

### Short Communication

## Spectrophotometric determination of copper in alloys with di-2-pyridylglyoxal-2-quinolyhydrazone

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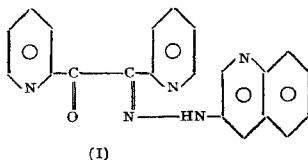
### Abstract

Di-2-pyridylglyoxal-2-quinolyhydrazone reacts with Cu(II) to form red coloured complex suitable for spectrophotometric determination of metal. The complex contains metal and ligand in 1:2 molar ratio and molar absorptivity is  $3.5 \times 10^4 \text{ l. mole}^{-1} \text{ cm}^{-1}$ . Copper has also been determined in several alloys.

**Key words:** Di-2-pyridylglyoxal-2-quinolyhydrazone (PQH), copper, spectrophotometric determination, alloys.

### 1. Introduction

Hydrazones, nitrogen-containing heterocyclic hydrazones in particular, have attracted much attention as analytical reagents because of high sensitivity, selectivity, easy synthesis and good yield. Their properties and use as analytical reagents have been described by many workers<sup>1-6</sup>. Synthesis of di-2-pyridylglyoxal-2-quinolyhydrazone (PQH, I) and its application in micro determination of copper is described in this paper. Copper has also been analysed in several alloys.



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## 2. Experimental

### 2.1. Apparatus

Spectrophotometric measurements were made with a Unicam SP 600 spectrophotometer and the pH measurements were made with a Beckman expandomatic SS-2 pH meter.

### 2.2. Reagents

The reagent was synthesised as follows. An ethanolic solution containing equimolar amounts of 2-hydrazinoquinoline and di-2-pyridylglyoxal was refluxed for four hours. Evaporation of solvent under reduced pressure and crystallization of residue from aqueous methanol yielded the reagent PQH, m.p. 165° (Found : C, 70.1; H, 4.18; N, 19.01; Calcd : C, 71.3; H, 4.24; N, 19.82%). The reagent solution was prepared in absolute ethanol by dissolving an appropriate amount and stored in amber glass bottles. Such solutions are stable for several weeks.

A stock solution of copper(II) was prepared by dissolving an appropriate amount of copper sulphate pentahydrate (Anal. A.R., B.D.H.) double distilled water, acidified with a few drops of dilute sulphuric acid. The solution was standardised volumetrically.

### 2.3. Procedure

To an aliquot containing 3.1 to 18.9  $\mu\text{g}$  of copper ion add an ethanolic solution of (0.0001 M) of PQH (2 ml). Adjust the pH range between 7.5 and 9.6, raise the volume to 10.0 ml, keeping 50% (v/v) ethanol water medium and measure the absorbance at 500 nm against the reagent blank. Spectra of the complex is shown in Fig. 1. The reagent does not show any absorbance in this region. The amount of copper present can be evaluated from the calibration curve drawn under identical conditions.

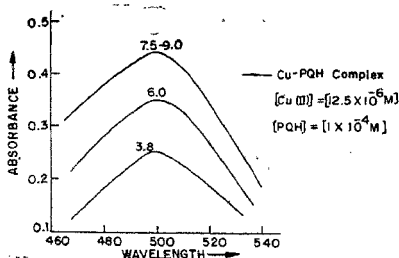


FIG. 1. Absorption spectra of copper complex at different pHs.

#### 2.4. Characteristics of complex

The absorption maximum of the complex occurs at 500 nm, in the pH range 7.5–9.6, maintaining 50% (v/v) ethanolic medium. In solution containing metal and ligand, turbidity appears when alcohol to water ratio is less than 1:3. More than 50% ethanol-water ratio did not enhance the colour markedly and 1:1 ethanol-water ratio was therefore maintained in subsequent studies. The absorbance of the complex was studied as a function of mole ratio of PQH to Cu(II). At least three fold excess of reagent is necessary to obtain constant and reproducible absorbance. Beer's law was obeyed up to 2.27 ppm and optimum concentration range as determined by Ringbom plot was 0.31–1.89 ppm. The sensitivity of the colour reaction in terms of Sandell's definition is 0.0018  $\mu\text{g}$  of Cu/cm<sup>2</sup> with molar absorptivity  $3.5 \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$ . The composition of the complex as determined by Job's method of continuous variation and mole ratio method showed that metal to ligand ratio is 1:2.

#### 2.5. Effect of diverse ions

In determination of 0.635  $\mu\text{g/ml}$  of Cu(II), the following ions do not interfere: Nitrate bromide (2000 ppm); fluoride, acetate, nitrite (1000 ppm); sulphite, iodide (500 ppm); nitrate, phosphate, thiocyanate (100 ppm); Ca(II), Sr(II), Ba(II), Mg(II) (500 ppm); Pb(II), Mo(VI), W(VI), Mn(II) (200 ppm); Sn(II), Sb(III), Al(III) (40 ppm); Ru(III), Rh(III), Os(VIII), Ir(III), Pt(IV) (20 ppm); however, EDTA, CN, thiourea, Fe(II), Co(II), Ni(II) and Pd(II) interfere seriously. In the case of Co(II), Ni(II) and Pd(II), the addition of a small amount of the foreign ion causes a marked increase in absorbance.

#### 2.6. Determination of copper in alloys

Copper in several alloys was separated by using the method of Patil and Shinde<sup>7</sup>. 5% solution of tri-*n*-octylamine (TOA) in benzene extracts copper quantitatively from 0.6 M HCl solution and after stripping copper from aqueous phase, it has been determined by recommended procedure. The results are summarised in Table I.

Table I

Determination of copper in alloys

Alloy	Composition %	Copper %	
		Required	Found
brass	Zn 31.9, Pb 1.45 Sn 1.37 and Fe 0.23	65.0	64.6
tin metal	Zn 2.57, Sn 9.61 Pb 0.35, Fe 0.06	87.1	87.3
CS 181/2	Fe 0.4, Ni 2.0, Mn 0.2 Mg 1.5, Si 0.27	4.0	3.8

Table II

## Sensitivities of the colour reactions of the various reagents for copper

Reagent	S. Sensitivity ( $\mu\text{g}/\text{cm}^2$ )	Ref.
Diethyldithiocarbamate	0.004/436 nm	8
1-(2-pyridylazo) naphthol/ $\text{CHCl}_3$	0.0014/530 nm	9
Neocuproine	0.0080/457 nm	10
Quinoline-2-aldehyde-2-quinoly- hydrazone	0.0010/545 nm	11
Thiothenoyl trifluoro acetone	0.0015/400 nm	12
Salicylaldehyde hydrazone	0.003/400 nm	13
Biacetyl bis(4-phenyl-3-thio- semicarbazone)	0.0077/530 nm	14

## 3. Conclusion

These studies show that di-2-pyridylglyoxal-2-quinolyhydrazone can be successfully used for the determination of copper(II). The procedure is simple and less time-consuming. Comparison of the sensitivities of the colour reaction with some other reagents has been made in Table II.

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