

Spectrophotometric determination of copper using o-vanillidine-2-amino-4-ethylbenzothiazole as a chromogenic reagent

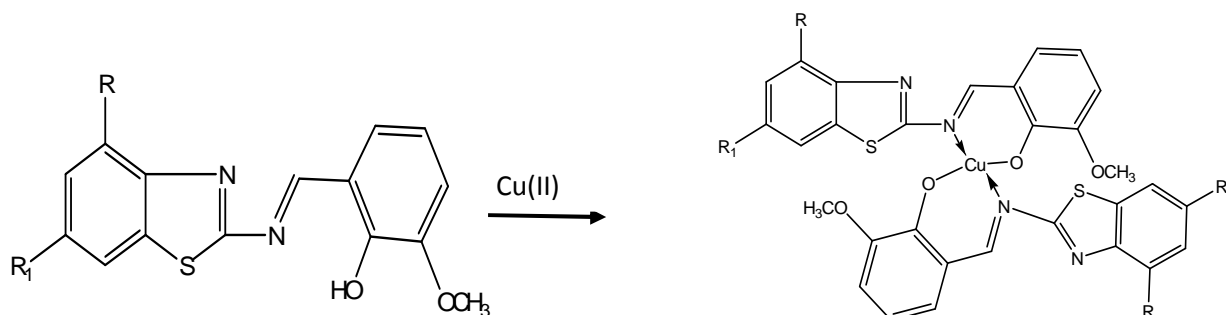
K. Shanthalakshmi^a and B. Muralidhar Rao^{b*}

^aDepartment of Chemistry, Regional Institute of Education, Mysore- (NCERT-New Delhi), Karnataka , India

^bGovinda Dasa College, Suratkal, D.K, Karnataka, India

ABSTRACT

A simple Spectrophotometric method is proposed for the determination of copper using o-Vanillidine-2-amino-4-ethylbenzothiazole (VEBT). The copper ions react with the Schiff's base at room temperature to form 1:2 [Metal: Ligand] complex. Beer's law obeyed over the range $0.41\mu\text{g mL}^{-1}$ to $3.78\mu\text{g mL}^{-1}$ of copper. Brownish yellow coloured complex formed was measured at λ_{max} 450nm in aqueous methanol solution. The proposed method offers the sensitivity, rapidity, selectivity and without any prior separation and extraction. The method is free from the interference of metal ions like zinc, cadmium, cobalt, iron, lead and mercury. The method has been successfully applied for the determination of trace amount of copper in Industrial effluents.



o-Vanillidine-2-amino-4-ethylbenzothiazole Schiff's base copper complex
Schiff's base [R=CH₃CH₂][R₁=H]

Keywords: Copper; o-Vanillidine-2-amino-4-ethylbenzothiazole; Absorption; Schiff's bases.

INTRODUCTION

Synthesis of new metal complexes of different ligand systems is important in chemistry, biology and medicine. Schiff's bases, having multidentate coordination sites are attractive analytical reagents, since many of them form complexes with transition metal ions [1-3]. Developing highly functional chelating agents such as Schiff's bases has been a great concern of many analytical chemists. Many investigations have been centred on the structure and bonding in Schiff's bases, but a few have been directly concerned with analytical applications. Schiff's bases form complexes with many transition metals to form either 1:1 (metal:ligand) or 1:2 (metal:ligand) complexes. The analytical methods based on complex formation are used more frequently. Owing to the relatively simple preparation procedures of Schiff's bases, it is possible to obtain ligands of different design and characteristics by selecting appropriate reactants. In search of new sensitive and selective organic reagent a thorough study of various benzothiazole azo dye and Schiff's bases has been made [4-13]

Schiff's bases derived from 2-amino-4-ethylbenzothiazole with o-Vanillin is synthesised and spectrophotometric methods for the determination of Copper ions from the Schiff's base was designed. This method was successfully applied for the estimation of trace amounts of Copper ions from the industrial effluents.

MATERIALS AND METHODS

2.1. Apparatus

The pH was determined with a model 7007 Digisun electronic pH meter with combined glass calomel electrode. Graphite furnace Atomic Absorption Spectrometer was used for the analysis of cations in water samples. Shimadzu UV double beam spectrophotometer was used for spectrophotometric measurements.

