

THE USE OF 1,10-PHENANTHROLINE IN A  
SPECTROPHOTOMETRIC METHOD FOR THE  
DETERMINATION OF COPPER IN ORES

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INTRODUCTION

For some time the general belief that spectrophotometric determinations are limited to micro, or at best, semi-micro quantities was widely accepted. Mellon (14, p. 86) in referring to absorption spectrophotometry pointed out the need for further study of various color systems to ascertain the upper limit for reliable work with modern instruments. In recent years, various spectrophotometric methods of analysis have been developed which make use either of the extinction coefficient of the color system at a given wave length, or of a reference curve correlating transmittancy or extinction at a given wave length with concentration. It has been found that the range of concentrations that can be determined effectively is surprisingly high.

Most of the common methods for the determination of copper are either gravimetric or titrimetric in nature; however, more recently 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.

Tartarini (16, p. 599-600), in a discussion of the new color reactions involving cuprous salts, reported that 1,10-phenanthroline forms a cupric complex which can be reduced with hydroxylamine in ammoniacal solution to give a highly colored cuprous compound. Previously, Blau (1, p. 647-498) had described the properties of 1,10-phenanthroline, along with the method of preparation. The use of 1,10-phenanthroline can be applied satisfactorily to the determination of copper. Formation of a complex cuprous salt such as  $\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)\text{X}$  is presumably responsible for the orange-brown color (16, p. 599).

1,10-phenanthroline has also been applied to a spectrophotometric method for the determination of iron (2, p. 60-64; 10, p. 869-871).

Moss and Mellon (15, p. 116-118) have made a critical spectrophotometric study of the cuprous-1,10-phenanthroline color system with particular attention to the effect of diverse ions, effect of concentration of reagents, solvents for the complex, and stability of the system. Optimum conditions were established under which the soluble colored complex could be used for the colorimetric determination of copper.

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 the light transmitted by the cuprous-1,10-phenanthroline color system at a wave length of 430 mμ. The work furnishes further evidence that spectrophotometric determinations are not limited to a micro scale, but are applicable in many cases to macro quantities.



## THEORETICAL CONSIDERATIONS

Colorimetric quantitative analysis is based upon the fundamental Lambert-Beer 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 the light entering the system;  $e$  is the molecular extinction coefficient, which is a measure of the absorption due to a single molecule;  $l$  is the length in centimeters of the absorbing medium through which the light passes; and  $c$  is the concentration of solute expressed in moles per liter.

Various colorimetric quantitative procedures have been developed of which the oldest and perhaps the most widely used involves visual comparison of the color produced by a solution containing an unknown concentration of a substance with that 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 solution appears to be the same. Since the transmission of light through the solution is an inverse function of both the length of the solution and the concentration of the colored

substance, the concentration of the desired constituent in the unknown solution may be easily calculated by solving the simple proportions involved.

Unfortunately, Beer's law often is not obeyed in visual colorimetry as a result of the use of polychromatic light. Furthermore, the eye of the observer is not sufficiently sensitive to distinguish between small variation in transmission, but in spite of these limitations, visual colorimetry finds extensive use in routine analysis.

The development of photoelectric colorimeters has partially overcome these limitations. In these instruments, incident light of a reasonably narrow spectral band width is provided by means of suitable light filters, and errors due to lack of visual acuity on the part of the observer are overcome by photoelectric measurement of the transmitted light.

The use of a prism or a diffraction grating in the spectrophotometer enables it to provide practically monochromatic incident light, and photoelectric measurement of transmission makes it possible to calculate concentrations from the fundamental Lambert-Beer equation.

By comparing the intensity of a ray which has passed through the colored solution with the intensity

of a similar ray after passage through a colorless solution of similar refractive index contained in an identical cell, a logical basis is established for the measurement of absorption. Such a comparison is necessary to compensate for losses by reflection and scattering at the boundaries of the cell containing the solution and also for the losses caused by scattering within the liquid itself. The ratio  $I/I_0$  is termed the transmittancy of the solution. The actual values of the intensities are not required in spectrophotometric analysis, only the ratio being significant. The logarithm of the reciprocal of the transmittancy is referred to as the extinction.

Two general procedures may be followed in determining the concentration of the desired constituent from transmittancy data.

