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### Synergetic Extraction and Spectrophotometric Determination of Copper in Iron

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## NOTE

### Synergetic Extraction and Spectrophotometric Determination of Copper in Iron

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#### Abstract

A method is developed for synergetic extraction and subsequent spectrophotometric determination of Cu(II). The Cu(II)-benzoinoxime-pyridine complex extracted into chloroform has a characteristic green color measurable at 440 nm. The system conforms to Beer's law and is free from a large number of cation interferences. A systematic study of copper separation from metal ions, such as Fe, Au, Co, Ni, Cr, Mn, Zn, Pb, and U, has been investigated and is reported.

$\alpha$ -Benzoinoxime (1, 2) has been used for the photometric determination of milligram amounts of copper in molybdenum and ferrous alloys, but the proposed methods are time consuming because they involved too many operational steps and also require the absence of cobalt and nickel. It seemed desirable, therefore, to develop a rapid method for the analysis of microamounts of copper with sufficient selectivity and sensitivity. In the work described here, it was found that the extractability of the copper-benzoinoxime complex into the organic phase could be increased by the addition of pyridine. The synergetic solvent extraction of Cu(II), from an aqueous solution of pH 3.5, with equal volumes of 0.0017 *M* benzoinoxime and 2 *M* pyridine solutions in chloroform, may be employed for its separation from a number of associated metal ions. The extracted green species

is also well suited for the spectrophotometric determination of copper at 440 nm.

## EXPERIMENTAL

### Apparatus

A Zeiss spectrophotometer (German) and 1-cm quartz cells were used for absorbance measurements. pH was measured on a Radiometer pH meter (Philips, Precision type).

### Reagents

All chemicals used in this work were of guaranteed grade.

### Extracting Solution

A 0.0017-*M*  $\alpha$ -benzoinoxime solution was prepared by dissolving a weighed amount of the reagent in chloroform. Equal volumes of reagent solution and of 2 *M* pyridine solution in chloroform were used for extractions.

### Standard Solutions of Copper(II)

A stock solution (1 mg Cu/ml) was prepared by dissolving Cu(II) sulfate pentahydrate in water, adding a few drops of concentrated sulfuric acid, and diluting to volume; the solution was standardized against thiosulfate. Freshly made standard solutions of lower concentration were obtained by appropriate dilution as required.

### Recommended General Procedure

An aliquot of solution containing about 40  $\mu$ g of Cu(II) was taken and adjusted to pH 3.5 in a 25-ml volume. The solution was then introduced into a separatory funnel and shaken with 10 ml of extracting solution for 15 sec. After separating the two phases, the green complex in the organic phase was measured at 440 nm against the reagent blank prepared in the same manner. The amount of copper was then computed from the calibration curve.

## RESULTS AND DISCUSSION

## Spectral Characteristics

The absorption spectrum of the Cu(II)-benzoinoxime complex extracted with pyridine at pH 3.5 is shown in Fig. 1. In the absence of pyridine, the complex did not extract. Addition of pyridine, however, ensures quantitative and rapid extraction of copper. Madera et al. (1, 2) have recommended a 5 to 7 min shaking period for quantitative extraction of the Cu(II)-benzoinoxime complex, but in the presence of pyridine only 15 sec of equilibration is adequate for complete extraction and development of the color.

The spectrum of the extracted complex has a maximum absorbance at 440 nm, and the molar absorptivity of the complex in chloroform is  $5.5 \times 10^2$  at this wavelength.

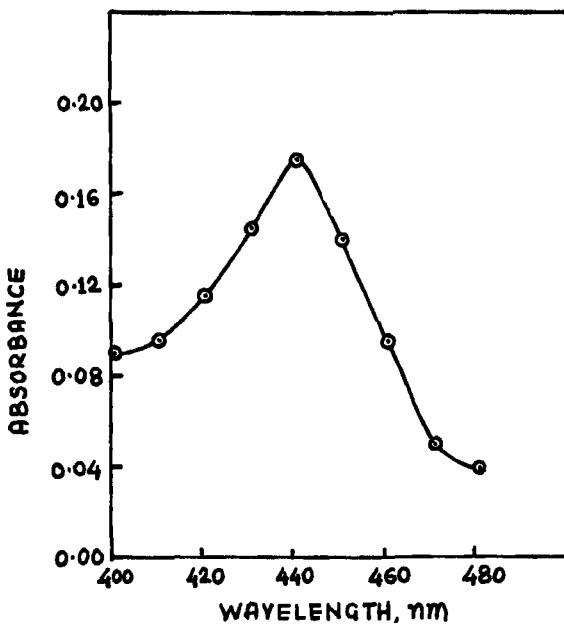


FIG. 1. Absorption spectra: 0.0017 M  $\alpha$ -benzoinoxime, 2 M pyridine, Cu(II) = 40  $\mu$ g.

