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DEVELOPMENT OF METHOD FOR EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF Cu (II) WITH OF 2-[2-(4-CHLORO BENZOTHIOZOLE) IMINO]-5- NITRO PHENOL AS AN ANALYTICALREAGENT

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ABSTRACT

A spectrophotometric method has been developed for the determination of Cu (II) using 2-[2-(4-Chloro Benzothiozole) imino]-5- nitro phenol as an extractive reagent. The reagent forms a coloured complex, which has been quantitatively extracted into n-butanol at pH 9.4. The method obeys Beer's law over a range from 1 to 10 ppm. The Molar absorptivity and Sandell's sensitivity calculated were 0.1404 × 10^4 L mol^{-1} cm^{-1} and 0.1778 μg/cm^2 respectively. The proposed method is very sensitive and selective. The method has been successfully applied to synthetic and commercial samples.

Keywords: Copper, Spectrophotometric determination, n-butanol, 2-[2-(4-Chloro Benzothiozole) imino]-5- nitro phenol

INTRODUCTION

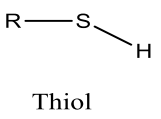
Copper is an important micro-nutrient for all living forms. As a natural element in the earth's crust, copper exists in most of the world's surface water and groundwater, although the actual concentration of copper in natural water varies geographically. Drinking water can comprise 20-25% of dietary copper [1]. The World Health Organization recommends a minimal acceptable intake of approximately1.3mg/day [2]. Copper play a crucial role in the functioning of organs and metabolic processes in human beings [3, 4]. In addition to being an essential nutrient for humans, copper is vital for the health of animals and plants, plays an important role in agriculture. Copper(II) ions are widely distributed in biological systems, a significant amount of research has centered on the search for relatively simple copper(II)

complexes which may display some of the properties of the metalloproteins [5]. In both humans and animals, the major target organs for copper deficiency are the blood and hematopoietic system, the cardiovascular system, connective tissue and bone, the nervous system and the immune system [6-8]. The excess concentration is harmful to human beings, causes metallic taste, nausea, vomiting, epi-gastric burning and diarrhoea. The accumulation of copper in the human liver and animals is a characteristic of Wilson's disease which produces neurological and psychiatric defects [9-11]. Copper at only very low level is an essential element and is toxic at higher levels in plants. Several compounds are known to react with the metal ions to give coloured complexes and have been employed for the quantitative extraction and spectrophotometric determination of metals at trace levels. A number of reagents such as oxime[12-15], hydrazone,[16] semicarbazone,[17-18] thiosemicarbazon[19-21]etc have been used for the determination of copper. However these methods suffer from limitations such as requirement of masking agents[12,22] interference of some ions[23-25] equillibrium time[25] for superior in sensitivity and selectivity to those reported in the literature, is developed for the extractive spectrophotometric determination of copper with CBZTINP . A close literature survey indicates that CBZTINP has far not been employed for analytical studies. The proposed method is free from limitations. The present investigation a novel method for the extractive spectrophotometric determination of copper, which is simple, sensitive, rapid and precise. It will be applied for the determination of copper at trace level in synthetic mixtures and alloys.

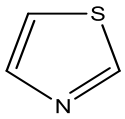
EXPERIMENTAL

The reagent2-[2-(4-Chloro Benzothiozole) imino]-5- nitro phenol was prepared as reported in the literature. The stock solution of Copper (II) was prepared by dissolving $CuSO_4.5H_2O$ in double distilled water containing dilute sulphuric acid, which was diluted to the desired volume with double distilled water and standardized by diethyldithiocarbamate method[26]. Absorbance and pH measurement were carried out on a Shimadzu UV- Visible 2100 spectrophotometer with 1cm quartz cells and digital pH meter with combined glass electrode respectively.