If Beer's law is obeyed by the color system, the fundamental equation may be used for calculating the concentration. This equation solved for concentration is

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

The molecular extinction coefficient  $e$ , for a color system is a constant at any given wave length and must



first be determined by the use of solutions of known concentration. Iron by salicylic acid (4, p. 162-163), thioglycolic acid (11, p. 8-14), 2,2'-bipyridyl (12, p. 52-55), o-phenanthroline and p-nitro-o-phenanthroline (10, p. 869-871), and salicylaldehyde (8, p. 76-79), and copper by ammonia (5, p. 387-389), and triethanolamine (9, p. 52-55) have been determined in this manner.

If there is dissociation, association, or ionization of the solute molecules with change in concentration, Beer's law will not necessarily be obeyed. If no change occurs in the solute molecules with concentration, Beer's law should apply in all cases. However, due to discrepancies in instrument construction, a color system which obeys Beer's law with one instrument may not necessarily do so with another. For this reason, it is not safe to rely upon a published value of the molecular extinction coefficient for a given system, and it should always be determined with the instrument to be used.

For a system which does not obey Beer's law, a reference curve may be constructed by plotting the transmittancy, reciprocal of the transmittancy, or the extinction as a function of 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 may be used for all systems regardless of their conformity or non-conformity to Beer's law, but is usually confined to those systems which do not conform. Determination of manganese in steel by permanganate (6, p. 27-29), nickel in steel by ammonia (7, p. 4-7), and iron by kojic acid (13, p. 642-643) are examples of this procedure.

## EXPERIMENTAL

### APPARATUS AND SOLUTIONS

Cenco-Sheard Spectrophotometer. All transmission measurements were made with a Cenco-Sheard spectrophotometer. In this instrument, light from an external six-volt, eighteen-ampere tungsten filament lamp is reflected by a mirror to a concave replica grating. The grating may be rotated in such a manner that a diffracted beam of light of any desired wave length is in focus at the exit slit. The diffracted beam returns slightly above the incident beam, passes through the absorption cell, and strikes a photovoltaic cell. The photovoltaic cell is connected to a galvanometer which correlates transmission with deflection of the scale.

In all transmission measurements, the intensity of the incident beam of light was regulated by means of the iris diaphragm so that the galvanometer pointer registered 100 when the "blank" solution was in position. By making this adjustment, the galvanometer reading for the colored solution represented per cent transmittancy directly, since transmittancy is defined as the ratio of the intensity of light transmitted by the colored



solution to the intensity of light transmitted by the "blank". Identical 1-cm. cells with fused corex windows were used for the colored solution and for the "blank".

1,10-Phenanthroline. A 0.1 per cent solution of the reagent was prepared by dissolving 0.5 gram of 1,10-phenanthroline monohydrate in 500 ml. of distilled water.

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

Hydroxylamine hydrochloride. A 10 per cent solution of hydroxylamine hydrochloride was prepared by dissolving 100 grams of the solid in distilled water and diluting to one 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 1 gram of electrolytically pure copper pellets in 10 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid. After the addition of 5 ml. of concentrated sulfuric acid, the solution was evaporated to dryness by means of an infra-red heat lamp. The copper sulfate thus formed was dissolved in distilled water, transferred to

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a 1000-ml. volumetric flask and diluted to volume at 20° C. By means of a micro-burette, 5 ml. of this solution were transferred to a 100-ml. volumetric flask and diluted to volume at 20° C. with distilled water. Each milliliter of this solution contained 0.05 milligram 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.

#### INSTRUMENT CALIBRATION

The calibration of the Cenco-Sheard spectrophotometer was checked according to manufacturer's specifications. The entrance slit was adjusted to a width of 0.5 millimeter and a mercury vapor lamp placed in front of it. The wave length indicator was set for 546 mμ and the position of the grating adjusted by means of the knurled screw on the grating support until the 546 mμ green line of the mercury spectrum was approximately in line with the cross hairs in the viewing tube. Only an approximate calibration was possible because one of the cross hairs was slightly misplaced.

No appreciable error is introduced by such a condition because determinations are made at the wave

length of minimum transmittancy as indicated by the spectral transmission curve for the system.

