

TITANIUM

THE SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN TITANIUM  
AND OTHER METALS WITH DICYCLOHEXANONE OXALYLDIHYDRAZONE

TECHNICAL REPORT

By

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TITLE

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ABSTRACT

Dicyclohexanone oxalyldihydrazone has been applied to the determination of copper in titanium alloys and other metals. This reagent reacts in alkaline solution with copper to form an intense blue colored complex which exhibits maximum absorption at a wave length of 600 m $\mu$ . The molar absorbancy of the complex is approximately 16,000. Other metals do not form colored complexes, thus allowing the direct determination of copper without extraction or preliminary separations. Ethanol stabilizes the complex in the presence of nickel, cobalt, and other metals.

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## INTRODUCTION

The determination of copper in titanium, steel, aluminum, and other metals is frequently required by research programs, foundry control work, and acceptance testing at Watertown Arsenal. Gravimetric determinations are always possible, but these, in most cases, require preliminary separations and purifications which may be quite involved. A further disadvantage of these methods is that the procedure is different for each type of base metal alloy. A colorimetric method utilizing neo-cuproine has been described by A. J. Frank, et al,<sup>1,2</sup> and is more universal in that it is applicable, with only slight modification, to many alloys. While this can be a highly accurate method, it requires considerable manipulation, including removal of chromium, a careful neutralization, and a chloroform extraction of the neo-cuproine complex. It has not been found satisfactory for occasional analyses because of the occurrence of high and irregular blanks.

Since difficulties were encountered with the neo-cuproine method for copper, an alternate procedure, preferably a photometric determination without extraction, was desired. A survey of the literature suggested that dicyclohexanone oxalyldihydrazone (trivial name, cuprizon) might be successfully used for copper determinations in titanium, aluminum, and other metals.

The use of dicyclohexanone oxalyldihydrazone was first described in 1952<sup>3</sup> by Wetlesen and Gran for the determination of copper in pulp and paper. In 1955 this reagent was applied to the determination of copper in blood by Peterson and Bollier.<sup>4</sup> Its application to ferrous alloys was described in 1956 by Haywood and Sutcliffe<sup>5</sup> and in 1957 by Wetlesen.<sup>6</sup>

This reagent was used at the Watertown Arsenal Laboratories for the analysis of several types of alloys for copper. A procedure was developed which can be applied with only slight modification to all the types of alloys tested. A method was found for stabilizing the copper color in the presence of cobalt and nickel and other metals which tend to cause instability.

## APPARATUS AND REAGENTS

Spectrophotometer - Beckman DU, with 1 cm cells.

Ammonium Citrate Solution - 500 grams of ammonium citrate dissolved in water and diluted to 1 liter.

Reagent Solution - 4 grams of dicyclohexanone oxalyldihydrazone dissolved in 1 liter of 50% ethyl alcohol.

dithizone extraction method.<sup>7</sup> These samples were dissolved in a dilute sulfuric acid-fluoboric acid solution and aliquots taken for analysis. The results are shown in Table I. The agreement among the three methods was excellent, especially since copper is known to segregate readily in titanium alloys.

The effect of alloying elements found in titanium alloys was investigated by the preparation of synthetic titanium alloy solutions. The solutions were all made-up to contain 100 mg of titanium, 0.235 mg of copper, and 10 mg of one of the following metal ions: Mn(II), Mo(VI), Fe(III), Cr(III), Cr(VI), V(IV), Sn(IV), W(VI), or Ni(II).

After color development of these solutions, readings were made of the transmittancies at intervals from 5 to 60 minutes. In each case, except in the presence of nickel, the color development was complete in 5 to 15 minutes and the color was stable up to 60 minutes. In the presence of nickel, full color development did not occur and fading was rapid. This effect had been noted in nickel steels by Wetlesen (see Reference 6), who recommended reading the transmittancy within 5 minutes in order to avoid appreciable fading. It was discovered in the course of the investigation at Watertown Arsenal Laboratories, however, that the solutions containing nickel could be stabilized by the addition of 95% ethanol. This effect is illustrated in Table II. The samples each contained 100 mg of titanium, 10 mg of nickel, and approximately 0.12 mg of copper.

Although Cr(III) will precipitate by itself when the solution is made alkaline, it does not precipitate in the presence of an excess of titanium. In large amounts it produces considerable color in the solution, but this effect is compensated for by the blank solution. Oxidation to Cr(VI) would eliminate the interfering color, but is not practical in titanium alloys since the simplest oxidation procedure, fuming with perchloric acid as has been recommended for steels, would precipitate the titanium. Other procedures would dilute the solution undesirably or would leave an excess of oxidant which would destroy the copper complex.

