



Spectrophotometric Determination of Copper(II) Using 1-(2-Pyridylazo)-2-naphthol in Micellar Solution of Cetyltrimethyl Ammonium Bromide

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A simple rapid new spectrophotometric method has been developed for the determination of copper at trace level using 1-(2-pyridylazo)-2-naphthol (PAN) in cationic micellar solution of cetyltrimethyl ammonium bromide (CTAB). The present method with the use of micellar system replaces the previous solvent extraction method, which reduces the cost and toxicity, while enhancing the sensitivity, selectivity and the molar absorptivity. The average molar absorption coefficient and Sandell's sensitivity was found $2.45 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and 2.6 ng cm^{-2} at λ_{max} 559 nm. Beer's law linear calibration graph was obtained over the concentration range from 0.12 to $5.0 \mu\text{g mL}^{-1}$, the stoichiometric composition of the chelate was 1:2 (Cu: PAN). The developed method was successfully applied for the determination of copper from alloys and real samples.

Keywords: Spectrophotometric, Copper, 1-(2-Pyridylazo)-2-naphthol, Micellar, Cationic, Cetyltrimethyl ammonium bromide.

INTRODUCTION

Copper plays an important role in living systems and is necessary constituent of many enzymes. It is utilized for production of hemoglobin. It enhances iron absorption and transport in gastrointestinal. Copper is utilized to maintain the level of myelin in nervous process, utilized for brain tissues and bone formation^{1,2}. Excess intake of copper is toxic and causes harmful to human kind, also effects the microbiological treatment of waste water³. In determination of Cu ion, the metal ion is chelated and insoluble complex formed is solubilized by the solvent extraction. Spectrophotometric techniques widely utilized commonly due to its simplicity, rapidity and low cost and maintenance. Several spectrophotometric techniques have been developed to replace the solvent extraction method by using the surfactants^{4,5}, due to solubilization ability of micellar system. Micellar systems enhances the molar absorptivities, sensitivities and replaces the previous steps of toxic solvent extraction⁶. Several spectrophotometric methods have been developed to replace the previous solvent extraction method by using the surfactants⁷. Micellar media is introduced to enhance the molar absorptivities, sensitivities and replaces the previous steps of toxic solvent extraction⁸⁻¹⁹. We have developed a new simple, sensitive and selective spectrophotometric method for the determination of copper(II) in various materials by using 1-(2-pyridylazo)-2-naphthol as chromogenic agent in cationic micellar solution of cetyltrimethyl ammonium bromide.

EXPERIMENTAL

A UV-visible scanning spectrophotometer (Cecil CE 9500 model) equipped with a 10 mm path length quartz cell was used. Atomic absorption spectrophotometer (Analyst-100 Perkin Elmer) with multi-elemental hollow cathode lamps was utilized. pH/ conductivity meter (Sension 156 HACH) with Sension Gel-filled pH electrodes was utilized. I.R spectrophotometer (260 Hitachi) was used.

Preparation of reagents: 1-(2-Pyridylazo)-2-naphthol (Merck) solutions of $8 \times 10^{-3} \text{ M}$ were made in 100 mL by dissolving its 0.1994 g in small volume of ethanol and diluted with 0.02 M CTAB surfactant solution. Copper(II) ions stock solutions of ($1000 \mu\text{g mL}^{-1}$) were made and were standardized²⁰. CTAB 0.02 M surfactant solution was prepared by dissolving its 0.02 g of CTAB in 1000 mL. Sodium tartrate tetrahydrate salt 0.1 % w/v and 2 % (m/v) hydroxylammonium chloride solution was prepared. However, 30 % NH_3 concentrated solution 10 mL volume was diluted in 100 mL volumetric flask. Whereas, 0.1 % w/v EDTA solution was prepared. Moreover, ($1000 \mu\text{g L}^{-1}$) stock solutions of thiosulphate, ascorbic acid, sodium acetate, sodium thiosulphate and ammonium molybdate were made. Metal ions solutions ($1000 \mu\text{g L}^{-1}$) were prepared by dissolving their appropriate salts and acidified²¹. Buffer solutions of pH 1-10 were prepared by using appropriate methods²², with appropriate volumes of the mixtures of 0.2 M KCl – 0.2 M HCl for (pH 1-4), 0.2 M CH_3COOH –

0.2 M CH_3COONa for (pH 5-6.0), 0.1 M KH_2PO_4 – 0.1 M NaOH for (pH 6.5-8.0) and 0.025 M sodium borate and 0.1 M HCl for (pH 9-10).

