.

The oldest and still most widely used of the various colorimetric quantitative procedures involves visual comparison of the color produced by a solution containing a definite concentration of an unknown substance with that of a solution produced by a color standard equivalent to, or containing a known concentration of, the desired constituent. The length of the column of the unknown solution is varied until the transmission through the standard and the unknown solutions appears to be the same. Since the transmission of light through the solution is an inverse function of both the length of the column of the solution and the concentration of the colored substance, the concentration of the desired constituent in the



unknown solution may be calculated by solving the simple proportion involved.

Beer's law is not always obeyed in visual colorimetry as a result of the use of polychromatic light. In addition, the eye of the observer is not sensitive enough to distinguish between small variations in intensities of transmitted light thereby introducing a serious error. In spite of these limitations, visual colorimetry finds extensive use in routine analytical work.

The development of photoelectric colorimeters has partially overcome these limitations. The photoelectric measurement of the transmitted light eliminates the error due to lack of visual acuity on the part of the observer. Incident light of a narrow spectral band width is provided by use of a suitable filter.

The spectrophotometer employs a prism or a diffraction grating to provide essentially monochromatic light, and the photoelectric measurement of the transmitted light makes it possible to calculate concentrations directly from the fundamental Beer-Lambert equation.

By comparing the intensity of a ray which has passed through the colored medium with the intensity of a similar ray after passage through a colorless medium of similar refractive index contained in an identical cell, a basis is established for the measurement of absorption.



A comparison of this type is necessary to compensate for losses by reflection and scattering at the boundaries of the cell containing the solution and also for losses caused by scattering within the cell itself. The actual values of the intensities are not required in spectrophotometric analysis; only the ratio is significant. The ratio  $I/I_0$  is called the transmittancy of the solution. The logarithm of the reciprocal of the transmittancy is referred to as the extinction.

There are two general procedures available for determining the concentration of the desired constituent using the spectrophotometer, depending upon the conformity or nonconformity to Beer's law. If Beer's law is obeyed by the system the fundamental equation may be used for calculating the concentration. The Beer-Lambert equation solved for concentration  $c$ , is

$$c = \frac{\log I_0/I}{el}$$

The molecular extinction coefficient  $e$ , is a constant at any given wave length for a color system and must be first evaluated by use of solutions of known concentrations. The determination of copper by ammonia (6, pp.387-389), and triethanolamine (10, pp.52-55); iron by 2,2'-bipyridyl (13, pp.52-55), o-phenanthroline and p-nitro-o-phenanthroline (11, pp.162-163), salicylaldehyde (9, pp.76-79), salicylic acid (5, pp.162-163) and

thioglycollic acid (12, pp.8-14) are examples of this procedure.

The failure to obey Beer's law may be attributed to any one or more of several properties. If there is dissociation, association, ionization of the solute molecules with change in concentration, or a discrepancy in the construction of the instrument, Beer's law need not necessarily hold. Because of the construction discrepancy in the instrument itself, one should not use a published value of the molecular extinction coefficient for a specified color system, but it should always be determined with the instrument to be used.

When a system does not obey Beer's law a reference curve must be constructed by plotting the transmittancy, reciprocal of the transmittancy, or the extinction as a function of the concentration for a series of solutions of known concentration. After determining respectively, the transmittancy, reciprocal of the transmittancy, or the extinction for an unknown solution, its concentration may be read directly from the reference curve. This procedure could be used regardless of conformity to Beer's law, but is usually confined to those systems which do not conform. Iron by kojic acid (14, pp.642-643), manganese in steel by permanganate (7, pp.27-29), and nickel in steel by ammonia (8, pp.4-7) have been determined in this manner.

## EXPERIMENTAL

### APPARATUS AND SOLUTIONS

Beckman Model B Spectrophotometer. All transmission measurements were made with a Beckman Model B spectrophotometer. Light from an internal tungsten filament lamp is reflected by means of a series of mirrors through a quartz prism. Here the light is diffracted and reflected through the absorption cells to the photocell. The prism may be rotated in such a manner that a diffracted beam of light of any desired wave length is in focus at the slit. The diffracted beam passes through the absorption cell and strikes the photocell. The photocell is connected to a galvanometer which is calibrated with both per cent transmission and extinction scales.