#### Analysis of Ferrous Alloys

Steels are readily analyzed for copper by the above procedure. It was found that with the exception of nickel and cobalt no common alloying element interferes. Both of these elements cause rapid fading of the copper color and, if present in high amounts, prevent its complete development. This is in accord with the findings of Wetlesen (see Reference 6), but in disagreement with Haywood and Sutcliffe (see Reference 5), who report no fading but speak only of interference due to background color by these elements.

Here, again, it was found that the addition of ethanol to the solutions repressed the interference of nickel and cobalt completely if they were present in normal alloying amounts in ferrous materials. In an alloy of the S816 type (40%Co, 20%Ni), this addition of alcohol does not prevent the interference, and some other method of analysis must be employed.

The color development time varies somewhat depending on the type of alloy. In all cases, however, full development took place in 20 minutes. This was selected, therefore, as the minimum elapsed time between the time of addition of the copper reagent and the reading of the percent transmittancy or absorbancy. The dicyclohexanone oxalyldihydrazone method is very rapid, both in elapsed time per determination and in working time. After the samples are in solution and cooled the work time per sample is about 10 minutes and the elapsed time before the end of an individual determination may be less than 30 minutes. This is much shorter than the time required for normal gravimetric procedures in which the copper is usually electro-deposited. In the latter procedures the working time and elapsed time may be measured in hours, especially in the case of bearing metals.

The precision found for the recommended method is excellent as shown by the range of six values for Standard 12F from 0.118 to 0.119. The accuracy is probably limited more by the care with which the blank correction is determined than by any limitation in the method itself. No study was made of the effect of temperature on the determination. Solutions were cooled only approximately to room temperature before the addition of reagents. Since no deviations were noted which might be ascribed to lack of temperature control this point was not investigated. However, all work was completed in an air-conditioned room, resulting in the temperature of all solutions at the time of reading being uniform at 22°C.

While a Beckman DU was used for this investigation, the use of a high-resolution instrument such as this is not essential. A Coleman spectrophotometer with a band width of 35 mmu is routinely being used with excellent results. It is probable that a filter photometer would be equally applicable. The reason for this is found in the broad, rather smooth absorption spectrum of the copper complex. This spectrum is shown in Figure II.

#### CONCLUSIONS

The dicyclohexanone oxalyldihydrazone method for copper is a nearly universal method for copper. It fails only in the presence of large amounts of cobalt or nickel. After dissolution of the sample all types of alloys can be analyzed by the same procedure, the single exception being the addition of alcohol to stabilize the color in some cases. The sensitivity of the method is such that analyses of alloys containing less than 0.005% copper are possible with reasonable accuracy, although for highest accuracy in this range an extraction method is undoubtedly preferable.

#### RECOMMENDATIONS

It is recommended that this method of copper determination in metallic alloys be adopted wherever possible to utilize its advantages of simplicity, speed, and low cost.

#### REFERENCES

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3. WETLESEN, C. U. and GRAN, G., *Svensk. Papperstich*, 55, 212 (1952).
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5. HAYWOOD, L. J. A. and SUTCLIFFE, P., *Analyst*, 81, 651 (1956).
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TABLE I  
COMPARATIVE COPPER VALUES IN TITANIUM BY THREE METHODS

<u>Sample</u>	<u>Type</u>	<u>Sample*</u> <u>Size</u>	<u>% Copper Found by</u>		
			<u>Cuprizone</u>	<u>Neo-Cuproine</u>	<u>Dithizone</u>
WA-5	10.5Co-4.5Fe	500 mg	.008	.0092	.0092
			.009	.0094	.0094
WA-7	2Cr-3Fe-2Mo	500 mg	.017	.014	.016
			.017	.018	.017
WA-44	2Sn	100 mg	.132	.133	.132
			.129	.136	.134

\*Sample size for cuprizone procedure.

