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Original Article

Use of 2-[{4-(1, 3- benzoimidazole-2- yl) phenyl} imino] -5- nitro phenol as an analytical reagent for extractive spectrophotometric determination of Cu (II)

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ABSTRACT

A spectrophotometric method has been developed for the determination of Cu (II) using 2-[{4-(1,3-benzoimidazole-2-yl)phenyl} imino]-5- nitro phenolas an extractive reagent. The reagent forms a coloured complex, which has been quantitatively extracted into n- butanol at pH-5.6 . The method obeys Beer's law over a range from 1 to 10 ppm. The Molar absorptivity and Sandell's sensitivity calculated were 0.1899×10^4 $LMol^{-1}cm^{-1}$ and 0.1315 µg cm^{-2} respectively. The proposed method is very sensitive and selective. The method has been successfully applied to synthetic and commercial samples.

Key words: Copper, Spectrophotometric determination, n-butanol, 2-[{4-(1,3-benzoimidazole-2-yl)phenyl} imino]-5-nitro phenol

INTRODUCTION

Copper is very important member of trace metals. Copper is an important micro-nutrient for all living forms. The world health organization recommends a minimal acceptable intake of approximately 1.3 mg/day[1].It plays a vital role in many fields either as metals or its salts such as industry, laboratory, medicine, food and beverage. Cu (II) play a crucial role in the functioning of organs and metabolic process in human being[2]. Cu (II) is an essential metal for plants, microorganism, animals and human being to perform specific biological function. The high concentration is harmful to human beings, causes nausea, vomiting, diarrhea. The accumulation of copper in the human liver and animals is a characteristic of wilson's disease which produces neurological and psychiatric defects[3-5]. 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,[6-9] hydrazone,[10]semicarbazone, [11-12] thiosemicarbazone[13-15],etc have been used for the determination of copper. However these methods suffer from limitations such as requirement of masking agents[6,16], interference of some ions, [17-19] equillibrium time[19] for superior in sensitivity and selectivity to those reported in the literature, is developed for the extractive spectrophotometric determination of copper with BIPINP. A close literature survey indicates that BIPINP 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 and so far not been employed for either coordination or analytical studies. It will be applied for the determination of copper at trace level in synthetic mixtures and alloys.

EXPERIMENTAL

The reagent 2-[{4-(1,3-benzoimidazole-2-yl) phenyl} 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[20]. 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.

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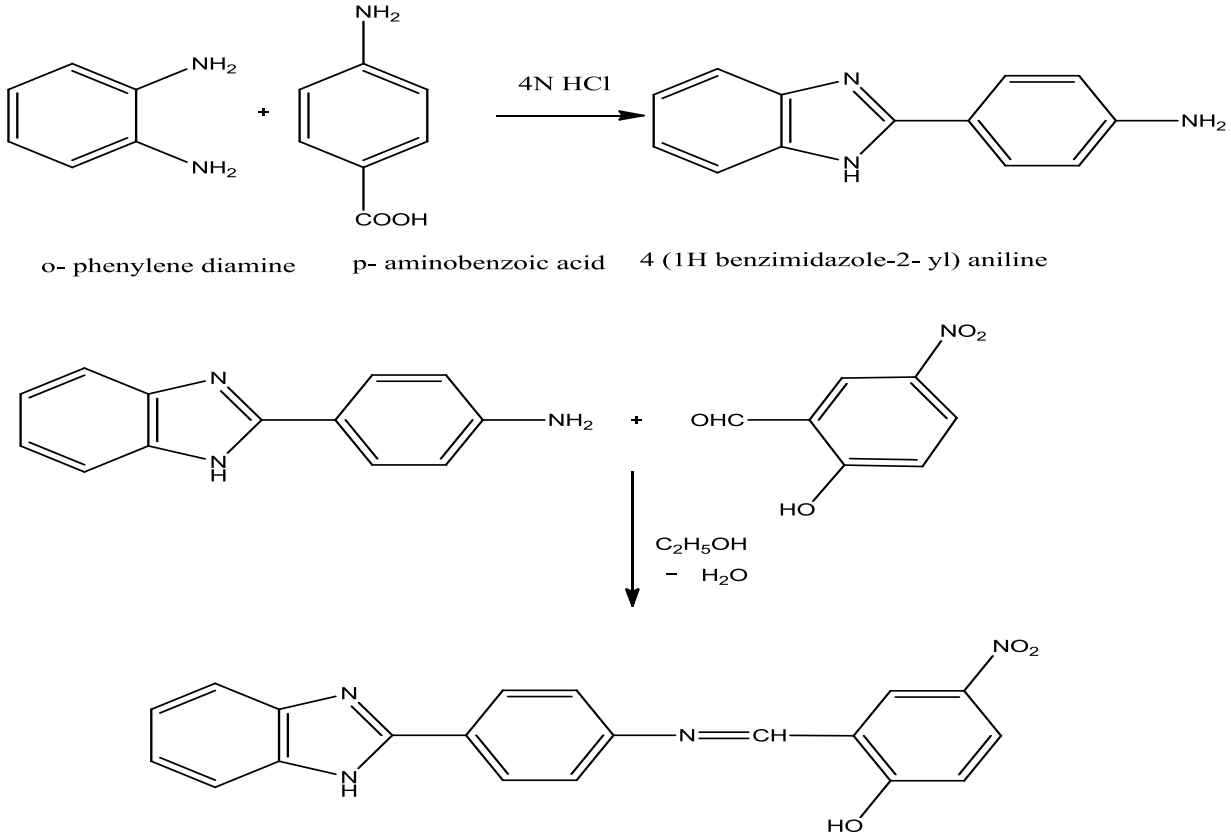
REACTION