2.2. Chemicals

All the reagents were of analytical grade and the solutions were prepared with doubly distilled water. Schiff's base solution (0.05% (w/v) were prepared by dissolving appropriate amounts of VEBT, in methanol^[14]. o-Vanillin was purchased from Sigma Aldrich (Germany), 0.2 M acetic acid and 0.2 M sodium acetates were used for pH adjustments.. 2-amino-4-ethyl benzothiazole synthesized starting from respective α -phenylthiourea^[15].

2.3. Methodology

2.3.1. Synthesis of o-Vanillidine-2-amino-4-ethylbenzothiazole

2-Amino-4-ethyl benzothiazole (1.80 g) was dissolved in absolute ethanol (15 mL) and then o-Vanillin (1.10 g) was added to the above solution along with a drop of piperidine. The mixture was refluxed for 3 hours and kept for eight hours. The yellowish orange solid obtained was filtered and washed several times with cold ethanol, dried and recrystallized from carbon tetrachloride to yield yellow crystalline solid.

2.3.2. Spectrophotometric determination of Copper ion

Preparation of Copper (II) standard solution

Copper (II) solution (1000 mg L^{-1}) was prepared by dissolving a known amount of Copper (II) sulphate penta hydrate in distilled water, adjusting the pH of the solution to 1.0 with dilute sulphuric acid and diluting the solution to a liter with distilled water. The concentration was determined by titrating with EDTA using 1-(2-Pyridyl azo)-2-naphthol (PAN) as indicator. Working solutions of the concentrations of 10^{-5}M were prepared by appropriate dilution of standard solution.

General procedure for the determination of Copper ions using VEBT Schiff's Base Standard solutions of VEBT Schiff's base of concentration 10^{-4}M were prepared in A.R methanol. Absorption measurements were made at 450 nm against the reagent blank from a solution, prepared by 1mL of the VEBT Schiff's base of the concentration 10^{-4}M , 1mL of $0.074 \mu\text{g mL}^{-1}$ to $0.91 \mu\text{g mL}^{-1}$ of Copper solution, 2 mL of 5.89 buffer solution and made up to 25 mL with methanol.

RESULTS AND DISCUSSION

3.1. Absorption Spectra of Synthesized Schiff's Bases and its Copper Complex

Absorption spectra of Schiff's bases VEBT and its corresponding Copper complex was scanned at pH 5.89. Absorbance decreased from 370 nm to 500 nm for all the four Schiff's bases. Copper complex of Schiff's bases show maximum absorptions at 450 nm. Hence 450 nm was chosen as the wavelength for the determination. Absorption spectra of VEBT, and its Copper complex is shown in the Figure 1.

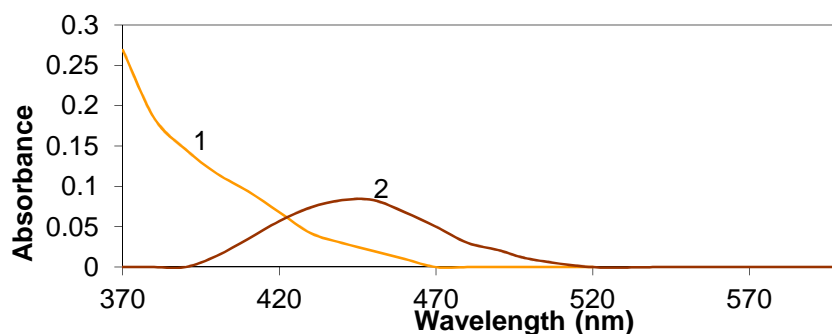


Figure 1: Absorption spectra of VEBT and Cu-VEBT
1. Absorption spectrum of VEBT 2. Absorption spectrum of Cu-VEBT

3.2. Effect of pH

The effects of pH on the absorbance of four Schiff's base Copper complex at 450 nm was studied under different pH conditions. Maximum absorbance for the complex was obtained at pH 5.89. Hence, pH 5.89 was selected for the determination of Copper. It is also found that, the addition of 2 mL of buffer solution of pH 5.89 was sufficient for the pH adjustments.

