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Original Research Article

Action of 4-[(*Z*)-(4-Methoxybenzylidene)amino]-5-methyl-4*H*-1,2,4-triazole-3-thiol as Chemosensor for the Trace Amount of Copper in Aqueous Media

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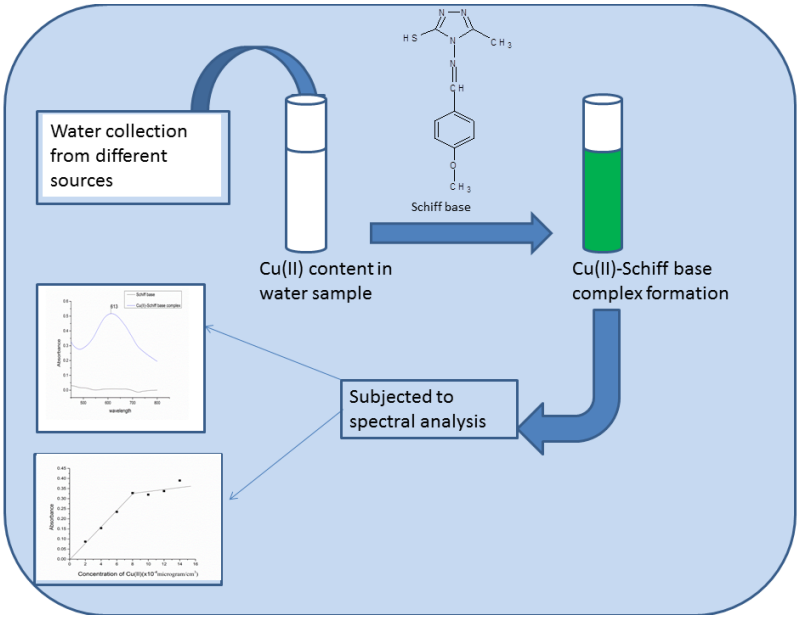
ABSTRACT

This research study evaluates a novel, sensitive, and selective spectrophotometric method for the estimation of copper(II) by using a new chromogenic reagent 4-[(*Z*)-(4-methoxybenzylidene) amino]-5-methyl-4*H*-1,2,4-triazole-3-thiol (MAMTT) (Schiff base). The maximum absorbance was found to be at 613 nm. Experimental conditions were optimized. Beer's law was seen in 12.7-50.83 µg/mL of copper concentration range. Calculated molar absorptivity, detection limit and quantification limit of the complex were 0.307×10^4 L $mol^{-1}.cm^{-1}$, 6.328 µg/cm^3 and 19.177 µg/cm^3, respectively. The study of interference of common ions was carried out. The current process was enforced for the estimation of copper in water samples.

GRAPHICAL ABSTRACT



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Introduction

Currently, the selective and sensitive checking of trace metal ions from various sources, particularly in water, have become more significant because of their poisonous impacts on biological and natural systems. Copper and its salts are utilized in foods, medicines, beverages, industries and laboratories. Therefore there is a requirement for a quick and definite analytical process for estimating the amount of copper in micro and semi micro levels. In spite of the way that there are various complexometric and gravimetric reagents for copper estimation, trouble arises when test sample bearing small amounts of copper needs to be analysed. Such errors can be minimised by adopting spectrophotometric techniques utilizing sensitive and selective reagents [1,2]. Spectrophotometry is the most broadly utilized analytical method for investigation because it is, economic, simple and easily accessible to most laboratories [3]. Numerous spectrophotometric reagents have been utilized for estimation of copper(II); however, most of these reagents have different restrictions, for example requiring more time for colour development, extraction, interference of ions and heating.