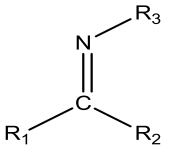
REACTION



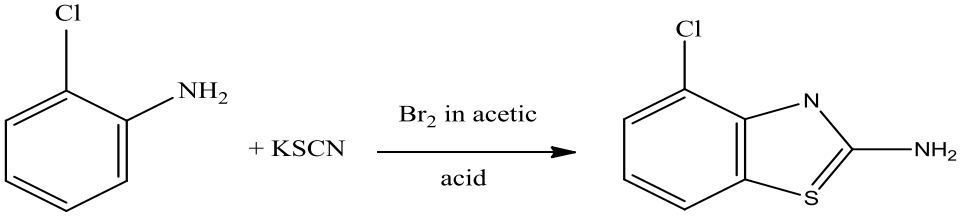
Thiol



Thiazole

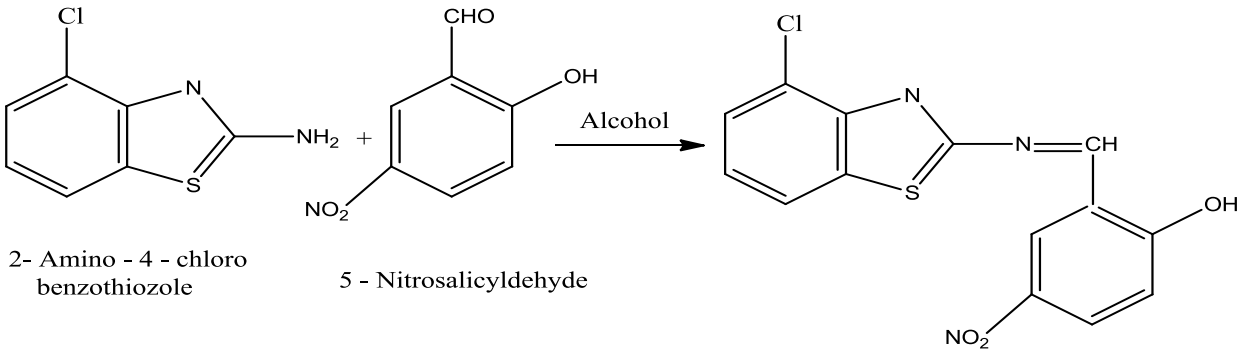


Schiff base



2 - Chloroaniline

2- Amino - 4 - chloro benzothiozole



2- Amino - 4 - chloro benzothiozole

5 - Nitrosalicyldehyde

2 - [2 - (4 - Chlorobenzothiozole) imino] - - nitrophenol

Procedure for the extraction

1.0 ml of aqueous solution containing 0.1 mg of copper metal and 1 ml of reagent were mixed in 50 ml beaker. The pH of the solution adjusted to 9.4 keeping the volume 10 ml. The solution was transferred to 100 ml separatory funnel. The beaker was washed twice with n-butanol and transferred to the same funnel. The two phases were shaken for two minutes and allowed to separate. The organic phase was collected in 10 ml measuring flask and made up to the mark with organic solvent, if required.

The amount of copper present in the organic phase determined quantitatively by spectrophotometric method by taking absorbance at 370 nm and in aqueous phase was determined by diethyldithiocarbamate method.

RESULTS AND DISCUSSION

The reagent CBZTINP forms light Green coloured complex with Cu (II), which was extracted into organic phase. The extraction of Cu(II) forms aqueous phase by CBZTINP in n-butanol is studied over a wide range experimental condition. The results of various studies are discussed below.

Extraction as a function of pH

The extraction of copper with2- [2- (4- Chloro Benzothiozole) imino] -5 – Nitro phenol has been studied over the P^H range 1- 10 and was observed that percentage extraction of Cu (II) is maximum at P^H 9.4.(Fig 1)

Absorption spectrum

The absorption spectrum of Cu(II) : 2- [2- (4- Chloro Benzothiozole) imino] -5 – Nitro phenol in n-butanol shows the maximum absorption at 370 nm. The absorption due to reagent at this wavelength is nearly negligible. Hence the absorption measurements were carried out at 370 nm.(Fig.2)

Influence of diluents

The suitability of diluents was investigated using organic solvents such as chloroform, ethyl acetate, ethyl/methyl ketone, toluene, n-butanol, carbon tetra chloride. The extraction of Cu (II) was quantitative with CBZTINP in n-butanol. Hence, n-butanol was used for further extraction studies as it gave better and quicker phase separation.