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 5.6 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 435 nm and in aqueous phase was determined by diethyldithiocarbamate method.

RESULTS AND DISCUSSION

The reagent BIPINP forms light Green colored complex with Cu (II), which was extracted into organic phase. The extraction of Cu(II) forms aqueous phase by BIPINP 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 with 2-[{4-(1,3-benzoimidazole-2-yl) phenyl} 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 5.6.

Absorption spectrum: The absorption spectrum of Cu(II) : 2-[{4-(1,3-benzoimidazole-2-yl) phenyl} imino]-5-nitro phenol in n-butanol shows the maximum absorption at 435 nm. The absorption due to reagent at this wavelength is nearly negligible. Hence the absorption measurements were carried out at 435 nm.

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 BIPINP 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-[{4-(1,3-benzoimidazole-2-yl) phenyl} 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 50 sec. are sufficient for the quantitative extraction of copper. The study of stability of colour of the Cu (II): BIPINP 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 BIPINP concentration gives linear and reproducible graph in the concentration range 1 to 10 ppm of copper (Fig.1). This shows that the Beer's law is obeyed in this range. The Molar absorptivity and Sandell sensitivity were calculated to be is 0.1899 $\times 10^4$ $Lmol^{-1}$ cm^{-1} and 0.1315 µg $/cm^{-2}$ respectively.
Nature of extracted species: The composition of extracted species has been determined by Job's continuous variation method (Table 2) Slope ratio method (Fig. 2) and Mole ratio method (Table 1). It shows that the composition of Cu (II): BIPINP 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 4).

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 ± 0.834.

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 3).

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.