Evolution of novel Schiff bases and their metal complexes presently attracting the thought of medicinal chemists. The versatile compounds such as Schiff bases and their complexes are synthesized from the condensation of carbonyl compounds with an amino compound. Schiff base complexes can be used for industrial purposes. It also exhibit a broad range of biological activities inclusive of antibacterial, antifungal, antimalarial, antiproliferative, anti-inflammatory, and antiviral properties. In various reactions many Schiff base complexes exhibit magnificent catalytic activity. The huge thermal and moisture stabilities of many Schiff base complexes were favorable for their application as catalysts in the high temperature conditioned reactions. The activity is usually enhanced by complexation hence to understand the properties of both ligands and metal can lead to the synthesis of highly active compounds. The impact of certain metals on the biological activity of these compounds has prompted a considerable hike in the study of their coordination behavior [4]. In our modern examinations, addition of copper(II) to the solution of 4-[(*Z*)-(4-methoxybenzylidene)amino]-5-methyl-4*H*-1,2,4-triazole-3-thiol [MAMTT](Schiff base) [5-7] resulted in a fast colour change from blue to dark green as shown in Figure 1 with an accompanying new band appearing at 613 nm in the absorption profile. However, the compound has not been recently applied for the spectrophotometric determination of copper(II).

A **B** **C**

Figure 1. Aqueous solutions of a) Schiff base, b) $CuSO_4.5H_2O$ and c) Schiff base-Cu(II) complex

Herein, we have proposed a novel, feasible and highly sensitive method for the spectrophotometric monitoring of copper(II) ion with a 4-[(*Z*)-(4-methoxybenzylidene) amino]-5-methyl-4*H*-1,2,4-triazole-3-thiol in an ethanol-water medium. Various experimental conditions,

e.g., the effect of pH, the amount of chromogenic agent, the effect of coexistence of ions, limit of detection and ranges of applicability of Beer's law have been studied. The method was successfully performed for the analysis of Cu(II) in water samples.

Materials and Methods

Apparatus

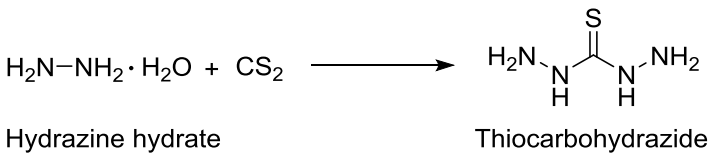
Spectrophotometric measurements were done using Agilent Cary WinUV software-based spectrophotometer. pH of buffer solutions was measured using Systronics μ 361 pH meter. High purity reagents were used.

Reagents, Solutions and Samples

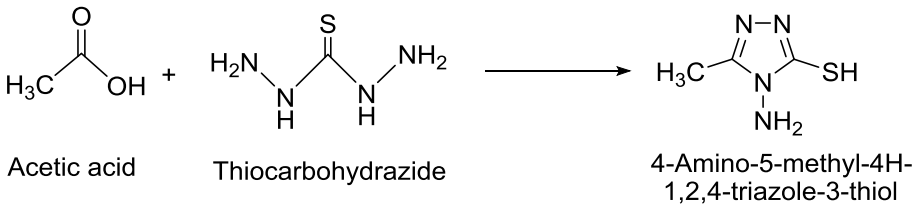
Stock solution of 0.02 M copper(II) sulphate pentahydrate was prepared. Different pH solutions from 1 to 12 were prepared using 0.2 M KCl and 0.2 M HCl (pH=1), 0.1M potassium hydrogen phthalate and varying amounts of 0.1 M HCl (pH=2–5), 0.1 M potassium dihydrogen phosphate and varying amounts of 0.1 M NaOH (pH = 6–8), 0.025 M borax and 0.1 M HCl (pH=9), 0.025 M borax and 0.1 M NaOH (pH=10), 0.05 M disodium hydrogen phosphate and varying amounts of 0.1 M NaOH (pH = 11and pH = 12) [8].