In all transmission measurements, the intensity of the incident beam of light was regulated by means of opening or closing the slit until the galvanometer needle registered 100 when the "blank" was in position. Since transmission has been defined as the ratio of the intensity of light transmitted by the colored solution to the intensity of light transmitted by the "blank" solution, this adjustment made the galvanometer reading for the colored solution represent percentage transmission directly. This procedure was followed in making all the



transmission measurements. The identical absorption cells used were constructed of corex glass in such a way that the solution thickness was one centimeter. The same cells were used throughout, one reserved only for the colored solution, the other for the "blank" solution.

2,2'-Bipyridyl. A 0.1 per cent solution was prepared by dissolving one gram in 0.2M hydrochloric acid and diluting to a liter with distilled water.

Ammonium hydroxide. A 6M and a 3M solution were prepared by suitable dilution of a 15M solution.

Hydroxylamine hydrochloride. A 10 per cent solution of hydroxylamine was prepared by dissolving 100 grams of the iron-free solid in distilled water and diluting to a liter.

Methyl carbitol (Diethylene glycol mono-methyl ether). A commercial grade of methyl carbitol was used.

Standard copper solution. A standard copper solution was prepared by dissolving exactly 0.1 gram of electrolytically pure copper pellets in 10 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid in a 1000-ml. volumetric flask. The solution was neutralized with 6M ammonium hydroxide until the first indication of the formation of the blue cupric ammonium complex. The solution was then diluted to the mark at 20°C with distilled water and thoroughly mixed. Exactly 500 ml.



of this solution were transferred to another 1000-ml. volumetric flask, diluted to the mark at 20°C., and thoroughly mixed. Each milliliter of this solution contained 0.05 mg. of copper. This was a convenient concentration for the standard solution since 1 ml. diluted to a final volume of 50 ml. gave a concentration of 1 milligram of copper per liter.

### THE COLOR REACTION

In order to produce the color system, the volume of the standard copper solution required to give the desired concentration of copper was accurately measured from a burette into a 50-ml. volumetric flask, 2 ml. of 6M ammonium hydroxide were then added to give the correct pH value and also to form the cupric ammonium complex. Ten milliliters of a 0.1 per cent solution of 2,2'-bipyridyl were added followed by 1 ml. of 10 per cent hydroxylamine hydrochloride which reduced all copper to the cuprous condition. Twenty milliliters of methyl carbitol were added and the solution was diluted to the mark at 20°C. and thoroughly mixed. The orange-brown color developed immediately. A "blank" solution was prepared by adding 2 ml. of 6M ammonium hydroxide, 10 ml. of a 0.1 per cent solution of 2,2'-bipyridyl, 1 ml. of a 10 per cent hydroxylamine hydrochloride solution, and 20

ml. of methyl carbitol, diluting to the mark at 20°C. and mixing thoroughly.

It was found by experiment the reagents must be added in the above order. In the case of 1,10-phenanthroline, Moss and Mellon (16, p.117) found that the copper must be in the form of the ammonia complex prior to the addition of the reagent and that the reagent must be added before reduction with hydroxylamine hydrochloride. The ammonia concentration is also a factor, but is easily controlled by adjusting the pH value of the copper solution with 6M hydrochloric acid or 6M ammonium hydroxide until the first indication of cupric ammonia complex formation. This end point is easily seen and is reproducible. The solution at this point is also neutral to litmus. The pH value and ammonia concentration are thus automatically controlled and no particular advantage is gained by buffering with ammonium acetate.

Transmittancy for each solution was measured over a range of wave lengths ranging from 400 to 700 mμ. The desired wave lengths were obtained by setting the wave length indicator. Transmittancy was determined at intervals of 10 mμ in the region of minimum transmission and at intervals of 20 mμ throughout the remainder of visible spectrum. The intensity of the incident light was adjusted by means of the slit width until the transmission of

the "blank" solution gave a reading of 100 on the galvanometer scale. The colored solution was then placed in the path of the light beam and the percentage transmittancy or the extinction read directly from the respective galvanometer scale.

The wave length of maximum absorption for the color system was determined by the use of seven solutions with concentrations of 1, 2, 3, 4, 5, 6, and 7 p.p.m. of copper. The spectral transmission curves for the seven solutions are shown in Figure 1, maximum absorption occurring at 430 m $\mu$  with every solution.