TABLE II  
EFFECT OF ALCOHOL ON STABILITY OF TRANSMITTANCY (T)  
IN PRESENCE OF NICKEL

<u>Time After</u> <u>Reagent Addition</u> <u>(minutes)</u>	<u>Alcohol (% by volume)</u>		
	<u>2.5</u>	<u>22.5</u>	<u>45.0</u>
5	63.0	51.2	54.1
10	59.2	49.0	50.3
20	65.0	48.1	48.8
30	--	48.2	48.1
60	--	49.7	47.8

TABLE III

ANALYSIS OF STANDARD SAMPLES

<u>Sample</u>	<u>Type</u>	<u>Percent Copper</u>	
		<u>Certificate Value</u>	<u>Found by Cuprizone</u>
NBS-8h	Steel, carbon	.054	.056
NBS-30e	Steel, 1Cr-.1V	.094	.094
NBS-73a	Steel, 14Cr	.080	.071
NBS-101d	Steel, 9Ni-18Cr	.181	.180
NBS-126a	Steel, 36Ni	.092	.074
NBS-132a	Steel, 6W-5Mo-2V	.120	.111
NBS-153	Steel, 2W-8Mo-8Co	.099	.098
NBS-85a	Aluminum, 1.5Mg-2Cu	2.48	2.48
NBS-53c	Lead, 10Sb-5Sn	.214	.214
NBS-54b	Tin, 7Sb-5Sn	3.19	3.18
NBS-94b	Zinc, 4Al	1.01	1.01
NBS-171	Magnesium, 3Al-1Zn	.011	.011
FZ-292	Zirconium	.0067*	.0068
5Y-303	Zirconium	.0013*	.0015