Synthesis of 4-[(Z)-(4-Methoxybenzylidene)amino] -5-methyl-4H-1,2,4-triazole-3-thiol [MAMTT]

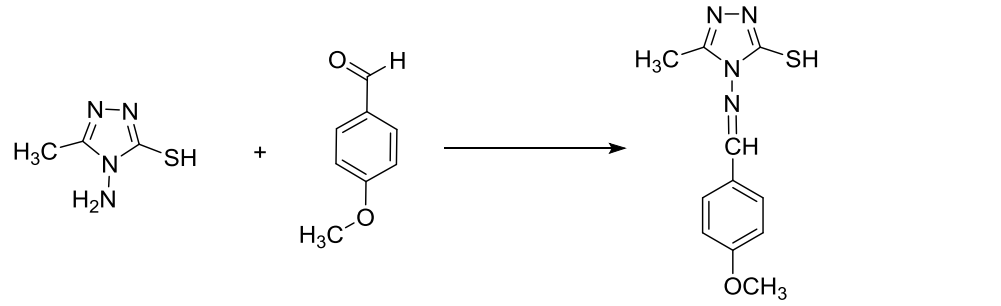
Thiocarbohydrazide (TCH) was prepared by the method reported by Earle S. Scotte and L. F. Audrieth [9] and subsequently modified by Gary R. Burns [10] (Scheme 1). Then 4-amino-5-methyl-4*H*-1,2,4-triazole-3-thiol (AMTT) was prepared by the method proposed by K. S. Dhaka, J. Mohan, V. K. Chadha and H. K. Pujari [11] (Scheme 2). Finally, the ligand was prepared by refluxing a mixture of 0.03 mole of AMTT and 0.03 mole of anisaldehyde in 50 mL of absolute alcohol for about 3 hours (Scheme 3).



Scheme 1. Preparation of TCH



Scheme 2. Preparation of 4-amino-5-methyl-4*H*-1,2,4-triazole-3-thiol



Scheme 3. Synthesis of 4-[(*Z*)-(4-methoxybenzylidene)amino]-5-methyl-4*H*-1,2,4-triazole-3-thiol [MAMTT]

Characterization

4-[(Z)-(4-methoxybenzylidene)amino]-5-methyl-4H-1,2,4-triazole-3-thiol: ^{1}H NMR (400 MHz; DMSO-d6, δ ppm): 8.06-8.08 (s, 2H, ArH), 8.12-8.14 (s, 2H, ArH), 13.8 (s,1H, SH), 3.3 (S, 3H, -CH_3), 3.83 (s, 3H, O-CH_3), 10.2 (s,1H, N=C-H); ^{13}C NMR (DMSO-d6, δ ppm): 11.21, 130.49, 138.93, 149.15, 161.75, 193.57. The IR spectrum (KBr film) of ligand has the bands in the region 3100 cm^{-1} (Figure 3) corresponding to ν(N-H), at 2931 cm^{-1} due to ν(-C-H), 1018 cm^{-1} due to ν(-O-CH_3) and in the region 1980 cm^{-1} due to ν(=C-H). Thioamide band which has a major contribution from ν (N-H) and minor contributions from ν(C=N) and ν(C-H), is observed at 1602 cm^{-1} in the spectrum of ligand. Yield 85%.

