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SUBJECT: Spectrophotometric Determination of Copper in Yttrium Metal with Neocuproine

TO: See Distribution

FROM: J. C. White

ABSTRACT

The neocuproine colorimetric method was applied to the determination of copper in yttrium metal. From 5 to 80 μg of copper was determined in the presence of as much as 500 mg of yttrium with a coefficient of variation of two per cent. Copper was reduced to copper(I) with hydroxylamine and complexed with neocuproine (2,9-dimethyl-1,10-phenanthroline). The colored complex was extracted into chloroform and its absorbance measured, after dilution with ethanol, at 457 mμ.

DISCLAIMER

SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN YTTRIUM METAL WITH NEOCUPROINE

R. G. Ball

Purpose

To apply the neocuproine colorimetric method to the determination of copper in yttrium metal and to establish the precision and limits of the determination.

Introduction

A rapid and accurate method was needed for the determination of copper in yttrium metal and its alloys. Although many methods have been proposed for the colorimetric determination of copper, most of them require a number of preliminary separations. The methods proposed by Chilton,[2] and Haddock and Evers[4] for the determination of copper in various other metals by use of sodium diethyldithiocarbamate give good results. The use of a more specific reagent, however, would eliminate the addition of complexing agents to mask interfering ions and simplify the extraction procedure. Hoste[5] has reported that 2,2'-biquinoline (cuproine) is a specific reagent for copper; however, the extraction techniques necessary have been found to be cumbersome and somewhat inefficient.[9] In 1952 Smith and McCurdy[7] found that 2,9-dimethyl-1,10-phenanthroline (neocuproine) reacted specifically with copper and that the colored complex formed in isoamyl alcohol is slightly more sensitive than its cuproine counterpart. Other reagents such as 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline[1] (bathocuproine) and 1,5-diphenyl-carbohydrazide[8] have been recommended as providing increased sensitivity.

Gahler[3] has offered a simplified procedure based on the work of Smith and McCurdy in which the copper(I)-neocuproine complex is extracted into chloroform and the color is developed and measured in an ethyl alcohol medium. The major advantages of the method lie in the insolubility of chloroform in water and the greater density of the organic phase than the aqueous phase which simplifies the collection of the organic solvent. This work was undertaken to apply Gahler's method to the determination of copper in yttrium metal.

Reagents and Apparatus

Standard copper sulfate solution, 5 g of Cu per ml. Dissolve approximately 20 g of reagent grade $CuSO_4 \cdot 5H_2O$ in water and dilute to one liter. Standardize by a conventional electrogravimetric procedure.

Hydroxylamine hydrochloride solution, 100 g per liter. Dissolve 20 g of reagent grade $NH_2OH \cdot HCl$ in water and dilute to 200 ml.

Sodium citrate solution, 300 g per liter. Dissolve 75 g of reagent grade $Na_3C_6H_5O_7 \cdot 2H_2O$ in water and dilute to 250 ml.

Yttrium chloride solution, 100 mg Y per ml. Dissolve 12.70 g of reagent grade Y_2O_3 in 50 ml of 6 N HCl. Dilute to 100 ml with water.

Neocuproine solution, 0.1 per cent (w/v). Dissolve 0.1 g of reagent grade $(CH_3)_2\ C_{12}H_6N_2 \cdot 1/2\ H_2O$ in absolute Ethanol and dilute to 100 ml with the alcohol.

Ethanol, absolute, reagent grade.

Chloroform, reagent grade.

Spectrophotometer, Beckman DU.

Cells, Beckman, 1-cm.