Preparation of sample solutions

Determination of copper ions in alloys sample²³: Alloy sample of copper ions 0.1-0.5 g of reference material Mallory was digested with concentrated HCl (15 mL) and concentrated HNO_3 (5 mL) in beakers. The sample solution was heated to reduce the volume to 5 mL on a hot plate. Then mixed 10 mL concentrated HCl , solutions in the sample solutions by filtering and diluting to a final volume of 25 mL. Alloy sample of reference material having the composition as Mallory (Cu 99.2, Cr 0.81)²³.

Determination of copper(II) ions in brass sample^{23,24}: The brass sample 1 g was digested with concentrated HNO_3 (15 mL) in a 250 mL beaker and mixed deionized water 25 mL, samples were dissolved by heating on hot plate and samples were taken to a volumetric flask of 1000 mL and made the maximum volume diluted up to maximum. Brass solution of 1 mL was diluted in 1000 mL volumetric flask. Diluted brass sample after complex formation was investigated.

Investigation of copper(II) ions in stream water sample: The stream water solution was collected from Khairpur, Sindh Province of Pakistan. The sample solution was filtered with filter paper and acidified with dil. HNO_3 ²⁵. The 5 mL sample was transferred to three different volumetric flasks of 10 mL and then added the optimized concentration of 1-(2-pyridylazo)-2-naphthol, appropriate buffers and 0.02 M CTAB for complex to the determination of Cu(II) ions by present method.

Procedure for determination of copper ions: 1 mol sample solution of copper, 2 mL buffer solution of pH 6.5, (1 or 2 mL) 0.02 M CTAB solution and 1 mL of 2×10^{-4} M 1-(2-pyridylazo)-2-naphthol solutions were added to 10 mL volumetric flask and solution was investigated.

RESULTS AND DISCUSSION

Copper(II) reacts with 1-(2-pyridylazo)-2-naphthol forms [Cu(II)-PAN] complex as shown in Fig. 1. UV-visible spectrum of 1-(2-pyridylazo)-2-naphthol gives greenish colour of ligand-to ligand charge transfer (LLCT) ($\pi \rightarrow \pi^*$)²⁶ of nitrogen atom of azo molecule at λ_{max} 471 nm and²⁷ at UV 250 nm for oxygen of C-O-H as shown in Fig. 2. UV-visible spectrum of red colour solution of copper(II)-PAN complex showed bathochromic shift of 88 nm charge transfer from ligand-to metal (LMCT) ($p\pi-d\pi$) at λ_{max} 559 nm as shown in Fig. 3. The stoichiometry of the complex was found 1:2 (Metal:Ligand). 1 m mole Cu(II) ions and 1-(2-pyridylazo)-2-naphthol molar ratio $1:2 \times 10^{-4}$ M was optimized for complex formation as shown in Fig. 4. The 0.02 M CTAB 1 mL showed maximum constant absorbance in 2 mg L^{-1} Cu(II)-chelate, that concentration is greater than cmc value (1.3 Mm)²⁸. Cu-PAN complex showed maximum constant absorbance at pH 6.5 as shown in Fig. 5. Molar absorptivity of the complex was found $2.45 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. Calibration graph showed linear range over the concentration of 0.12-5.0 $\mu\text{g mL}^{-1}$, the correlation coefficient with experimental data was 0.999 as shown in Fig. 6. Detection limit and Sandell's sensitivity was found 0.12 $\mu\text{g mL}^{-1}$ and 2.6 ng cm^{-2} as given in Table-1. The metal-complex showed absorbance

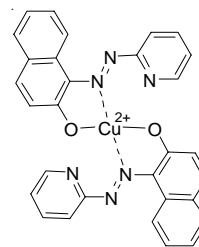


Fig. 1. Proposed structure for Cu(II)-PAN

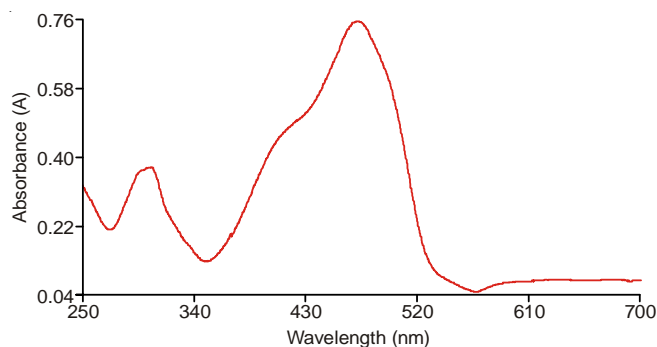


Fig. 2. UV-visible spectrum of 1-(2-pyridylazo)-2-naphthol (PAN) at (λ_{max} 471.4 nm) at neutral pH