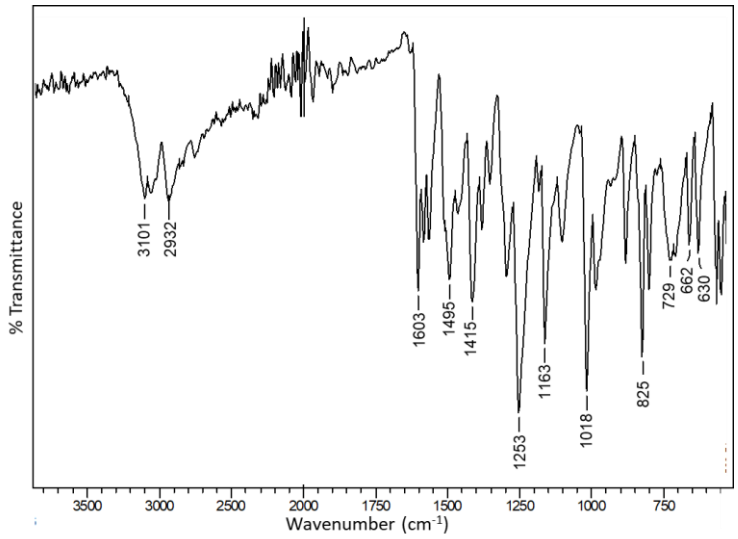


Figure 2. IR spectrum of MAMTT

Procedure

Verification of Beer-Lambert's law

To each set of different 10 mL standard flask varying volumes in microliters, of Cu(II) solution was added. 2 mL of Schiff base solution was transferred in equal proportion to all the standard flasks, followed by the addition of 5 mL of pH resistant solution (pH = 5) [12-14] and then made up to the mark by adding alcohol. The maximum absorbance was found at λ_{max} = 613

nm against the blank. The calibration plot was prepared.

Results and Discussion

Absorption Spectra of Copper Sulphate Solution and Schiff Base

The reaction of Schiff base with Cu(II) ion results in a stable Cu(II)-Schiff base complex and shows maximum absorbance at 613 nm, as shown in Figure 3. At this wavelength, the absorbance due to blank solution is negligible. It is probable from Figure 3 that at 613 nm, the spectrophotometric determination of Cu(II) is feasible. Further investigations were conducted at this wavelength.

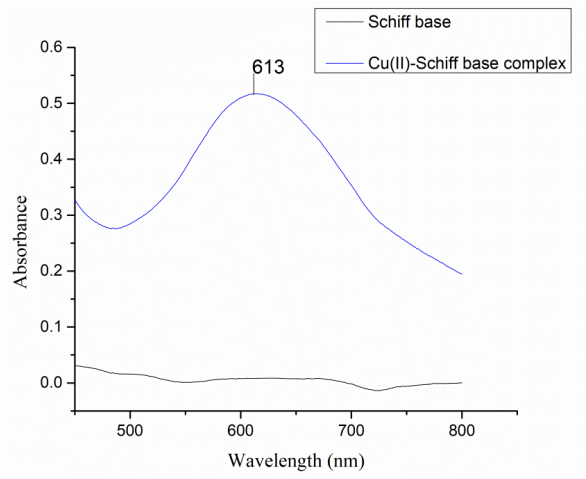


Figure 3. Absorption spectra of Schiff base versus its copper complex

Effect of Reagent Concentration

The significant variable which could influence the absorbance intensity of the complex is the concentration of Schiff base. The impact of Schiff base concentration was investigated in the concentration range $1x10^{-3}$ to $1x10^{-2}$ M. The absorbance of complex was increased on incrementing the concentration of chromogenic reagent. It was found that the concentration range of the reagent should be $3.0x10^{-3}$ to $3.2x10^{-3}$ M. The absorbance maximum of the colored complex corresponds to 1.6 mL of $3.2x10^{-3}$ M concentration, showing no effect on further addition of Schiff base (Figure 4).

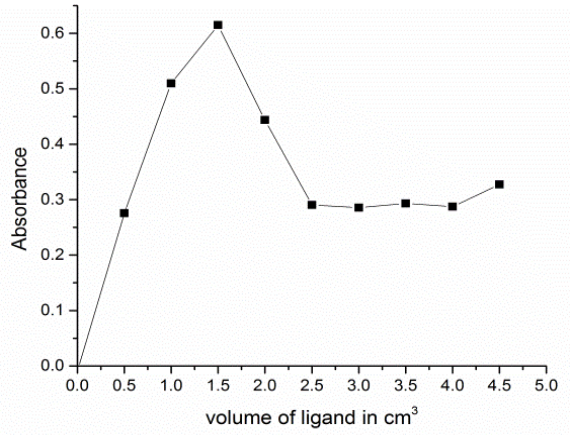


Figure 4. Effect of MAMTT concentration on the absorbance of Cu(II)-MAMTT complex

Effect of pH on Absorbance of Complex

Measurement of complex absorbance at 613 nm using varying pH solutions showed that maximum color intensity was developed by the usage of pH = 5 solution (Figure 5). Hence, further analytical study of the complex was done by keeping the solution pH = 5.