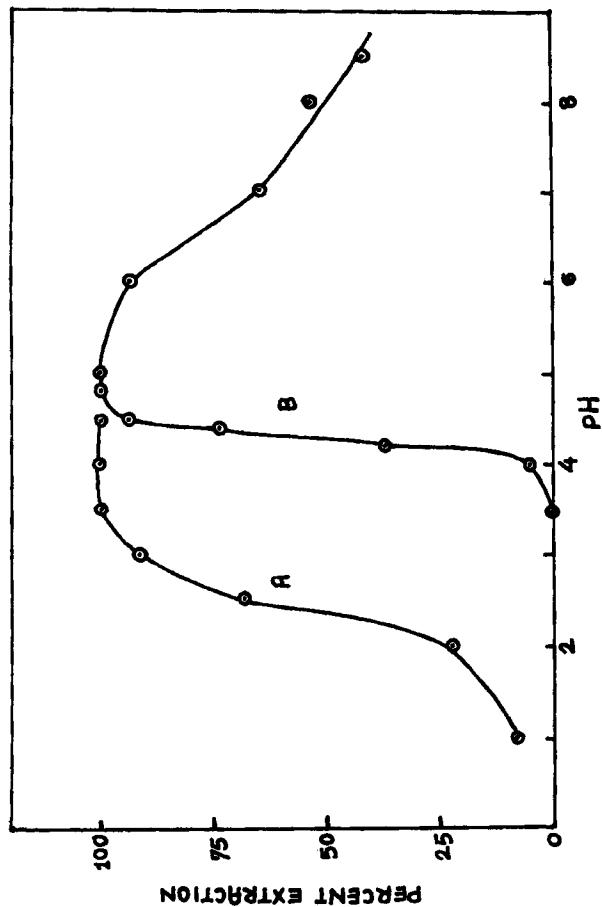


FIG. 2. Extraction of Cu(II)-benzoinoxime complex with pyridine (A) and without pyridine (B) as a function of pH.

### Effect of pH

The extraction of copper was studied at pH 1 to 8 (Fig. 2). In the absence of pyridine, extraction of the Cu(II)-benzoinoxime commences at pH 4, becomes quantitative at pH 5, and then decreases. In the presence of pyridine, however, extraction commences at pH 1 and becomes quantitative at pH 3.5. (After extraction the pH of the aqueous extract was found to be approximately 7.4.) Pyridine thus shows a synergistic effect on the extraction of Cu(II)-benzoinoxime complex from acidic solution.

### Calibration Curve

The Cu(II)-benzoinoxime-pyridine system conforms to Beer's law over the concentration range of 20 to 100  $\mu\text{g}$  of copper per 10 ml of the organic phase at 440 nm (Fig. 3).

### Stability of the Color

As per the general procedure, the absorbance of the Cu(II)-benzoinoxime-pyridine complex was measured at elapsed intervals of 0, 0.25, 0.5,

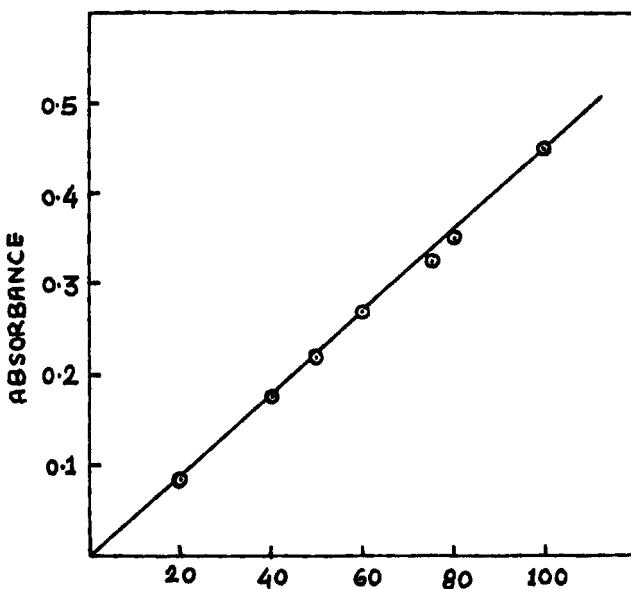


FIG. 3. Calibration curve at 440 nm.

1, and 2 hr. The absorbance was stable for 30 min. Hence the complex should be measured within 30 min of the extraction.