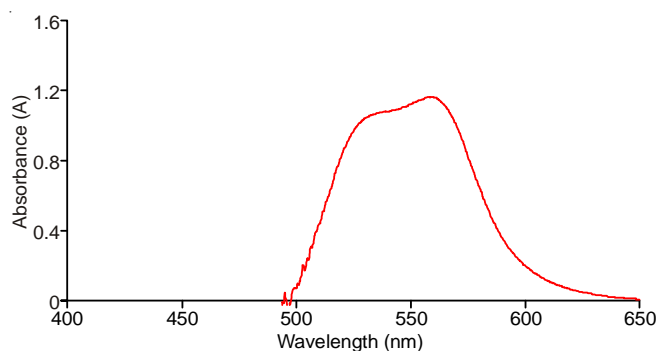


Fig. 3. UV-visible spectrum of Cu(II)-PAN at (λ_{max} 559.4 nm) pH 6.5

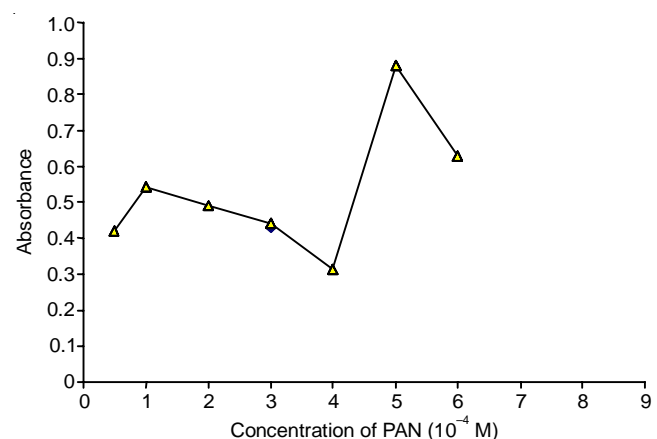


Fig. 4. 1-(2-pyridylazo)-2-naphthol (PAN) molar ratio effect on absorbance of Cu(II)-PAN complex in 0.02 M cetyltrimethyl ammonium bromide (CTAB)

maximum constant up to 5 min. At ordinary temperature Cu-PAN complex showed stable absorbance measurement, till 24 h. Cu(II)-PAN complex in micellar solution was stable than solvent extraction system²⁹. The method developed was validated to the determination of copper ions in certified reference material Mallory (Table-3), synthetic mixtures (Table-4) and

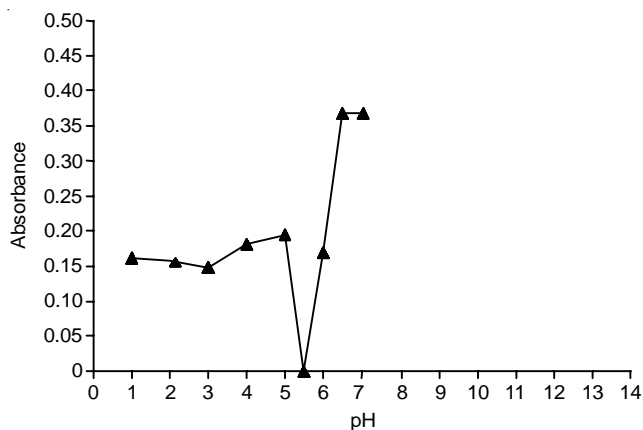


Fig. 5. pH graph for Cu(II)-PAN complex in 0.02 M cetyltrimethyl ammonium bromide (CTAB)

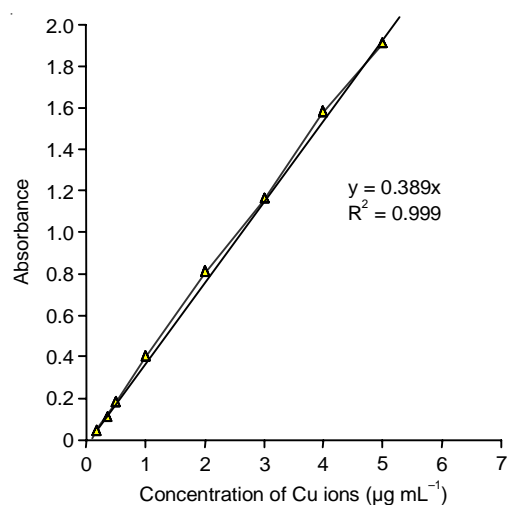


Fig. 6. Calibration graph for Cu(II)-PAN complex in 0.02 M cetyltrimethyl ammonium bromide (CTAB)

in real samples (Table-5) to verify the accuracy and the precision of the method. The average Cu ions found ($n = 7$) in the reference material with a precision as relative standard deviation RSD was up to 0.91 %.