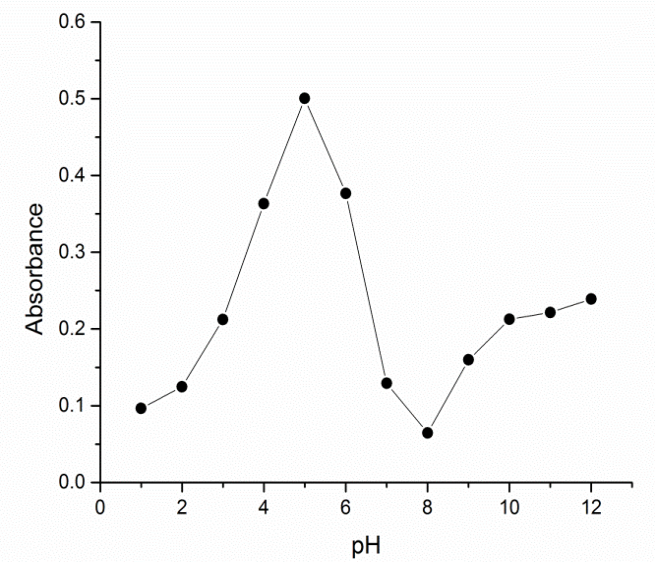


Figure 5. Impact of pH on absorbance of Cu(II)-MAMTT complex

Beer's Law Sensitivity and Calibration Plot

Under the optimum conditions, the calibration curve for the estimation of Cu(II) was obtained (Figure 6). The Beer's law was observed in the range of 12.7-50.83 µg/mL Cu(II) concentration.

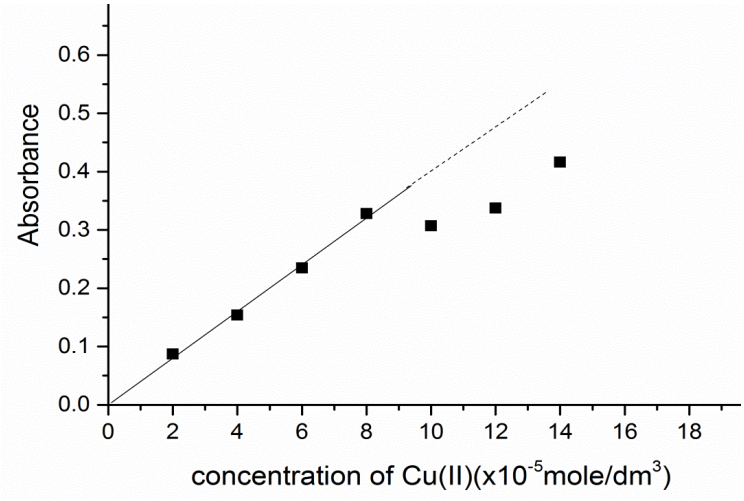


Figure 6. Beer's law plot for Copper(II)-Schiff base complex

Stoichiometry of Complex

The composition of the complex was found to be 1:2 (M:L), as estimated by mole ratio method (Figure 7) and Job's continuous variation method (Figure 8). Stability constant of the complex was found to be 3.08 x 10^4 (Figure 9) which was estimated by Turner Anderson method.