#### CONFORMITY TO BEER'S LAW

To determine whether the cuprous-2,2'-bipyridyl color system conforms to Beer's law, the extinction values of seven standard copper solutions were determined at the wave length of maximum absorption and plotted as a function of the concentration. The curve is shown in Figure 2. The curve follows a straight line until a concentration of 6 p.p.m. is reached and then it begins to curve downward. The maximum concentration for which the molecular extinction coefficient can be used is therefore 6 p.p.m.

The molecular extinction coefficient was determined by solving the Beer-Lambert equation for  $e$ , and calculating the value of  $e$  from this equation by determining

the extinction values for a series of copper solutions of known concentration. The values obtained are shown in Table I. Above 6 p.p.m. the values for the molecular extinction coefficient were too divergent to be of any value and are not recorded.

TABLE I

## Determination of Molecular Extinction Coefficient

P.p.m. Copper	Molecular Extinction Coefficient
1	4,768
2	4,768
3	4,747
4	4,784
5	4,742
6	4,768
Average	4,762



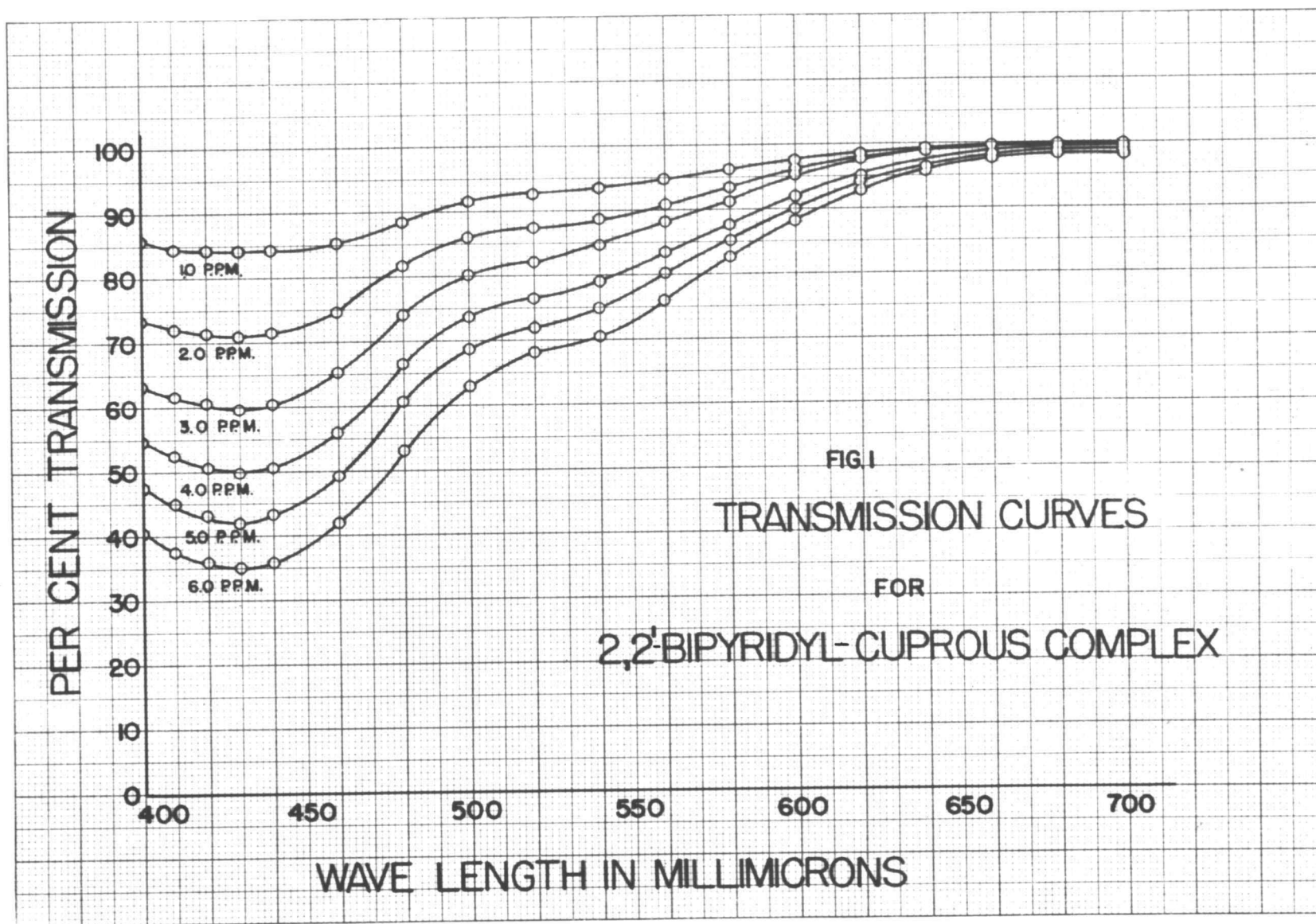
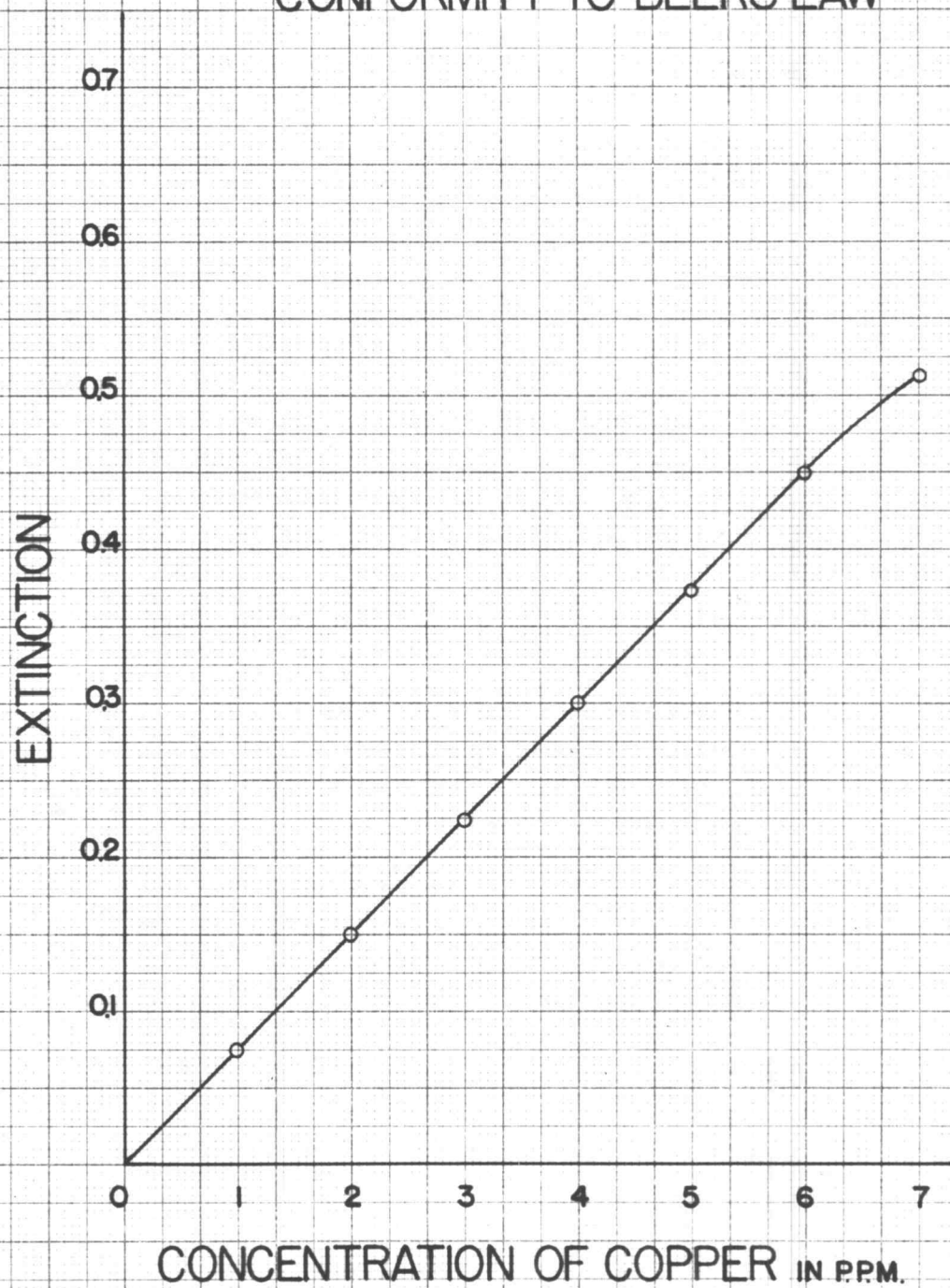


