Spectrophotometric Determination of Copper After Selective Extraction with α-(2-Benzimidazolyl)-α′,α″-(*N*-5-nitro-2-pyridyl hydrazone)-toluene in the Presence of Brij 58

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The spectrophotometric determination of Cu(II) with α-(2-benzimidazolyl)-α',α"-(*N*-5-nitro-2-pyridylhydrazone)-toluene has been investigated. The optimum conditions of pH, stability, concentration of ligand and surfactant were evaluated. This method is a simple and sensitive method for determination of Cu(II) and offers a selective separation of Cu(II) from sample solution containing 1ppm below amount of Ni(II), Co(II), Zn(II) and Sn(II). Copper was determined by measuring the absorbance of Cu(II)-BINPHT complex extracted with benzene in Brij 58 surfactant at 410 nm. Beer's law is obeyed over the concentration range 0~2.5 μgmL^{-1} and the detection limit (S/N=2) is 0.06 μgmL^{-1}. The relative standard deviation at the 0.3 μgmL^{-1} is 2.4% (N=7). The method was applied for the determination of Cu(II) in various milks.

Introduction

In analytical chemistry, hydrazones was used in detection, determination and isolation of compounds containing the carbonyl group and hydrazones act as multidentate ligands with metals (usually transition elements), forming coloured chelates. These chelates are then used in selective and sensitive determination of the metals.[1~5]

Cu(II) is widely distributed in foods of plant tissue and animal organ. For this reason, several methods have been developed for the determination of copper including the use of hydrazones.[6~9]

In a previous work,[10,11] the author synthesized 2-pyridinecarbaldehyde-5-nitro-pyridylhydrazone and 2-hydroxybenzaldehyde-5-nitropyridylhydrazone and it showed a sensitive reagent for Fe(II) and Co(II). In this work, we synthesized a new reagent, in which a benzimidazolyl group was introduced in the azomethine moiety of α-(2-benzimidazol-yl)-α',α"-(*N*-5-nitro-2-pyridylhydrazone) toluene [BINPHT], and proposed a simple and rapid extraction method for a selective separation of Cu(II) from sample solution with benzene and spectrophotometric determination of micro amounts of Cu(II). And, the effect of surfactants on the absorbance of the Cu(II)-BINPHT complex was also carried out.

Experimental Section

BINPHT was synthesized according to Scheme 1 as follows. The synthesis of 2-chloro-5-nitro-pyridine has been described previously.[10]

Synthesis of α-(2-benzimidazolyl)-α',α"-(*N*-5-nitro-2-pyridyl hydrazone)toluene. BINPHT was synthesized by refluxing equimolar amount of 2-benzoylbenzimidazole[12] and 5-nitro-2-pyridylhydrazine in etanol solution for 5 hr. The product was recrystallized from each solvent used in the synthesis and dried at 110 °C for 10 hrs under reduced pressure to dark brown crystal.

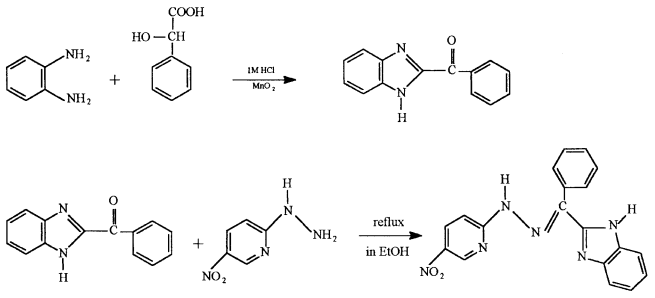
The product was characterized by infrared spectroscopy using KBr pallet method. The spectra had absorption peaks assigned to the stretching vibration of an azomethine bond (-N=C<) around 1603 cm^{-1} and melting point of BINPHT was about 280 (Scheme 1).

Reagent and Apparatus. Analytical-reagent grade chemicals and distilled, deionized water used through out. A stock standard solution of copper (50 ppm) was prepared from Cu(II) atomic absorption spectroscopy standard solution and working standard solutions were prepared by dilution. An acetic acid-sodium acetate buffer solution (pH 6.0) was used. Surfactant solutions were prepared by dissolving suitable amounts of surfactants in water with gentle heating.

α-(2-benzimidazolyl)-α',α"-(*N*-5-nitro-2-pyridyl hydrazone) toluene (1.7×10^{-3} M) was prepared by dissolving 0.61 g of the reagent in 1000mL of absolute methanol.