### THE COLOR REACTION

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 micro-burette into a 50-ml. volumetric flask. Two milliliters of 6 M ammonium hydroxide were added to give the desired pH and to form the cupric ammonium complex. Ten milliliters of a 0.1 per cent solution of 1,10-phenanthroline were added followed by 1 ml. of 10 per cent hydroxylamine hydrochloride to reduce all copper to the cuprous state. Twenty milliliters of methyl carbitol were next added, methyl carbitol being the most satisfactory solvent (15, p. 116). The solution was diluted to the mark with distilled water at 20° C. and thoroughly mixed. The orange-brown color of the system developed immediately. A "blank" solution was prepared by adding 2 ml. of 6 M ammonium hydroxide, 10 ml. of 0.1 per cent 1,10-phenanthroline, 1 ml. of 10 per cent hydroxylamine hydrochloride, and 20 ml. of methyl carbitol to a 50-ml. volumetric flask, diluting to the mark with distilled water at 20° C. and mixing thoroughly.



It is important that the reagents be added in the order given above. Moss and Mellon (15, p. 117) found that the copper must be in the form of the ammonia complex before addition of the reagent and that the reagent must be added before reduction with hydroxylamine hydrochloride. Ammonia concentration is also a factor, but is easily controlled by neutralizing the copper solution to litmus with 6 M hydrochloric acid or 6 M ammonium hydroxide and adding exactly 2 ml. of 6 M ammonium hydroxide. No particular advantage is gained by buffering with ammonium acetate since the addition of a definite amount of ammonium hydroxide to the neutral solution gives the proper pH adjustment.

All transmission measurements reported in this work were made with a Cenco-Sheard spectrophotometer. Transmittancy for each solution was measured over a range of wave lengths varying 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. The intensity of the incident light was adjusted by means of the entrance slit, exit slit, and the iris diaphragm 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 read on the

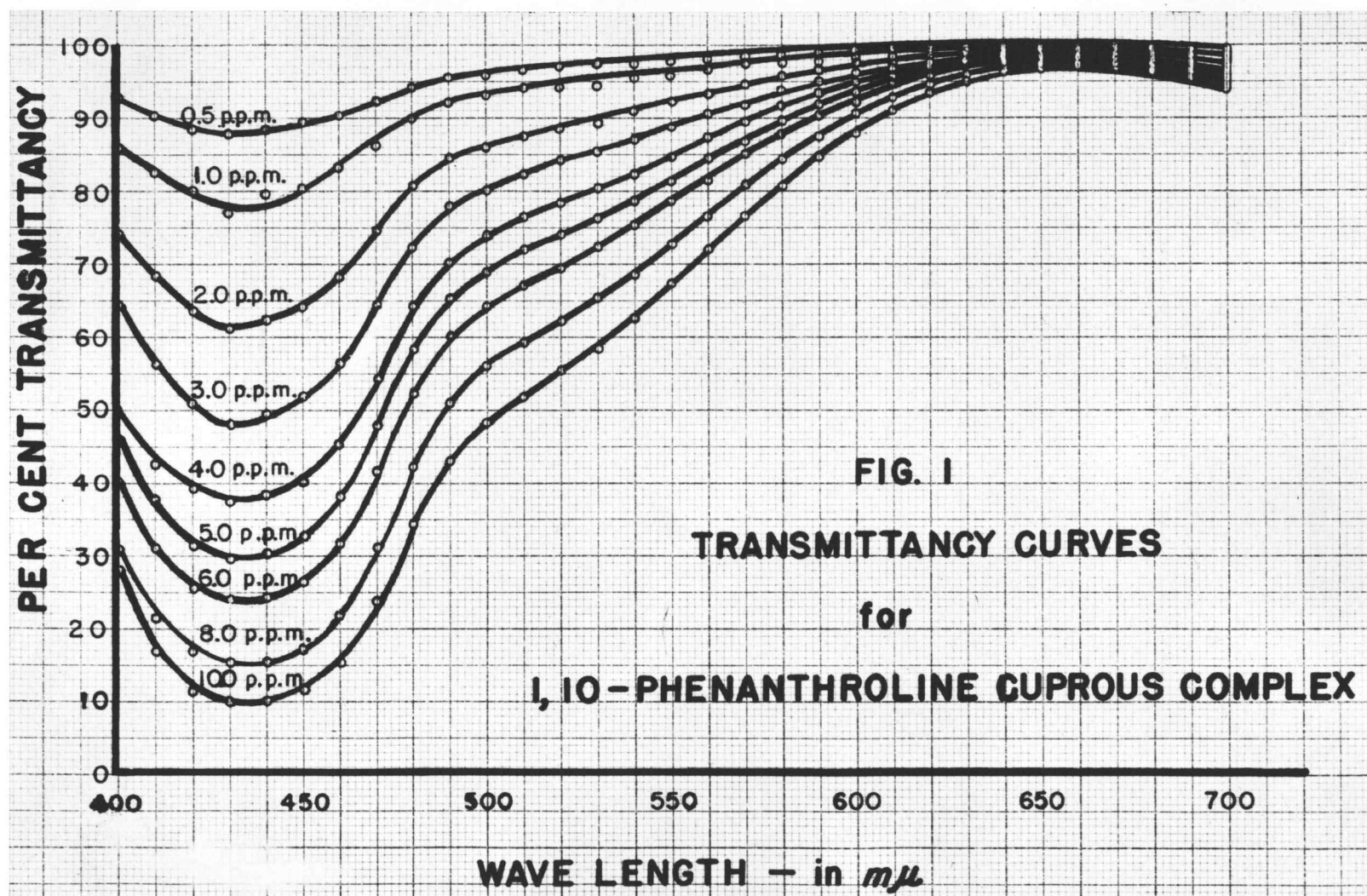
galvanometer scale.