FIG. 2

## CONFORMITY TO BEER'S LAW



### DETERMINATION OF COPPER IN ORES

The method was tested by application to the determination of copper in ores in which copper had previously been determined by the iodide titrimetric method (4, pp.254-257). Since the system obeyed Beer's law up to a concentration of 6 p.p.m., a weight of ore was taken which provided a concentration in this range at the dilutions used.

A sample varying from 0.1 to 0.2 gram depending upon the copper content was accurately weighed and transferred to a 250-ml. beaker. Ten milliliters of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid were added to the sample and the covered mixture was warmed on a hot plate until solution had been effected or until only a white, siliceous residue remained. Concentrated ammonium hydroxide was slowly added with constant stirring to the hot solution until all the iron was precipitated as the hydrous ferric oxide and the deep blue copper complex was formed. The mixture was filtered into a 1000-ml. volumetric flask, and the residue washed with 3M ammonium hydroxide until the washings showed no blue color. The ferric hydroxide in the residue was dissolved with a minimum of dilute hydrochloric acid and washed through the filter paper into the original beaker until all the yellow color of ferric chloride had

disappeared from the filter paper. The solution was heated on a hot plate and the iron reprecipitated with concentrated ammonium hydroxide. The mixture was again filtered into the same 1000-ml. volumetric flask and washed with 3M ammonium hydroxide until the washings were colorless. The solution was acidified with hydrochloric acid and neutralized to the first appearance of the cupric ammonia complex with dilute ammonium hydroxide, diluted to the mark at 20°C., and thoroughly mixed.

Four milliliters of this solution were accurately measured into a 50-ml. volumetric flask by means of a burette. Two milliliters of 6 M ammonium hydroxide, 10 ml. of 0.1 per cent 2,2'-bipyridyl solution, 1 ml. of 10 per cent hydroxylamine hydrochloride solution, and 20 ml. of methyl carbitol were added to the copper solution, diluted to the mark at 20°C. and thoroughly mixed. A "blank" solution was prepared using the same concentrations of all the reagents except the copper solution.

The extinction was read directly from the galvanometer scale at a wave length of 430 mμ. The percentage of copper in the sample was calculated by use of the molecular extinction coefficient.

The following example illustrates the method of calculation:

Experimental data: weight of sample - 0.1018 gram;



extinction value 0.249; average molecular extinction coefficient - 4,762.

The Beer-Lambert equation solved for  $c$  gives

$$c = \frac{\log 1/T}{e \times l} \quad \text{moles of iron per liter}$$

Therefore,

$$c = \frac{\log 1/T \times \text{at. wt. Cu}}{e \times l} \quad \text{gram of Cu per liter.}$$

Since the final solution contained 0.004 of the original sample in 50 ml. of solution,

$$\begin{aligned} \% \text{ Cu} &= \frac{(63.57)(1000)(5)(\log 1/T)}{(4,762)(1)(0.1018)(80)} \\ &= \frac{(63.57)(1000)(5)(0.249)}{(4,762)(1)(0.1018)(80)} \\ &= 20.39\% \end{aligned}$$

### RESULTS

The method was applied to the determination of the copper content of four oxides, six ores, and two mattes. The results are shown in Table II along with values obtained by the iodide titrimetric method. In no case was the difference between the two methods greater than  $\pm 0.09$  per cent and the average difference was - 0.01 per cent. Since the extinction scale could be read only to the third decimal place, the average of several readings was taken. Results were duplicated on the same sample with a precision of  $\pm 0.01$  to  $\pm 0.11$  per cent.