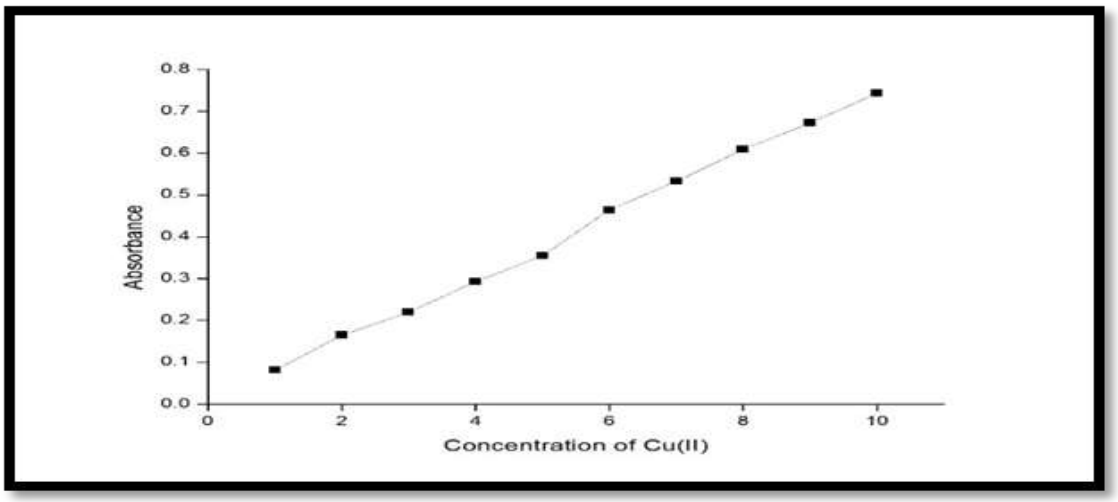


Fig. 1. Calibration plot of Cu (II) with BIZPINPH

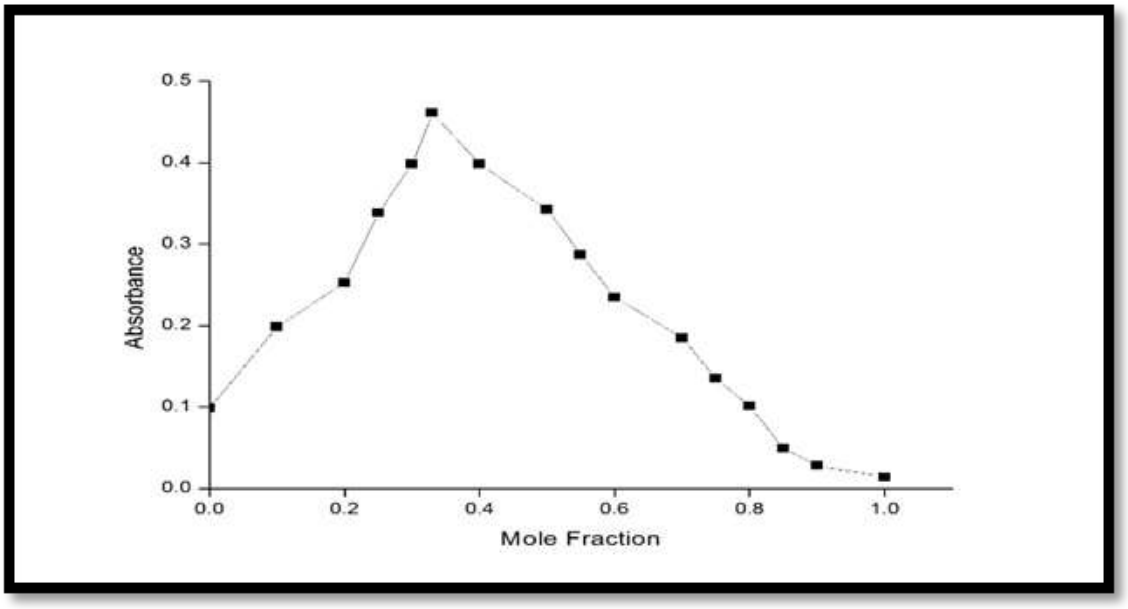


Fig. 2. Job's continuous variation method

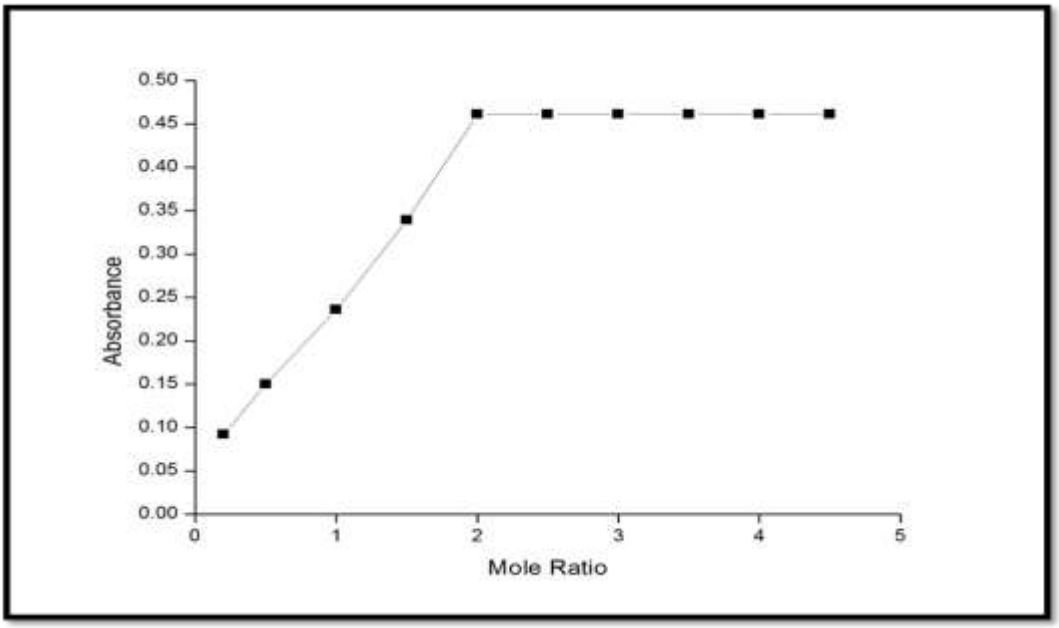


Fig 3 Mole ratio of Cu(II):BIZPINPH

Table 1. Mole ratio of Cu(II):BIZPINPH

Sr.no.	BIZPINPH/Cu(II)	Absorbance
1	0.2	0.092
2	0.5	0.184
3	1.0	0.236
4	1.5	0.339
5	2.0	0.461
6	2.5	0.461
7	3.0	0.461
8	3.5	0.461
9	4.0	0.461
10	4.5	0.461

Table2. Job's continuous variation method

Sr.No.	Volume of BIZPINPH (in ml)	Volume of Cu (II) (in ml)	Mole fraction $\frac{[Cu\ (II)]}{Cu\ (II) + (BIZPINPH]}$	Absorbance
1	2.0	0.0	0.0	0.099
2	1.8	0.2	0.1	0.198
3	1.6	0.4	0.2	0.253
4	1.5	0.5	0.25	0.338
5	1.4	0.6	0.3	0.398
6	1.33	0.67	0.335	0.461
7	1.2	0.8	0.40	0.398
8	1.0	1.0	0.50	0.342
9	0.9	1.1	0.55	0.287
10	0.8	1.2	0.60	0.235
11	0.6	1.4	0.70	0.185
12	0.5	1.5	0.75	0.135
13	0.4	1.6	0.80	0.101
14	0.3	1.7	0.85	0.049
15	0.2	1.8	0.90	0.028