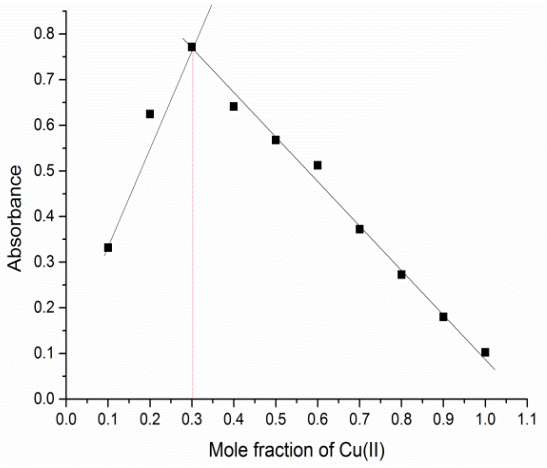


Figure 7. Mole ratio plot for Cu(II)-MAMTT complex

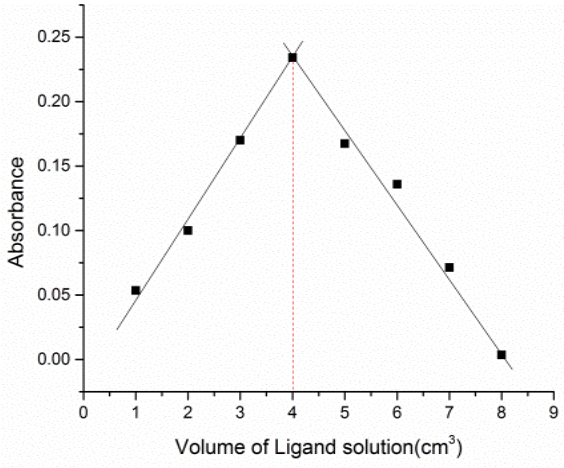


Figure 8. Job's continuous variation plot for Cu(II)-MAMTT complex

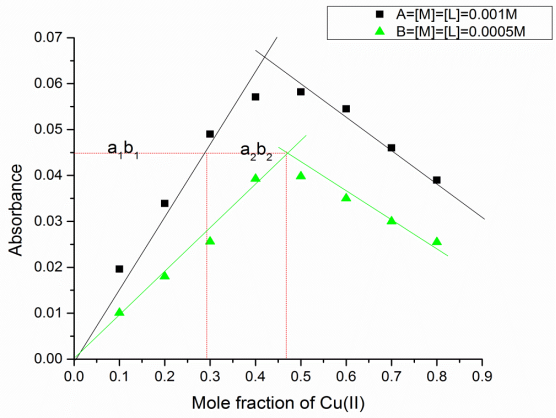


Figure 9. Modified Job's plot of Cu(II)-Schiff base complex

Effect of Diverse Ions

Along with the presence of diverse ions, the absorbance value of the complex Cu(II)-Schiff base containing 40 µg of Cu(II) was studied. The results are presented in Figure 10.

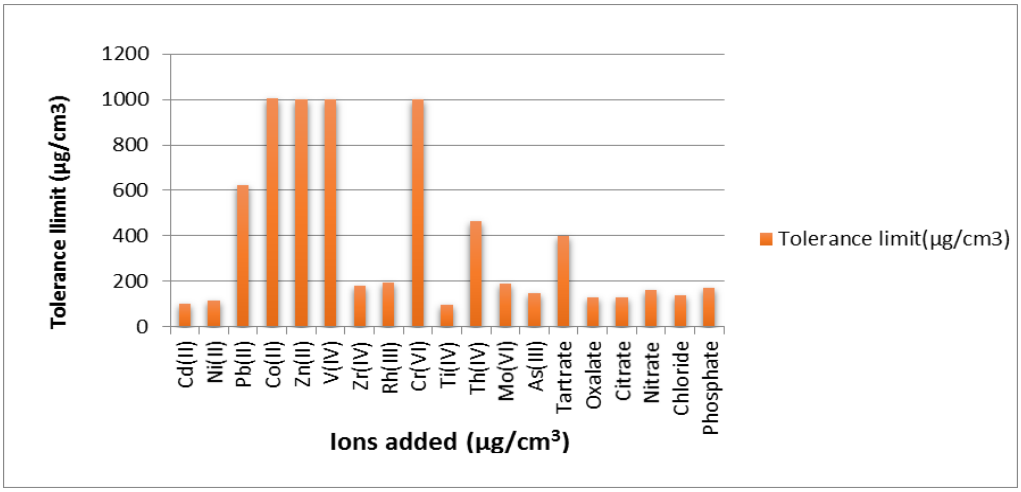


Figure 10. Study of interference of diverse ions

The above data suggests that several associated anions and cations do not interfere when they are present in large quantities.