TABLE II

Results Obtained with 2,2'-Bipyridyl

Sample No.	Nature of Sample	Copper by Iodide Method	Copper by 2,2'-bi-pyridyl Method	Deviation	Percentage Error
		%	%	%	%
1	ore	10.43	10.48	+0.05	+0.477
2	ore	11.16	11.16	0.00	0.000
3	ore	12.04	12.00	-0.04	-0.332
4	ore	20.33	20.37	+0.04	+0.197
5	ore	19.40	19.31	-0.09	-0.466
6	ore	18.63	18.61	-0.02	-0.107
7	oxide	15.02	15.05	+0.03	+0.200
8	oxide	14.00	14.03	+0.03	+0.214
9	oxide	13.23	13.22	-0.01	-0.088
10	oxide	22.31	22.30	-0.01	-0.052
11	matte	21.61	21.63	+0.02	+0.093
12	matte	14.09	14.02	-0.07	-0.497

## DISCUSSION

The spectrophotometric method which has been developed has proved that it may be applied to the determination of copper in ores with the copper content as high as 22.31 per cent. By proper dilution the range may be extended further. The careful dilution of the copper solutions cannot be overemphasized as any error introduced by this means would be greatly magnified in the final calculations. The results obtained from the 2,2'-bipyridyl method compare favorably with those obtained by the iodide titrimetric method (4, p.257) and by the triethanolamine method (10, p.53).

Moss and Mellon (16, p.116) found that an organic solvent was needed to prevent precipitation of the 1, 10-phenanthroline cuprous complex. The 2,2'-bipyridyl cuprous complex was water soluble, but very unstable in aqueous solutions. A solvent of 40 per cent methyl carbitol was found to stabilize the complex for 30 minutes. No color formation at all was noted when 40 per cent ethyl carbitol was used as the solvent.

The spectrophotometric method for copper using 2,2'-bipyridyl has an advantage over the visual colorimetric method since it does not require the use of a series of colored standards and eliminates entirely the erroneous matching of color shades by eye. Its chief advantage over

the photoelectric colorimetric method consists of the elimination of a search for a suitable light filter. The 2,2'-bipyridyl cuprous system was found to be stable for 30 minutes in contrast to the 24-hour stability of the 1,10-phenanthroline-cuprous system (16, p.117). The spectrophotometric determination of copper using 2,2'-bipyridyl has an advantage over the determination of copper using ammonia (6, p.388) and triethanolamine (10, p.52) because of its greater sensitivity, but is inferior to the 1,10-phenanthroline method both in its sensitivity and stability (3, p.24).

#### EFFECT OF DIVERSE IONS

A study of the interference of the more common diverse ions revealed a striking similarity to the results obtained by Moss and Mellon (16, p.117) in their 1,10-phenanthroline-copper study. Only serious interference was encountered with cadmium, chromic, cobaltous, cyanide, ferric, nickelous, thiosulfate, and zinc ions. None of these are present in interfering quantities in copper ores or are removed in the course of the procedure. The results obtained are shown in Table III.



TABLE III  
EFFECT OF DIVERSE IONS

Ion	Added as	Concentration in p.p.m.	Inter- ference	Approximate Limiting Concentration p.p.m.
Aluminum	$\text{Al}_2(\text{SO}_4)_3$	500	Precipitates	100
Ammonium	$\text{NH}_4\text{Cl}$	500	Negligible	-
Bismuth	$\text{Bi}(\text{NO}_3)_3$	20	Precipitates	15
Cadmium	$\text{CdCl}_2$	25	Fading	20
Chloride	$\text{NH}_4\text{Cl}^-$	500	Negligible	-
Chromic	$\text{CrCl}_3$	25	Change in hue	20
Cobaltous	$\text{CoCl}_2$	20	Change in hue	5
Cyanide	KCN	5	Fading	0
Lead	$\text{Pb}(\text{NO}_3)_2$	200	Precipitates	100
Nickelous	$\text{Ni}(\text{NO}_3)_2$	20	Change in hue	5
Nitrate	$\text{NaNO}_3$	500	Negligible	-
Oxalate	$\text{K}_2\text{C}_2\text{O}_4$	500	Fading	300
Potassium	$\text{KNO}_3$	500	Negligible	-
Sodium	$\text{NaNO}_3$	500	Negligible	-
Sulfate	$\text{Na}_2\text{SO}_4$	500	Negligible	-
Thiosulfate	$\text{Na}_2\text{S}_2\text{O}_3$	10	Fading	5
Zinc	$\text{ZnSO}_4$	20	Fading	10

## SUMMARY

A spectrophotometric method has been developed for the determination of copper in ores by use of 2,2'-bipyridyl. The method depends upon the formation of a cupric complex in ammoniacal solution and subsequent reduction of the copper with hydroxylamine hydrochloride to form an orange-brown highly colored cuprous compound. A 40 per cent methyl carbitol solution was found to be necessary in order to provide a stable color system. Extinction measurements were made at 430 m $\mu$ , the wave length of maximum absorption. The system obeyed Beer's Law up to a concentration of 6 p.p.m. warranting the use of the molecular extinction coefficient in determining the copper content of the samples.