*\*Average values at several laboratories using neo-cuproine method.*

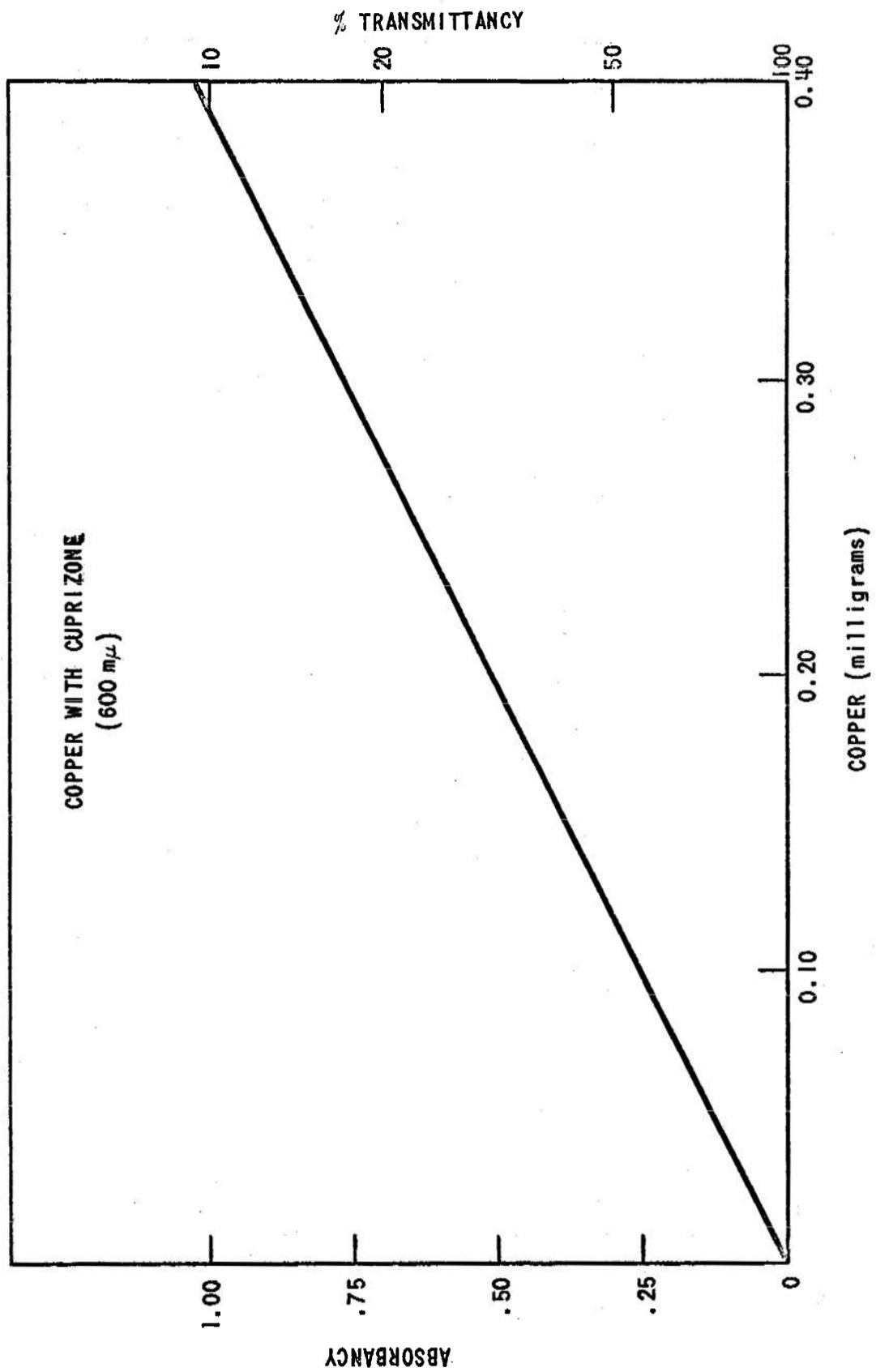


FIGURE 1

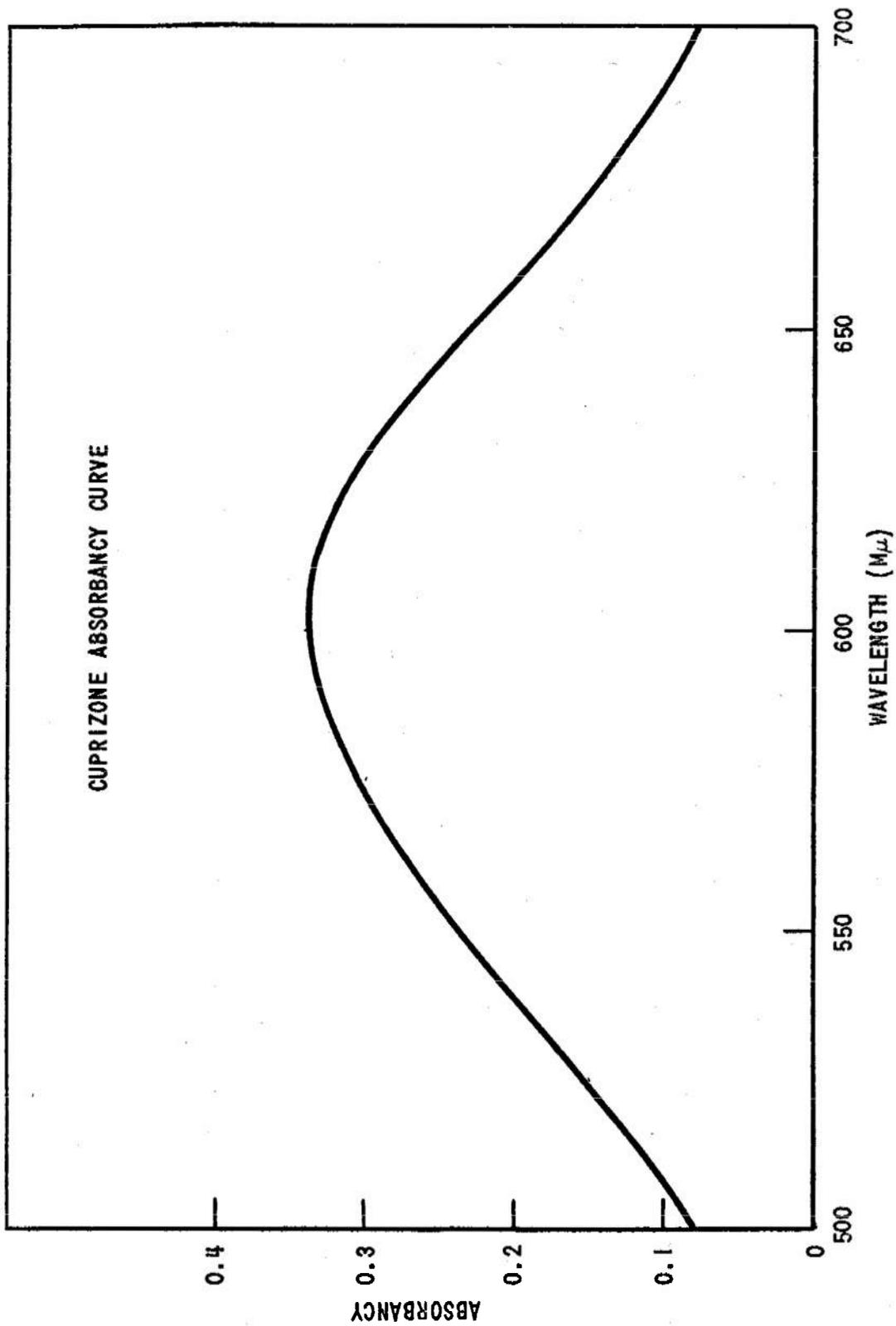


FIGURE 2

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