Precision and Accuracy

To evaluate the precision and accuracy of the method, the amount of Cu(II) was determined in four different samples under the reliable experimental conditions. The results are mentioned in Table 1. The relative error and relative standard deviation are not exceeding ±0.42% and ±0.3%. Therefore the method is found to be more precise and accurate. Table 2 gives the entire analytical data.

Table 1. Determination of Cu(II) ions in copper sulphate solution.

Cu(II) (µg/mL)		Standard deviation	Relative standard deviation	Relative error
Taken	Found*			
12.7	12.4	0.044	0.301	-2.5
25.4	25.1	0.054	0.282	-1.0
38.1	38.0	0.035	0.190	-0.13
50.8	50.4	0.027	0.142	-0.74

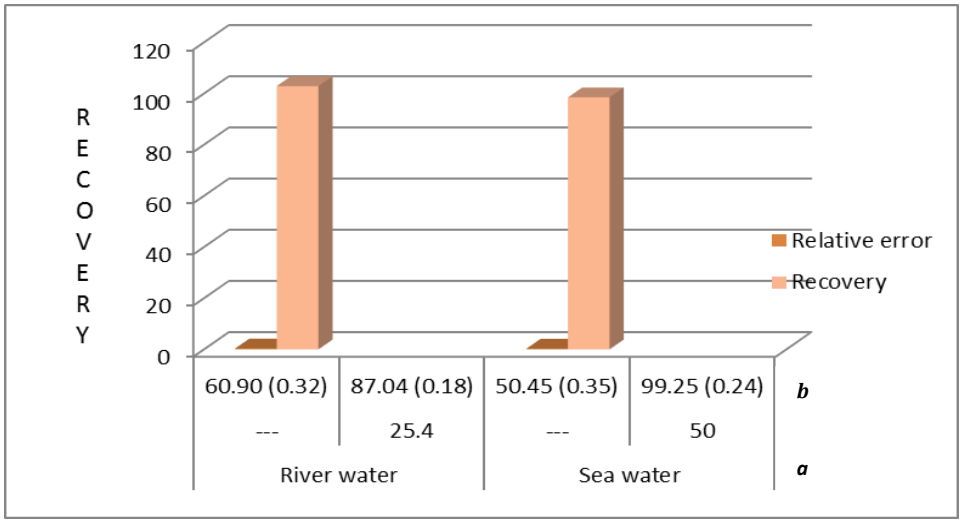
(*Average of five determinations)

Table 2. Physico-chemical properties of Cu(II)-Schiff base complex.

Characteristics	Results
λ_{max}	613
Optimum pH range	5
Beer's law validity range	12.7-50.83 µg mL^{-1}
Composition of the complex	1:2
Standard deviation in the determination of Cu(II) from12.7 – 50.83 µg/mL	0.04
Relative standard deviation	0.2287
Molar absorptivity	0.307x10^4 L $mol^{-1}.cm^{-1}$
Sandell's sensitivity	0.020 µg/cm^2
Detection limit	6.328 µg/cm^3
Quantification limit	19.177 µg/cm^3

Applications: Analysis of Water

The analytical applicability of the current process was evaluated by the determination of Cu(II) in river water, tap water, well water and rainwater (10 µg/mL). The filtration of the various samples of water collected from different resources were carried out. Then the Solution was spiked by taking requisite amount of Cu and diluted [15-18]. Then absorbance of each sample was measured to find out the amount of Cu(II)present. The results are presented in the form of graph (Figure 11).