3.3. Characteristics of the Copper Complexes

Light yellowish orange solutions of VEBT, solution change to brownish yellow solution immediately on the addition of Copper ions at 5.89 pH in methanol solution with maximum absorption at 450 nm and was stable for at least half an hour.

3.4. Spectral data of Copper Complex

Beer Lambert's Range, optical Characteristics, such as, molar absorptivity, Sandell's sensitivity, slope, intercept, correlation coefficient are shown in Table 1

A typical plot showed unequivocally, that the stable 1:2 [M-L] complexes are formed at pH 5.89 (λ_{\max} 450 nm). Calibration graph obtained by the recommended procedure was linear over the range $0.41\mu\text{g mL}^{-1}$ to $3.78\mu\text{g mL}^{-1}$ in the final solution.

Table- 1 Spectral data for the determination of Copper ions using VEBT, Schiff's base as spectrophotometric reagent

Parameters	Cu-VEBT
Colour	Brownish yellow
λ_{\max} (nm)	450
Stability (minutes)	30
Molar absorptivity, (ϵ_{\max}) $\text{L mol}^{-1} \text{cm}^{-1}$	2.99×10^3
Beer Lambert's Range ($\mu\text{g mL}^{-1}$)	0.074-0.91
Sensitivity ($\mu\text{g cm}^{-2}$)	2.142×10^{-3}
Regression (r^2)	0.9855
Slope	0.9373
Intercept	0.00365
Correlation Coefficient	0.9927

Table-2: Effect of various Cations and anions ($0.059 \mu\text{g mL}^{-1}$ Copper added)

Ions / Substance	Amount added ($\mu\text{g mL}^{-1}$)	Copperfound ($\mu\text{g mL}^{-1}$)with VEBT	Error ($\mu\text{g mL}^{-1}$)
Cl^-	70	0.056	-0.003
SO_4^{2-}	103	0.050	-0.009
NO_3^-	90	0.059	0.0
F^-	38	0.063	0.004
PO_4^{3-}	122	0.072	0.013
DMG	1194	0.052	-0.007
EDTA (0.1M)	0.05mL	-	-
Thiourea	170	0.0	-0.059
Hg^{+2}	1.25	0.051	-0.008
Pb^{+2}	1.08	0.040	-0.019
Fe^{+2}	2.02	0.050	-0.009
Cd^{+2}	2.12	0.054	-0.005
Zn^{+2}	2.02	0.0501	-0.008
Co^{+2}	1.95	0.057	-0.002
Ni^{+2}	1.09	0.048	-0.011

3.5. Effect of foreign ions on the determination of metal ions

Effect of foreign ions on the determination of Copper in 5.8×10^{-5} M Copper solution buffered at pH 5.89. The tolerance amounts of foreign ions are as shown in Table2. The tolerance limit of foreign ions was taken as that value,

which caused an error of not more than $\pm 5\%$ in the absorbance. Most of the cations do not interfere with the determination of Copper.

3.6. Determination Copper in the Industrial Effluents

The effluent samples were collected from four different industries around Mysore. Treated effluent solutions were completely evaporated, they were digested with 10 mL of Conc. HNO_3 , until all the brown fumes of nitric acid subside [16]. The residues obtained were extracted with dilute acetic acid and made up to 25 mL with redistilled water in a volumetric flask. The estimations of Copper ions were carried out as described under general procedure using VEBT, as analytical reagents and absorption measurements were made at 450 nm against the reagent blank and the results are presented in the Table 3. The results obtained by the proposed method agreed with the certified values.

Table 3 Results obtained for the determination of Copper in the industrial effluents

Industrial effluents	VEBT as analytical reagent($\mu\text{g mL}^{-1}$)	AAS method($\mu\text{g mL}^{-1}$)
Glowtronics	0.021	0.02
Marc batteries	0.023	0.02
Allcoats	0.029	0.03
Tritan Valves	0.36	0.35

CONCLUSION

Schiff's bases VEBT, Copper complex was synthesized. And used for the determination of copper in Industrial effluent. The reagent form brownish yellow copper complex at pH 5.89, with a stoichiometric ratio of 1:2 [Copper to ligand]. The method is relatively free from interference with most of the metal ions like Zinc, Cadmium, Cobalt, Lead, Mercury and Iron.

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