Effect of salting out agent

The presence of 0.1M salts of various alkali and alkaline metals does not show any effect over the absorbance value of Cu (II): 2-[2-(4-Chloro Benzothiozole) imino]-5- nitro phenol complex extract. Therefore, no salting out agent was required during the extraction.

Effect of reagent concentration

Various volumes of 0.1% reagent solution were added to the sample solution containing 50µg of copper at respective P^H values. The absorbance remained nearly constant when the volume of the reagent solution used was more than 1 ml. Therefore, 1 ml of 0.1 % reagent was chosen for the quantitative determination of the metal.

Effect of equilibrium time and stability of the complex

The study of change in absorbance with variation in equilibrium time extraction of the complex into organic solvent shows that equilibrium time of 60 sec. are sufficient for the quantitative extraction of copper. The study of stability of colour of the Cu (II): CBZTINP complex with respect to time shows that the absorbance due to extracted species is stable up to 48 hours, after which slight decrease in absorbance is observed. Throughout the experimental work, for practical convenience, the measurements have been carried out within one hour of extraction of copper.

Calibration plot

A calibration plot of absorbance against varying copper concentration and fixed CBZTINP concentration gives linear and reproducible graph in the concentration range 1 to 10 ppm of copper.This shows that the Beer's law is obeyed in this range.The Molar absorptivity and Sandell sensitivity were calculated to be is 0.1404×10^4L mol^{-1} $cm^{-1}$and 0.1778 µg /cm^{-2} respectively.

Nature of extracted species

The composition of extracted species has been determined by Job's continuous variation method(Fig.3), Slope ratio method and Mole ratio method(fig.4). It shows that the composition of Cu (II): CBZTINP complex is 1:2.

Effect of divalent ions and foreign ions

The effect of other ions present in various amount indicated no interference in the spectrophotometric determination of 50 µg of copper. The ions which show interference in the spectrophotometric determination of copper were overcome by using appropriate masking agents (Table 2).

Precision and Accuracy

The precision and accuracy of the developed spectrophotometric method has been studied by analyzing five solutions each containing 50 µg of copper in the aqueous phase. The average of five determinations was 50.04 and variation from mean at 95% confidence limit was ± 0.1319.

Applications

The proposed method was successfully applied for the determination of copper from various alloys and synthetic mixtures. The results found to be in good agreement with those obtained by the standard known method. (Table 1).

CONCLUSION

The proposed method is highly sensitive and selective than the other reported methods for extractive spectrophotometric determination of microgram amounts of copper. It offers advantages like reliability and reproducibility in addition to its simplicity, instant colour development and suffers from less interference. It has been successfully applied to the determination of copper at trace level in synthetic mixtures and alloys.

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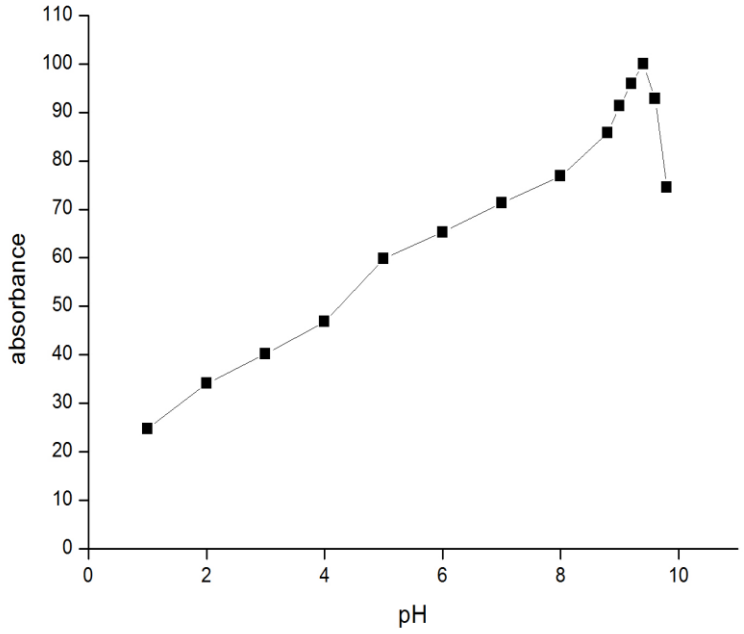