[a] Samples were collected at Thokkottu, Mangaluru
[b] values in parenthesis are the relative standard deviations for n = 3

Figure 11. Analysis Cu(II) in various samples of water

Conclusion

The proposed process is found to be simple, speedy and accurate. It does not require heating and extraction and also the reagent is readily available. The synthesized Schiff base was characterized by IR and NMR spectroscopic techniques. The color change was very much sharp on the addition of Schiff base solution to the metal solution, which reveals the formation of complex. The interference of other ions in the determination of copper is negligible. This method of determination of copper works under acidic condition. This process can be used for the estimation of minute quantity of Cu(II) in various water samples.

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Conflict of Interest

The authors declare that they have no competing interests.

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References

[1] M. Acquarone, M. Paiusco, *Physica C*, **1993,** *210*, 373–385. [CrossRef], [Google Scholar], [Publisher]

[2] K.B. Chandrasekhar, K.H. Reddy, T.S. Reddy, *J. Indian Chem. Soc*., **2003**, *80*, 930–933. [Google Scholar]

[3] F.J. Huo, C.X. Yin, Y.T. Yang, J. Su, J.B. chao, D.S. Liu, *Anal. Chem*, **2012**, *84*, 2219–2223. [CrossRef], [Google Scholar], [Publisher]

[4] A.M. Abu-Dief, I.M.A. Mohamed, *J. Basic Appl.*, **2015**, *4*, 119–133. [CrossRef], [Google Scholar], [Publisher]

[5] H. Schiff, *Eur. J. Org. Chem.*, **1864,** *131***,** 118–119. [CrossRef], [Google Scholar], [Publisher]

[6] U. Schiff, *Biodiversity heritage Library,* **1866**, *2,* 201–257. [Publisher]

[7] P.R. Reddy, S. Rajeshwar, B. Satyanarayana, *J. Photchem. Photobiol. B*, **2016**, *160*, 217–224. [CrossRef], [Google Scholar], [Publisher]

[8] K. Ravindhranath, Rasayan *J. Chem.*, **2012**, 5, 38–41. [Google Scholar], [Publisher]

[9] E.S. Scott, L.F. Audrieth, *J. Org. Chem.*, **1954,** *19*, 742–748. [CrossRef], [Google Scholar], [Publisher]

[10] G.R. Burns, *Inorg. Chem.*, **1968,** *7*, 277–283. [CrossRef], [Google Scholar], [Publisher]

[11] K.S. Dhaka, J. Mohan, V.K. Chadha, H.K. Pujari, *Indian J. Chem.*, **1974**, *12*, 288. [Google Scholar]

[12] G. Shafiee, M Ghaedi, A. Taghvamanesh, A. Mohamadizadeh, *Asian J. Chem.*, **2007,** *19*, 1065–1074. [Google Scholar], [Publisher]

[13] A.S. Hankare, V.D. Barhate**,** *Int. J. Curr. Pharm. Res.*, **2014,** *6*, 30–33. [Google Scholar]

[14] D. Admasu, D.N. Reddy, K.N. Mekonnen, *SpringerPlus*, **2016**, *5*, 1169. [CrossRef], [Google Scholar], [Publisher]

[15] R.A. Nalawade, A.M. Nalawade, G.S. Kamble, M.A. Anuse, *Spectrochim. Acta A*, **2015**, *146*, 297–306. [CrossRef], [Google Scholar], [Publisher]

[16] T.S. Lobana, R. Sharma, G. Bawa, S. Khanna, *Coord. Chem. Reviews*, **2009**, *253*, 977–1055. [CrossRef], [Google Scholar], [Publisher]

[17] S.E. Ghazy, R.M. El-Shazly, M.S. El-Shahawi, G.A. Al-Hazmi, A. A. El-Asmy, *J. Iran. Chem. Soc.*, **2006,** *3*, 140–150. [CrossRef], [Google Scholar], [Publisher]

[18] K.C. Sarker, M.R. Ullaha, *Int. J. Chem. stud.*, **2013**, *1*, 5–14. [Google Scholar], [Publisher]

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