Procedure

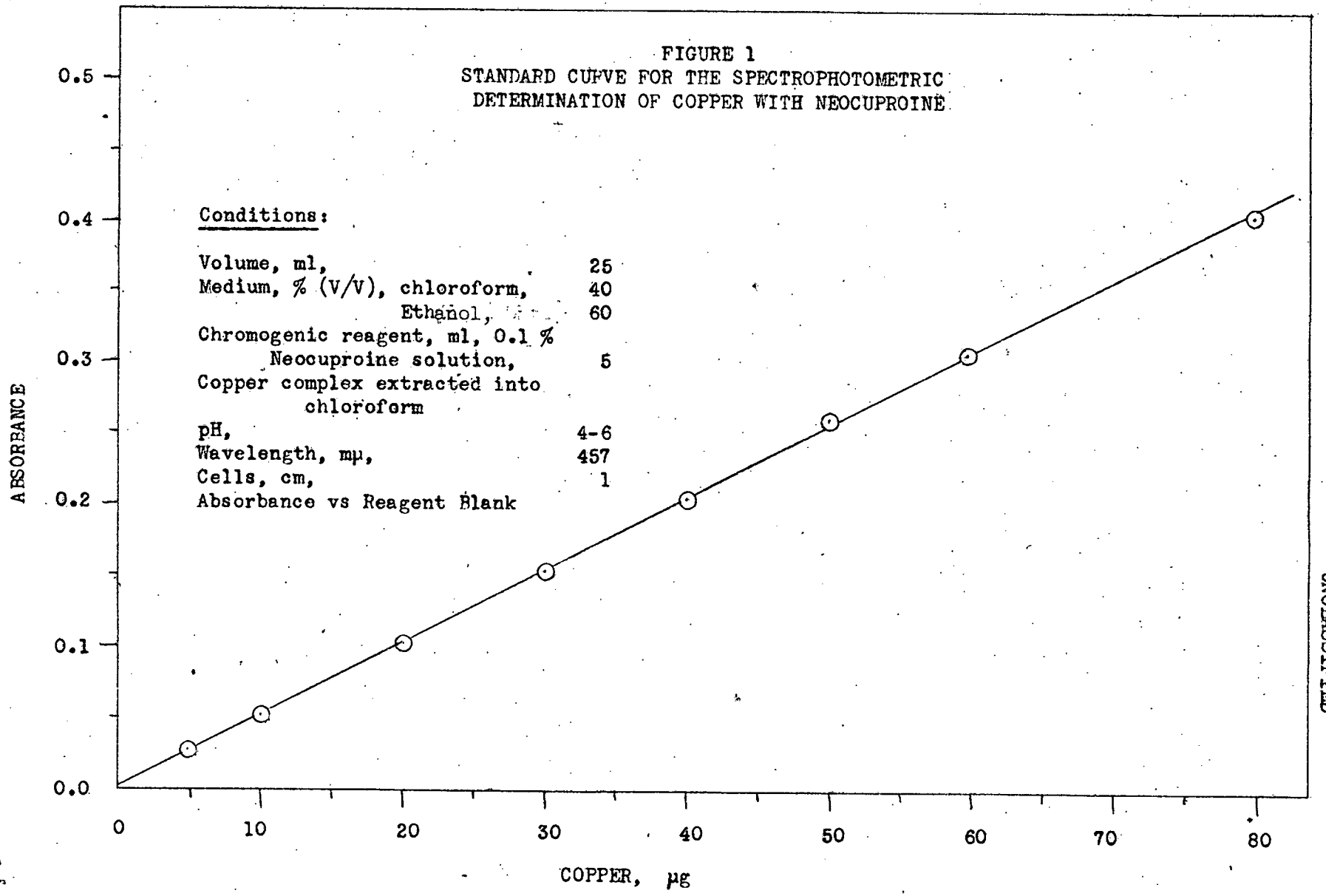
Dissolve a weighed sample in 6 N HCl. Add sufficient HNO_3 to oxidize any iron present; then evaporate the solution to a small volume. Transfer the sample to a volumetric flask and dilute to volume with water (if an aliquot is to be taken). Transfer an aliquot of 20 ml or less which contains 5 to 70 µg of Cu into a 125-ml separatory funnel. Add 5 ml of $NH_2OH \cdot HCl$ solution (100 g/l) and 10 ml of $Na_3C_6H_5O_7$ solution (300 g/l). Adjust the pH of the sample to 4 to 6 with NH_4OH, if necessary. Add 5 ml of the neocuproine reagent (0.1 per cent in ethanol) and 10 ml of chloroform. Shake the sample for approximately 30 seconds and allow the two phases to separate. Draw off the chloroform (bottom) phase into a 25-ml volumetric flask which contains 3 to 4 ml of absolute ethanol and dilute to volume with absolute ethanol. Measure the absorbance of the copper-neocuproine complex at 457 mµ in a 1-cm cell vs an extracted reagent blank. Determine copper by the standard curve technique.

Discussion

The results of the determination of copper in standard samples which contain 100 mg of yttrium are presented in Table I. From 5 to 80 µg of copper in a volume of 25 ml was determined in the presence of as much as 500 mg of yttrium. One extraction of the copper(I)-neocuproine complex into chloroform was found to give quantitative recovery of the copper. The average molar absorbance index was determined to be 8400 with a coefficient of variation of 2 per cent. This figure is in close agreement with the literature value of 8000.[8] A standard curve which graphically presents these data is shown in Figure 1.

Although yttrium is not considered an interference in the colorimetric determination of copper with neocuproine, it must be complexed with citrate or it will hydrolyze from solution and be carried into the chloroform phase, thus causing an error in the absorbance measurement. Therefore, it was necessary to establish the yttrium tolerance level for the copper determination and these data are shown in Table II. As much as 500 mg of yttrium(III)

FIGURE 1
STANDARD CURVE FOR THE SPECTROPHOTOMETRIC DETERMINATION OF COPPER WITH NEOCUPROINE



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can be present without causing any significant deviation in the copper determination; however, yttrium is precipitated during the extraction when 1 g is present even though an excess of citrate is added.