All absorbance measurements were made with a Perkin-Elmer 552S spectrophotometer using 1-cm quartz cells. All pH measurements were made with a NOVA-310 pH Meter . A Hitachi IR 435 infrared spectrophotometer and Yamato Model MP-1 melting point were used.

General procedure. One mL of the sample solution containing 0.1-2.0 mg of Cu(II) was taken in a 50 mL separatory funnel. 1.7×10^{-3} M BINPHT solution 4 mL, 4 mL of buffer solution (pH 6.0) and 1.0 mL of 5.0×10^{-2} M surfactant solution were added, then adjusted the volume to about 10 mL



Scheme 1

with deionized water. This was equilibrated with benzene (10 mL) then stirred for 5 min. After phase separation, the organic solvent was passed through Whatman No. 41 filter paper to remove water droplets. The absorbance of the organic phase was measured at 410 nm against a reagent blank as reference.

Results and Discussion

Cu(II) reacts with BINPHT giving a pale brown in neutral medium and intensive in weak acidic solution. The spectral characteristics, effect of variables and foreign ions on Cu(II) -BINPHT absorbance and applications of the system are discussed below.

Spectral characteristics. The absorption spectra of the Cu(II)-BINPHT complex extracted with benzene and BINPHT hydrazone in methanol show a maximum absorption at 410 nm and 340 nm, respectively (Figure 1) and the absorbance of the Cu(II)-BINPHT complex showed the maximum values at pH of the range 5.5-6.5. In more acidic or more alkaline solutions, the absorbance decreased because of incomplete complex formation and hydrolysis of the complex. Buffer solution of acetic acid-acetate solution (pH=6) was chosed for subsequent studies.

The Cu(II)-BINPHT complex in aqueous medium of pH 5.5-6.5 has a low solubility. The solubility of the Cu(II)-BINPHT complex was improved by addition of suitable surfactant.

The effects of cationic surfactants [cetyltrimethylammonium bromide (CTMAB), dodecyltrimethylammonium bromide (DTMAB)], nonionic surfactants [Brij 58, Triton X-100] and anionic surfactant [sodium dodecyl sulfate (SDS)] on the absorbance of Cu(II)-BINPHT complexes were studied. As shown in Table 1, Brij 58, the nonionic surfactant gave an enhancement of absorbance but in the anionic and cationic surfactants showed no effect or diminished on the absorbance of the Cu(II)-BINPHT complex. The use of the surfactant of Brij 58 was most effective in improving absorbance and the stable color development. This suggests that Cu(II)-BINPHT complex interacts with the nonionic surfactant and forms the micellar medium, hydrophobic solvation of the chelate and improves solubility. The absorbance

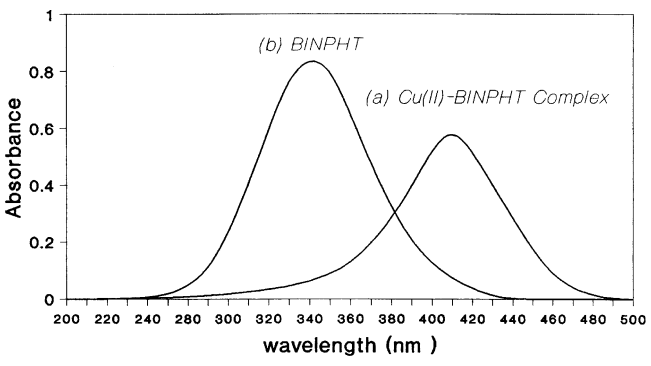


Figure 1. Absorption spectra (a) Cu(II)-BINPHT complex extracted with benzene. (b) BINPHT in methanol solution. Cu(II): 2.0 ppm, BINPHT: 6.8×10^{-4} M, Brij 58: 1.0×10^{-3} M, pH 6.

Table 1. Absorbance characterisitics of Cu(II)-BINPHT complex in the different surfactants

Surfactant	Concentration (M)	λ_{max} (nm)	Absorbance
None	-	408	0.608
CTMAB	1×10^{-3} M	411	0.620
DTMAB	1×10^{-3} M	411	0.300
SDS	1×10^{-3} M	411	0.394
Tritron X-100	1×10^{-3} M	412	0.388
Brij 58	1×10^{-3} M	415	0.670

Cu(II): 2.0 ppm, BINPHT: 6.81×10^{-4} M, pH 6.0.

increased with a increase of Brij 58 concentration untill 5.0×10^{-3} M, but the absorbance diminished with further increase of Brij 58. So, 5.0×10^{-3} M of Brij 58 was selected for further investigations.