The wave length of maximum absorption for the color system was determined by the use of nine solutions with concentrations of 0.5, 1, 2, 3, 4, 5, 6, 8, and 10 p.p.m. of copper.

The spectral transmission curves for the nine solutions are shown in Figure 1, maximum absorption occurring at 430 mμ.

ADVANCE BOND

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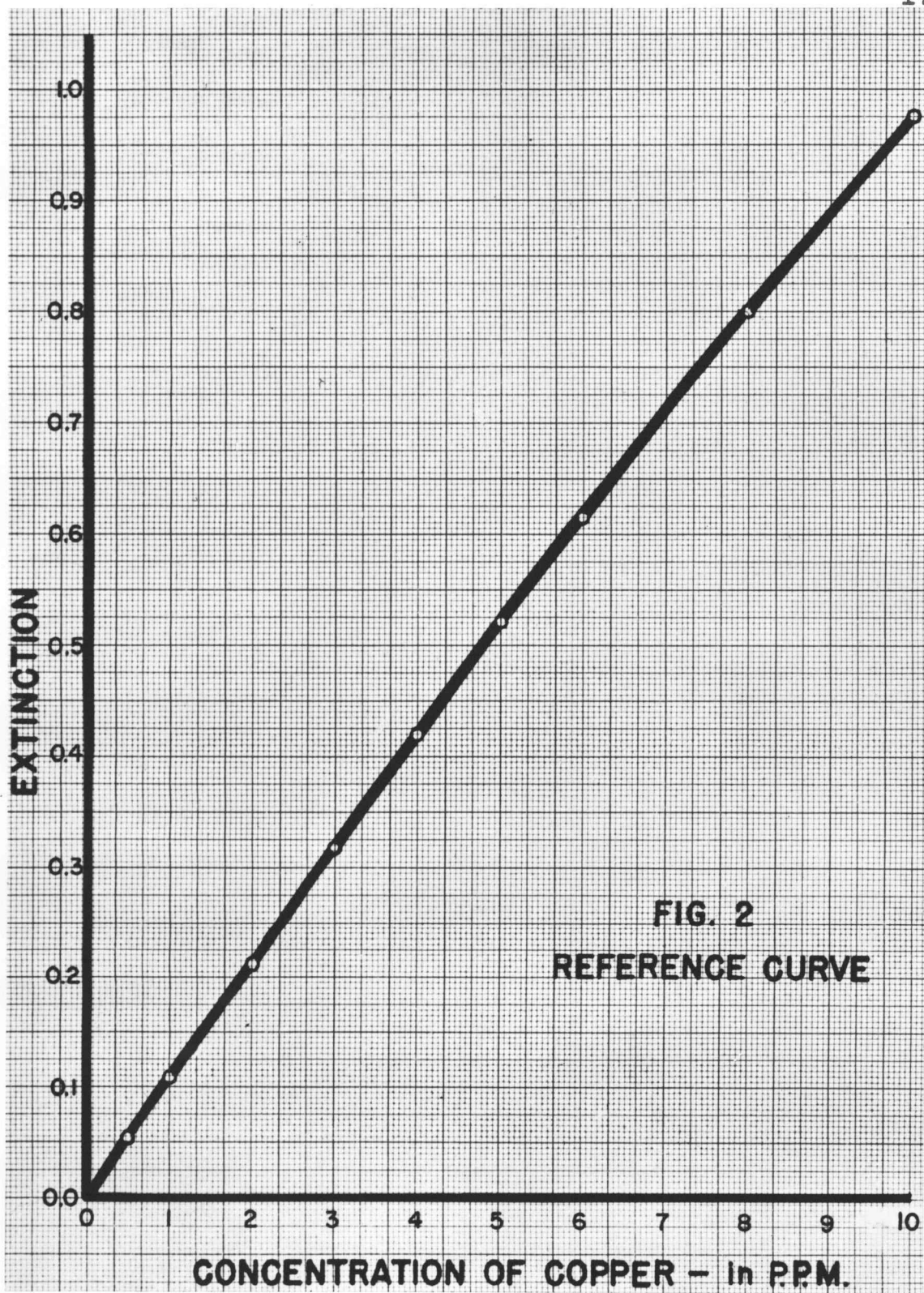