Effect of foreign ions in the determination of copper:

The cations Cr(IV) and Co(II), showed much interference in the determination of Cu(II)-PAN complex at the lower concentration level as given in the Table-2, 1 mL EDTA was added, as masking agent to remove interference of Cr(IV) and Co(II) before further addition of perchloric acid. Besides this Co(II) ions interference was removed with masking agent *o*-phenanthroline. At higher concentration level ascorbic acid, Cl⁻, I⁻, Br⁻ and SCN⁻ does not show interference³⁰. Na₂tartarate at 1500 µg mL⁻¹ concentration level have not shown any interference in the absorbance of the Cu(II)-PAN complex. Citrate, phosphate, fluoride, thiocyanate, fluoride, citrate and phosphates were used as masking agents to remove the interference of the foreign ions²³. Tolerance limit of foreign ions is given in Table-2.

TABLE-2
EFFECT OF FOREIGN IONS ON Cu(II)-PAN (µg)

Metal ion/salt	Cu(II)
Na ₂ tartarate	1500
KSCN, KClO ₃	1000
NaF, CH ₃ COO ⁻	600
Na ₂ citrate, Pb(II) ^a	500
Al(III)	300
Bromide, Iodide, Chloride, Borate, Na ₂ C ₂ O ₄	200
EDTA, ^c Cyanate, ^e Fe(II), ^a Mn(II), Zn(II), Hg(II)	100 ^b
Co(II)	10
Ni(II)	100
Cd(II)	100
Cr(III)	50
Cr(IV)	8

TABLE-1
ANALYTICAL PARAMETERS OF Cu(II)-PAN IN CETYLTRIMETHYL AMMONIUM BROMIDE

Parameters	Cu(II)
Wavelength (λ/nm)	559
pH	6.5
Surfactant/0.02 M CTAB (mL)	1.0
1-(2-Pyridylazo-2-naphthol) concentration (M)	2.0 × 10 ⁻⁴
1-(2-Pyridylazo-2-naphthol) (molar excess, M:R)	1:2
Linear range (µg mL ⁻¹)	0.12-5.0
Molar absorption coefficient (L mol ⁻¹ cm ⁻¹)	2.45 × 10 ⁴
Sandell's sensitivity (ng cm ⁻²)	2.6
Detection limit (µg mL ⁻¹)	0.12
Correlation coefficient (R ²)	0.999
Reproducibility (% RSD) ^a	0.91

TABLE-4
PERCENTAGE RECOVERY OF KNOWN AMOUNT OF Cu(II) IONS

Cu(II)	0.50	0.49	98
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Conclusion

The results obtained in the determination of copper(II) ions were comparable with the recently reported methods, while the present method is more sensitive and has shown significant improvement in Beer's law linear range and in the detection limit than the reported³¹⁻³⁴. Sensitivity and selectivity of proposed method is higher than solvent extraction methods^{26,35}. The present method is precise, sensitive, selective, reproducible simple, rapid and versatile than the reported existing spectrophotometric methods as shown in Table-6.

TABLE-3
DETERMINATION OF COPPER(II) IN ALLOY SAMPLES

Alloy certified (%) composition	Metal ion	Metal (µg) present	Metal (µg) found	RSD (%)	Relative error (%)	Recovery (%)
Mallory	Cu(II)	25.00	24.98	0.91	0.08	99.92

TABLE-5
DETERMINATION OF COPPER(II) IN REAL SAMPLES

Sample	Analyte ion	Proposed method (µg mL ⁻¹)	RSD (%)	AAS method (µg mL ⁻¹)	RSD (%)	Recovery (%)
Diluted brass sample	Cu(II)	0.655	0.4	0.664	0.4	98.64

TABLE-6
COMPARISON OF COPPER(II) DETERMINATION METHODS USING 1-(2-Pyridylazo-2-naphthol)

M ion	Method	Reference
Cu	In triton X-100 at λ_{\max} 520 nm, ϵ $1.14 \times 10^5 \text{ mol}^{-1} \text{ cm}^{-1}$, linear concentration 0.01-0.60 $\mu\text{g mL}^{-1}$	32
Cu	In CCl_4 at λ_{\max} 565 nm, ϵ $2.27 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ linear concentration 0.3-12.0 $\mu\text{g mL}^{-1}$	30
Cu	In triton X-100, at λ_{\max} 555 nm, ϵ $5.21 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$, linear concentration 0.08-4.00 $\mu\text{g mL}^{-1}$	31
Cu	In SDS at λ_{\max} 581 nm, ϵ $2.08 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ linear concentration 0.05-4.50 $\mu\text{g mL}^{-1}$, D.L 4 ng mL^{-1}	24
Cu	In SDS, ϵ $1.6 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$, linear concentration 0.5-3.0 $\mu\text{g mL}^{-1}$, D.L 3.9 ng mL^{-1}	32
Cu	In CTAB, ϵ $2.45 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$, linear concentration 0.12-5.0 $\mu\text{g mL}^{-1}$ D.L 2.6 ng mL^{-1}	*Present method

*Present method is more sensitive and selective L

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