### **Effect of Cations**

The interference study showed that a few cations, namely Sn(II), Au(III), Fe(III), and Ru(III), interfere seriously in the determination of copper by the recommended procedure. There was no interference from 5 mg of the following metallic ions: Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Pb(II), Bi(III), Ce(III), Cr(III), Te(IV), Th(IV), V(V), Mo(VI), and U(VI). The system could also tolerate 6 mg of Pd(II), 2 mg of W(VI), and 4 mg of Re(VII), but complexing anions interfere severely and must be absent.

### **Reproducibility and Sensitivity**

In a test of reproducibility of the method, 10 samples each containing 40  $\mu$ g of copper were prepared according to the standard procedure and measured at 440 nm. The average absorbance was 0.175 with a standard deviation of 0.005 absorbance unit. As little as 0.023  $\mu$ g of Cu per milliliter can be detected, which indicates the high sensitivity of the method.

## **SEPARATION STUDIES OF COPPER**

### **Separation of Copper from Fe(III) and Au(III)**

Fe(III) and Au(III) interfere in the extraction and determination of copper by the proposed method. However, separation of these two elements could be accomplished by prior extraction with 4-methyl-2-pentanol from 6 *M* hydrochloric acid solution (3, 4). Under these conditions copper is not extracted even in traces. The aqueous extract is adjusted to pH 3.5 and then copper is extracted as described in the recommended procedure. Some results are summarized in Table 1. The recovery of copper as well as of iron and gold from binary mixtures is almost quantitative (> 99.8%).

### **Separation of Copper from Cobalt, Nickel, Chromium, Manganese, Zinc, Lead, and Uranium**

The high distribution coefficient of Cu(II) on extraction with a mixture of chloroform solution of  $\alpha$ -benzoinoxime and pyridine at pH 3.5 may be

used for the separation (and subsequent photometric determination) of copper from metal ions such as Co, Ni, Cr, Mn, Zn, Pb, and U. The results of separation are shown in Table 1. The recovery of copper is more than 99.8%. The recovery of separated metal ions in the aqueous extract (estimated by standard procedure) is also almost quantitative (98.5 to 99.5%).

### PRACTICAL APPLICATIONS

The proposed method was applied to the separation and determination of copper in steel and brass. The results obtained are shown in Table 2.

TABLE 1

Separation of Copper from Synthetic Mixtures. Copper(II) = 40  $\mu$ g. Extracting solution = equal volumes of 0.0017 M  $\alpha$ -benzoinoxime and 2 M pyridine

Ions added	Percentage recovery of copper from duplicate analysis
Fe(III), 5 mg	99.8
Co(II), 1 mg	100.0
Ni(II), 1 mg	100.0
Cr(III), 1 mg	100.0
Mn(II), 5 mg	100.0
Zn(II), 5 mg	100.0
Pb(II), 5 mg	100.0
U(VI), 1 mg	100.0
Au(III), 200 $\mu$ g	100.0
Fe (5 mg) + Au (200 $\mu$ g)	99.8
Fe (2 mg) + Au (100 $\mu$ g)	100.0
1 mg each of Ni, Co, Cr, Mn, Zn, Pb, and U	100.0

TABLE 2  
Determination of Copper in Standard Samples

Sample	Composition	Copper	
		Declared %	Found %
33 d (Bureau of Analysed Samples, U.K.)	C 2.30, Si 1.63, Mn 0.63, Ni, 2.38, Cr 0.52, Mo 0.48	1.54	1.53, 1.53
Brass	Cu + Zn	63.20	63.19, 63.19

## ANALYTICAL PROCEDURE

### Determination of Copper in Steels

Dissolve a known weight ( $\sim 0.5$  g) of alloy steel in 9 ml of concentrated sulfuric acid and 50 ml of water, add 10 ml of concentrated nitric acid, heat almost to dryness, and then dilute to 100 ml. Take an aliquot of this solution in a separatory funnel and add hydrochloric acid to give a concentration of 6 M. Shake with 10 ml of 100% 4-methyl-2-pentanol for 1 min to remove iron. Under these conditions copper is not extracted (3). Evaporate the aqueous phase to 5 ml, dilute to 20 ml with distilled water, adjust the pH to 3.5, and extract and determine the copper as described earlier.

### Determination of Copper in Brass

Dissolve about 1.035 g of brass in nitric acid, evaporate to dryness, extract with 0.5 M sulfuric acid, and dilute to 250 ml. An aliquot portion of this solution is analyzed by the general procedure. The results are reported in Table 2.

Reproducibility of results was satisfactory on all samples analyzed, and the results were also found to be accurate within  $\pm 0.5\%$ .

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