Data concerning the stability of the color of the copper-neocuproine complex are presented in Table III. The complex was found to be quite stable for a period of at least 4 days and probably longer. Maximum color formation occurred immediately upon addition of the copper complex to the ethanol medium. Reproducibility of the individual measurements from day to day were well within the precision of the method.

In order to demonstrate the feasibility of using the method, the recovery of copper standard additions in actual yttrium samples was determined. These data are shown in Table IV. Standard additions of copper ranging from 5 to 50 μg were recovered quantitatively in every case.

One of the most important advantages of this method for the determination of copper is the specificity of neocuproine for copper. Various authors have reported that no cation other than copper(I) forms a colored complex that is extractable.(3,6,7) However, certain anions cause interference--e.g., cyanide and sulfide. Sulfate, fluoride, perchlorate, phosphate, niobate, molybdate, tantalate, tungstate, and vanadate do not interfere.(3)

Summary

The neocuproine colorimetric method was successfully applied to the determination of copper in yttrium metal. From 5 to 80 μg of copper was determined in the presence of as much as 500 mg of yttrium. The molar absorbance index at 457 mμ was determined to be 8440 with a coefficient of variation of 2 per cent. The copper(I)-neocuproine complex was extracted into chloroform and the absorbance measured after dilution with ethanol. The colored complex thus extracted was found to be quite stable and free from interference of other ions.

Table I

Spectrophotometric Determination of Copper in Solutions of Yttrium with Neocuproine

Conditions:	Volume, ml	25
	Medium, % (v/v), chloroform	40
	ethanol	60
	Copper extracted into chloroform	
	Y(III) present prior to separation, mg	100
	pH	4 to 6
	Wavelength, mμ	457
	Cells, cm	1
	Absorbance measured vs a reagent blank	

Copper Taken, μg	Absorbance	Molar Absorbance Index
None	0.000*	-
4.93	.027	8720
9.86	.054	8720
19.7	.103	8300
29.6	.157	8460
39.4	.206	8290
49.3	.262	8460
59.2	.310	8320
78.9	.409	8230
Average,	$\bar{X}$ =	8400
Standard Deviation,	S =	200
Coefficient of Variation,	V =	2%

* vs Water.

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Table II

Yttrium(III) Tolerance Level in the Determination of Copper with Neocuproine

Conditions: Cf. Table I
Copper taken, µg 19.7

Yttrium(III) Present,* mg	Absorbance	Error, Per Cent
None	0.104	None
100	.103	None
500[a]	.105	< 2
1,000[b]	.119	* 16

* Prior to separation by extraction.
a Yttrium precipitated during extraction but redissolved.
b Yttrium precipitated and some was carried into the chloroform phase.

Table III

Stability of the Copper-Neocuproine Complex

Conditions: Cf. Table I

Copper Present, µg	Absorbance			
	Immediate	24 Hrs	48 Hrs	96 Hrs
None	0.000*	0.000	0.000	0.000
5	.027	.029	.030	.028
10	.054	.053	.054	.054
20	.103	.100	.100	.099
30	.157	.154	.154	.153
40	.206	.202	.204	.204
50	.262	.258	.258	.259
60	.310	.307	.305	.306

* vs Water.

Table IV

Recovery of Standard Additions of Copper to Yttrium Samples

Conditions: Cf. Table I
Yttrium sample tested, OR-9
Sample taken, mg 50

Copper Added, µg	Absorbance	Copper Found, µg	Error
4.93	0.027	4.93	0.0
9.86	.055	10.3	.4
29.6	.156	30.0	.4
39.4	.210	29.9	.5
49.3	.259	49.3	0.0

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Laboratory Procedure

SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN YTTRIUM METAL WITH NEOCUPROINE

Reference

Gahler, A. R., "Colorimetric Determination of Copper with Neo-Cuproine," Anal. Chem. 26, 577 (1954).

Procedure

1. Dissolve weighed sample in HCl. Add sufficient HNO_3 to oxidize the iron and evaporate solution to a small volume.

2. Transfer to volumetric flask and dilute to volume with water (if an aliquot is to be taken).

3. Transfer sample containing 5 to 200 µg Cu into a separatory funnel (up to 20 ml).

4. Add 5 ml of hydroxylamine hydrochloride solution (100 g/l).

5. Add 10 ml of sodium citrate solution (300 g/l).

6. Adjust pH to 4 to 6 with ammonium hydroxide (if necessary).

7. Add 5 ml of the neocuproine reagent (0.1 g/100 ml in absolute ethanol).

8. Add 10 ml of chloroform.

9. Shake about 30 seconds, allow the two phases to separate and draw off the chloroform phase into a 25-ml volumetric flask containing 3 to 4 ml of absolute ethanol.

10. Dilute to volume with absolute ethanol.

11. Measure the absorbance at 457 mµ in a 1-cm cell vs an extracted reagent blank.

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