The influence of the amount of BINPHT on the absorbance of solution containing 2 ppm of Cu(II) was studied under the conditions established above. The absorbance increased with increase in the amount of BINPHT up to 4 mL (6.8×10^{-4} M), remained constant from 6.8×10^{-4} M to 11.9×10^{-4} M and decreased slowly thereafter. Thus, 6.8×10^{-4} M was selected to ensure a sufficient excess of the reagent throughout the experimental work.

Solvent extraction. After complexation under optimum conditions, the extraction of Cu(II)-BINPHT complex with benzene is studied because the complex was not stable in aqueous medium. The extraction equilibrium was very fast and no change is observed in the absorbance of the Cu(II)-BINPHT complex for 6 hrs. That is, the absorbance of the Cu(II)-BINPHT complex remains practically constant for 6 hrs in benzene.

Solvent extraction was able to establish the selective separation of Cu(II) from the sample solution containing 1 ppm below amount of Ni(II), Co(II), Zn(II) and Sn(II) ion, respectively.

The molar ratio of the complex was studied under the established experimental conditions by the molar ratio and continuous variation method.[13] The two methods showed that the composition of the complex is 1 : 2.

Linear range and detection limit. Beer's law is obeyed over the concentration range of 0-2.5 μg mL^{-1}. The molar absorptivity was calculated to be 3.81×10^4 $mol^{-1}cm^{-1}L$. Maximum molar absorptivity is observed in Cu(II)-BINPHT methanol solution. The detection limit (S/N=2) was 0.06 μg mL^{-1} and the relative standard deviation at the 0.3 μg mL^{-1} of Cu(II) level was 2.4% (n=7).

Interference. To assess the usefulness of this method, the effects of foreign ions which often interfere the determination of Cu(II) were studied. The tolerance limits given in Table 2 are the concentrations that cause error of less than ±2.0% in the absorbance of 2 ppm Cu(II) solution.

Sn(II), Zn(II), Co(II) and Ni(II), which form strong complexes with BINPHT, give strong interference and EDTA shows the strong interferent effect by forming complex with Cu(II) in stead of BINPHT compared with some other reagents.

Table 2. Tolerance limit of foreign ions on the analysis of 2.0 ppm Cu(II)

Tolerance limit (ppm)	Foreign ions
100	Ca(II), Cl^-, NO^{3-}, Malonate ion
10	Sm(III), Gd(III), Yb(III), Au(II)
5	Pb(II), Zr(IV), U(IV), Al(III)
1	Zn(II), Ni(II), Sn(II), Co(II), EDTA

Table 3. Analytical results of Cu(II) in various milk samples

Sample	BINPHT	method	AAS
	Cu(II) found (ppm)	RSD (%)	Cu(II) found (ppm)
Raw milk	4.4×10^{-2}	2.4	4.8×10^{-2}
Choco milk	7.3×10^{-2}	2.8	7.5×10^{-2}

Determination of copper in milk samples. 100 mL of milk was added dropwise to a heated crucible to evaporate it without frothing, then heated strongly to 450-500 °C for 1hr after the moisture has been removed. We took utmost care to avoid loss by sputtering. The dark ash was dissolved in the minimum of strong nitric acid and evaporated, then dissolved in the minimum of dilute nitric acid once again. After filtering the ash and making up the filterate volume to 10 mL, we pipetted 1 mL aliquot and determined it's Cu(II) concentration (in all cases adjusted the pH to 5-6 with sodium acetate). Results for these analyses are given in Table 3. The results shown in Table 3 are in reasonable agreement with those determined by the AAS.

Conclusion

α-(2-benzimidazolyl)-α',α''-(*N*-5-nitro-2-pyridylhydrazone)toluene is a new spectrophotometric reagent for the determination of Cu(II). The method described are very sensitive and selective for the direct determination of Cu(II). The complex between BINPHT and Cu(II) in the presence of Brij 58 is very stable and more sensitive than that in the absence of surfactant. The Cu(II)-BINPHT complex in Brij 58 has an maximum absorbance at 410 nm and obeys the Beer,s law in the range of 0-2.5 μg/mL. Molar absorptivity is 3.81×10^4 $mol^{-1}cm^{-1}L$.

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