REFERENCE CURVE

To ascertain conformity or non-conformity of the cuprous-1,10-phenanthroline color system to Beer's law, the extinctions of the 9 standard copper solutions were determined for the wave length of maximum absorption and plotted as a function of the concentration. The curve is shown in Figure 2. No portion of this curve was a straight line indicating that Beer's law was not being obeyed. The deviation from a straight line may have been caused by limitations of the instrument used in the work, since Moss and Mellon (15, p. 118) working at Purdue university have shown, by using a General Electric recording spectrophotometer, that the system does obey Beer's law for concentrations ranging from 0.5 to 10.0 p.p.m.

Non-conformity to Beer's law required the use of a reference curve for subsequent determination of the copper content of ores. A large graph was constructed correlating extinction with concentration on which the extinction and concentration could be read to four significant figures. This curve was used throughout the remainder of the work for determination of copper concentration from transmittancy data.



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 (3, p. 254-258). Since the reference curve had been constructed for copper concentrations ranging from 0.5 to 10.0 p.p.m., a weight of ore was taken which provided a concentration within this range at the dilutions used.

A sample varying from 0.7 to 1.2 grams depending upon the copper content was accurately weighed, transferred to a casserole and covered with a watch glass. Ten milliliters of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid were added to the sample and the mixture was warmed on a hot plate until solution had been effected or only a white siliceous residue remained. The solution was allowed to cool, 5 ml. of concentrated sulfuric acid were added, and the solution was evaporated to dryness by means of an infra-red heat lamp. The copper sulfate in the residue was dissolved by adding 20 ml. of distilled water and heating on a hot plate.

If no iron was present in the sample, concentrated ammonium hydroxide was added to the hot solution



until the deep blue color of the cupric-ammonia complex was formed. The mixture was cooled, filtered into a 1000-ml. volumetric flask, and the residue washed with 3 M ammonium hydroxide.

If iron was present, concentrated ammonium hydroxide was slowly added with constant stirring to the hot solution until the hydrous ferric oxide was completely precipitated and the blue copper complex was formed. The mixture was cooled, filtered into a 1000-ml. volumetric flask and the residue washed with 3 M ammonium hydroxide. The ferric hydroxide in the residue was dissolved with a minimum of concentrated hydrochloric acid and washed through the filter paper into the original casserole until all the yellow 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 cooled, filtered into the same 1000-ml. volumetric flask, and the residue washed with 3 M ammonium hydroxide until the washings emerged colorless. The solution was neutralized to litmus with 6 M hydrochloric acid, diluted to the mark with distilled water at 20° C. and thoroughly mixed.

By means of a micro-burette, 1 ml. of this solution was transferred to a 50-ml. volumetric flask

and the following reagents were added in the order named: 2 ml. of 6 M ammonium hydroxide, 10 ml. of 0.1 per cent 1,10-phenanthroline, 1 ml. of 10 per cent hydroxylamine hydrochloride, and 20 ml. of methyl carbitol. The solution was diluted to the mark with distilled water at 20° C. and thoroughly mixed. A "blank" was prepared containing the same concentrations of all reagents except the copper.

Transmission measurements of this solution in a 1-cm. cell were made at 430 mμ. The entrance slit was set at a width of 1.0 mm. and the exit slit at a width of 10 mμ. The percentage of copper in the sample was calculated by use of the reference curve.

The following example illustrates the method of calculation:

Experimental data: weight of sample--0.9376 gram; percentage transmittancy of the colored solution--39.7 per cent.

$$T = 0.397$$

$$1/T = 2.5189$$

$$E = \log 1/T = 0.4012$$

From the reference curve, the concentration of copper corresponding to an extinction of 0.4012 is 3.813 p.p.m. Since the concentration of the final solution was one-fiftieth of the original,

$$\text{percentage copper} = \frac{(3.813)(50)(100)}{(0.9376)(1000)}$$

$$= 20.33 \text{ per cent}$$

The calculations may be easily and rapidly performed.