Fig. 1. Effect of P_H on the % extraction of Cu (II): CBZTINP

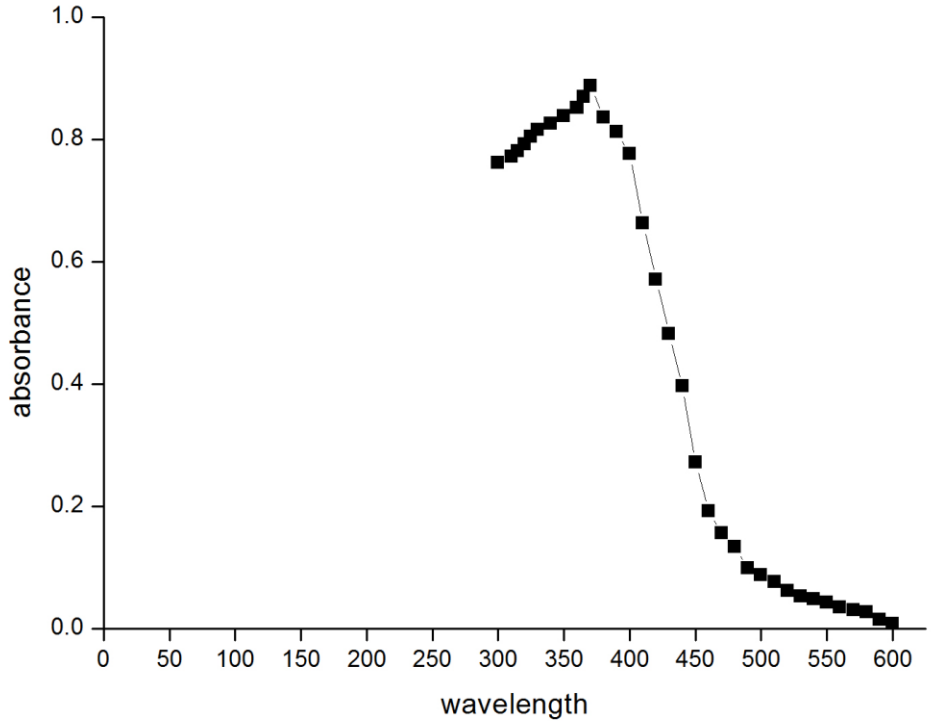

Fig.2. Absorption spectrum of Cu (II): CBZTINP

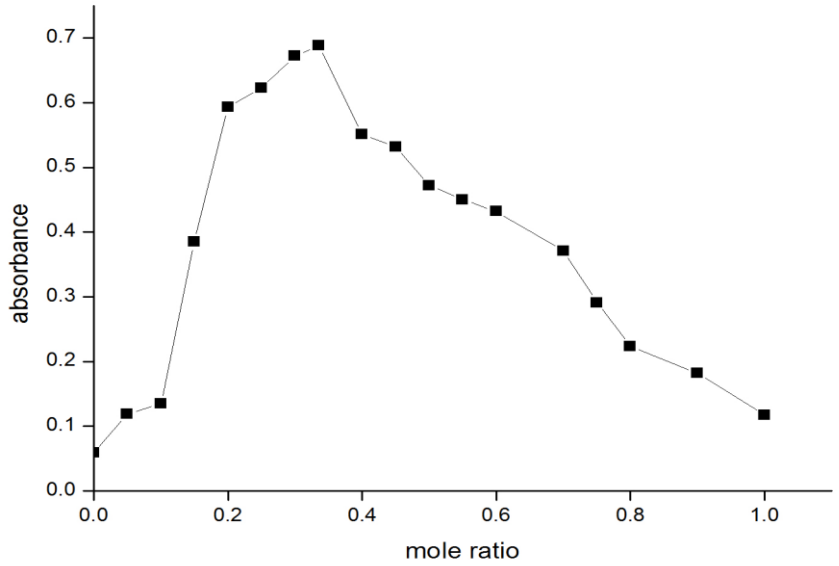

Fig. 3.Job's continuous variation for Cu (II): CBZTINP

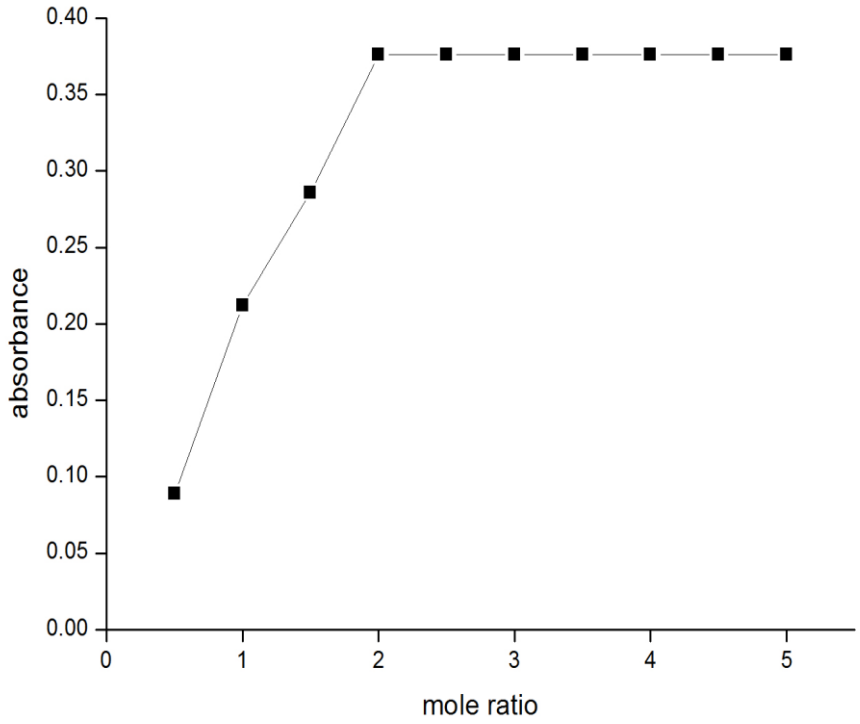

Fig.4. Mole ratio of Cu (II): CBZTINP

Table 1: Determination of Cu (II) Using CBZTINP from different samples

Sr.No.	Sample	Amount of Cu (II)	
		Standard method	**Present method**
1	**Alloys** Brass Monel metal	 60.0%% 63.0 %	 59.94% 62.58 %
2	**Capsule/ tablets** supradyn Multivitamin capsule	 3.39mg 5.9 mg	 3.27 mg 5.83 mg
3	Synthetic mixture Cu (55) + Zn (45) Cu(100)+ Zn(100)+ Cd(100)	 55 µg 100 µg	 54.89 µg 9.97 µg

Table 2: Effect of divalent ions and foreign ions

Sr.No.	**Ion**	**Amount added In mg**	**Absorbance**
1	---	---	0.443
2	Li+	11.0	0.443
3	Na+	12.0	0.443
4	K+	9.0	0.443
5	Mg+2	8.0	0.443
6	Ca+2	7.0	0.443
7	Ba+2	6.0	0.443
8	V+5	4.0	0.443
9	Al+3	6.0	0.443
10	Pb+2	5.0	0.443
11	Bi+2	7.0	0.443