

NOTE

Extractive Spectrophotometric Determination of Copper with *p*-Methylisonitrosoacetophenonehydrazone

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A simple and rapid extractive spectrophotometric method for the determination of Cu(II) is studied. The complex formed between Cu(II) and *p*-methylisonitrosoacetophenonehydrazone is extracted into chloroform from aqueous solution of pH 7.0. The extracted species has an absorption maximum at 510 nm and obeys Beer's law over a range of 0.1–1.0 $\mu\text{g mL}^{-1}$ of Cu(II); the molar absorptivity being $6.28 \times 10^3 \text{ L mole}^{-1} \text{ cm}^{-1}$. Interference from foreign ions has also been studied.

Spectrophotometric methods coupled with a separation technique like solvent extraction can be advantageously applied for the determination of metals at low concentration. Hydrazoximes^{1,2} have been used for the extraction and spectrophotometric determination of metals at trace levels. *p*-Methylisonitrosoacetophenonehydrazone (HIMAPH) forms coloured complex with Cu(II). The present work describes a method for the extractive spectrophotometric determination of Cu(II) in aqueous solution using HIMAPH as a reagent and chloroform as the extracting solvent.

A Beckman DU-2 spectrophotometer with optically matched quartz cells of 1 cm optical path was used for absorbance measurements and pH values were determined with an ELICO-LI 120 pH meter.

All chemicals and solvents used were of analytical reagent grade. A stock solution of copper having a strength of 1 mg/mL was prepared by dissolving copper(II) sulphate (AR) in sulphuric acid and standardised by the benzoin-oxime method³. Working solution of copper was prepared using double distilled water. The reagent HIMAPH was synthesized as the procedure reported by Day⁴ for the preparation of phenylglyoxyhydrazoxime. Standard solutions of diverse ions were prepared from their chloride, nitrate or sulphate; or from sodium, potassium or ammonium salts using double distilled water.

Procedure

An aliquot of copper solution containing 0.1–30 $\mu\text{g mL}^{-1}$ of copper was treated with 2 mL of 0.5 M sodium acetate and 1 mL of 15% ethanolic solution of HIMAPH and pH of the solution was adjusted to desired value using dilute solutions of NH_4OH and/or HNO_3 . The resulting mixture was equilibrated for 2 min with 10 mL of chloroform. The organic layer was separated and its

absorbance was measured at 510 nm against a reagent blank prepared under identical conditions.

Amounts of copper in unknown solutions were determined from the standard calibration curve. To study the interference, the respective foreign ions were added to the aqueous phase before extraction and pH adjustment.

Copper can be quantitatively extracted by HIMAPH into chloroform from an aqueous solution of pH 6.0–7.2. The organic solvents can be arranged in the following order on the basis of their extraction coefficient values:

chloroform > diethyl ether > isobutanol > benzene > toluene > *n*-butanol
> carbon tetrachloride > ethyl methyl ketone = ethyl acetate > nitrobenzene.

The absorption spectrum of Cu : HIMAPH complex in chloroform shows an absorption maximum around 510 nm and the Beer's law is obeyed over the concentration range 0.1–10 $\mu\text{g mL}^{-1}$ of copper. Molar absorptivity of the extracted species is $6.28 \times 10^3 \text{ L mole}^{-1} \text{ cm}^{-1}$. One mL of 1% ethanolic solution of HIMAPH was adequate for complete extraction of 50 μg of copper and the colour of the complex was found to remain stable for 54 h at room temperature.

Effect of foreign ions: Copper (50 μg) was determined in the presence of various ions. The following ions, when present in amounts indicated do not interfere in the spectrophotometric determination of copper: 10 mg of Li(I), Na(I), K(I), Sr(II), Mn(II); 5 mg each of Ba(II), Ca(II), Mg(II), Pb(II), Al(III), Bi(III), As(III), V(V), Mo(VI), W(VI); 10 mg each of chloride, bromide, iodide, fluoride, chlorate, bromate, iodate, sulphate, thiosulphate, persulphate, sulphite, nitrate, nitrite, cyanate, acetate, pyrophosphate, perchlorate, thiourea, thiocyanate. The interference by the ions Ag(I), Pd(II), Fe(III), Zn(II), Zr(IV), Th(IV), Ce(IV), U(VI), cyanide, citrate, tartrate, oxalate and EDTA can be removed using appropriate masking agents as shown in Table-1.

TABLE-1
MASKING AGENTS REQUIRED TO SUPPRESS THE INTERFERENCE
OF FOREIGN IONS

Interfering Ions	Masking agent added
Ag(I)	Potassium iodide
Pd(II)	Thiourea
Zn(II)	Sodium fluoride
Fe(III)	Thiourea
Zr(IV), Th(IV), Ce(IV), U(VI)	Sodium fluoride
Cyanide	Boiling with HNO_3 and formaldehyde
Citrate	Sodium molybdate
Tartrate	Sodium molybdate
Oxalate	Sodium molybdate
EDTA	Boiling with HNO_3

The composition of the extracted species was found to be 1:2 (Cu : HIMAPH) by Job's continuous variation method and mole ratio method.

Thus the present method proved to be very rapid and simple and provides an excellent recovery of copper in presence of most of the common ions.

The method was found to be quite suitable for the determination of copper in alloys such as brass and cupro-nickel. The results of the analysis were found to be in good agreement with those obtained by diethyldithiocarbamate method. The results are presented in Table-2.

TABLE-2
ANALYSIS OF ALLOY SAMPLES

Sr. No.	Alloy	Copper Found (%)	
		Present method Average	Diethyldithiocarbamate method Average
1.	Brass	61.01	51.03
2.	Cupro-nickel	74.87	74.80

Results are the average of three independent determinations.

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(Received: 17 November 1998; Accepted: 1 June 1999)

AJC-1741