The results obtained by this method agree very closely with those obtained by the iodide titrimetric method, and with the triethanolamine spectrophotometric method which gives further proof that constituents of macro quantities may be determined satisfactorily with the spectrophotometer.

The method may be easily carried out and possesses several advantages over the ammonia and triethanolamine methods for copper, but does not possess any advantages over the 1,10-phenanthroline method (3, p.24).

The color system is stable for 30 minutes, long enough to permit measurements conveniently.

Of the diverse ions which interfere, only iron is normally present in copper ores and it is removed during the course of the procedure.

## LITERATURE CITED

1. Blau, Fritz. Ueber neue organische Metallverbindungen. Bin Beitrag zur Kenntniss der Metallake. Monatshefte fur Chemie 19:647-698. 1898.
2. Fortune, W. B. and M. G. Mellon. Colorimetric determination of iron with o-phenanthroline. Industrial and engineering chemistry (analytical edition) 10:60-64. 1938.
3. Gruzensky, Paul Milnore. The use of 1,10-phenanthroline in a spectrophotometric method for the determination of copper in ores, Thesis, Oregon State College, June 1951.
4. Mahin, Edward G. Quantitative analysis. 4th ed. New York, McGraw-Hill, 1932. 623p.
5. Mehlig, Joseph Parke. A spectrophotometric method for the determination of iron in ores. Industrial and engineering chemistry (analytical edition) 9:162-163. 1937.
6. ———. Spectrophotometric determination of copper in ores and mattes. Industrial and engineering chemistry (analytical edition) 7:387-389. 1935.
7. ———. Spectrophotometric determination of manganese in steel. Industrial and engineering chemistry (analytical edition) 7:27-29. 1935.
8. ———. Spectrophotometric determination of nickel in steel with ammonia. Chemist analyst 34:4-7. 1945.
9. ——— and Dorothy Durst. Application of salicylaldoxime to the spectrophotometric determination of iron in ores. Chemist analyst 38:76-79. 1949.
10. ——— and Dorothy Durst. Application of triethanolamine to the spectrophotometric determination of copper in ores. Chemist analyst 37:52-55. 1948.



11. \_\_\_\_\_ and Henry Russel Hulett. Spectrophotometric determination of iron with o-phenanthroline and nitro-o-phenanthroline. Industrial and engineering chemistry (analytical edition) 14:869-871. 1942.
12. \_\_\_\_\_ and Maurice Joseph Shepherd, Jr. Application of thioglycolic acid to the spectrophotometric determination of iron in ores. Chemist analyst 35:8-14. 1946.
13. \_\_\_\_\_ and Maurice Joseph Shepherd, Jr. Spectrophotometric determination of iron in ores with 2,2'-bipyridyl. Chemist Analyst 36:52-55. 1947.
14. \_\_\_\_\_ and Maurice Joseph Shepherd, Jr. Spectrophotometric determination of iron in ores with kojic acid. Analytical chemistry 21:642-643. 1949.
15. Mellon, M. G. Light absorption spectrometry. Industrial and engineering chemistry (analytical edition) 17:81-88. 1945.
16. Moss, M. L. and M. G. Mellon. Colorimetric determination of copper with 1,10-phenanthroline. Industrial and engineering chemistry (analytical edition) 15:116-118. 1943.
17. \_\_\_\_\_ and M. G. Mellon. Colorimetric determination of iron with 2,2'-bipyridyl and with 2,2',2"-terpyridyl. Industrial and engineering chemistry (analytical edition) 14:862-865. 1942.
18. Tartarini, G. Nuove reazioni cromatiche dei sali rameosi. Gazzetta chimica italiana 63:597-600. 1933.