### RESULTS

The method was applied to the determination of the copper content of four oxides, two mattes, and seven ores. The results are shown in Table I along with the values obtained by the iodide titrimetric method. In no case was the difference between the two methods greater than  $\pm 0.10$  per cent and the average difference was  $-0.02$  per cent. The percentage error ranged from  $-0.710$  to  $+0.383$  per cent with an average of  $-0.169$  per cent. Since the scale of the galvanometer can only be read with an accuracy of 0.1 scale division corresponding to about 0.06 per cent copper in a sample containing 20 per cent copper, the average of several readings was taken for the transmittancy. Results were duplicated on the same samples with a precision of  $\pm 0.01$  to  $\pm 0.18$  per cent.



TABLE I

Results Obtained with 1,10-phenanthroline

Sample No.	Nature of Sample	Copper by Iodide Method	Copper by 1,10-phenanthroline Method	Deviation	Percentage Error
		%	%	%	%
1	oxide	22.31	22.33	+0.02	+0.089
2	oxide	13.23	13.21	-0.02	-0.151
3	oxide	14.00	13.98	-0.02	-0.143
4	oxide	15.02	14.94	-0.08	-0.533
5	matte	21.61	21.68	+0.07	+0.224
6	ore	10.43	10.47	+0.04	+0.383
7	ore	11.16	11.15	-0.01	-0.090
8	matte	14.09	13.99	-0.10	-0.710
9	ore	12.04	11.98	-0.06	-0.498
10	ore	20.33	20.27	-0.06	-0.295
11	ore	7.27	7.25	-0.02	-0.275
12	ore	18.63	18.66	+0.03	+0.161
13	ore	19.40	19.33	-0.07	-0.361

## DISCUSSION

The results show that the spectrophotometric method which has been developed may be applied to the determination of copper in ores for copper concentration at least as high as 22.31 per cent. The range of concentration to be determined may be extended further by proper dilution or by changing the length of the absorption cell. A careful dilution of the copper solutions is important, as any error introduced thereby would be greatly multiplied in the final calculations. Results of the analysis compare favorably with those obtained by the iodide titrimetric method (3, p. 257) and by the triethanolamine spectrophotometric method (9, p. 53).

Since the color reaction is carried out in ammoniacal solution, iron must be absent irrespective of the fact that it also forms a colored complex with 1,10-phenanthroline (2, p. 61). The separation may be effected by double precipitation of the iron as the hydrous ferric oxide with ammonia. In the spectrophotometric determination of copper in ores with ammonia, iron was separated in this manner (5, p. 388).

Moss and Mellon (15, p. 117) have made an extensive study of the effect of diverse ions. Of the cations whose compounds are soluble under the conditions employed, only cadmium, cobalt, nickel, and zinc

interfere, presumably by complex formation with the reagent. Metals which form a precipitate in basic solution are removed in the course of the procedure. Among the anions investigated, only cyanide, dichromate, and thio-sulfate interfere appreciably.

The spectrophotometric method for copper using 1,10-phenanthroline 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 matching of color shades by eye. Its advantage over the photoelectric colorimetric method consists of the elimination of a search for suitable light filters.

It has been shown that the color system is stable for 24 hours, permitting spectrophotometric measurements to be made conveniently (15, p. 118).



## SUMMARY

A spectrophotometric method has been developed for the determination of copper in ores which depends upon the formation of a cupric complex with 1,10-phenanthroline in ammoniacal solution, and subsequent reduction with hydroxylamine hydrochloride to give an orange-brown highly colored cuprous compound. Methyl carbitol is the most effective solvent for the complex. Transmittancy measurements of the color system were made at 430 mμ, the wave length of maximum absorption. The copper concentration is related quantitatively to the transmittancy and can be calculated by the use of a reference curve correlating extinction with concentration. Beer's law was not obeyed in this work, probably due to limitations of the instrument used.

Results obtained by this method agree very closely with those obtained by the iodide titrimetric method, and the triethanolamine spectrophotometric method, thus giving further proof that constituents in macro quantities can be determined satisfactorily by spectrophotometric methods.

The method is easily carried out and possesses several advantages over existing colorimetric methods for copper.

Of the diverse ions which interfere with the color system, only iron is normally present in a copper ore and it is removed in the course of the procedure.

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