16	0.0	2.0	1	0.014

Table 3: Determination of Cu (II) Using BIPINP from different samples

Sample	Amount of Cu (II)	
	Standard method	**Present method**
Alloys		
Brass	60.0%%	59.97%
Cupronickel	35.0 %	34.5 %
Capsule/ tablets		
Austrin	32.86mg	32.84mg
supradyn	0.862mg	0.860mg
Multivitamin capsule	5.9 mg	5.84 mg
Revital	0.50mg	0.45mg
Synthetic mixture Cu(10)+ Zn(10)+ Cd(10)	10ppm	9.97ppm

Table 4: Effect of divalent ions and foreign ions

Sr.No.	Ion	Amount added In mg	Absorbance
1	Zn2+	7.0	0.355
2	Ba2+	4.0	0.355
3	Ca2+	14.0	0.355
4	Ni2+	13.0	0.355
5	Fe2+	8.0	0.355
6	Pb2+	16.0	0.355
7	K2+	11.0	0.355
8	Mg2+	8.0	0.355
9	Co2+	10.0	0.355
10	Na+	16.0	0.355
11	Mo(II)	13.0	0.355
12	Mn(II)	11.0	0.355

13-	Cl^-	12.0	0.355
14	Br^-	16.0	0.355
15	NO_2^-	17.0	0.355
16	SO_3^-	12.0	0.355
17	CN^-	18.0	0.355
18	SO_4^{2-}	11.0	0.355
19	NO_3^-	14.0	0.355
20	Oxalate	13.0	0.355
21	Thiourea	17.0	0.355

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