International Journal of Science and Research Archive
eISSN: 2582-8185
Cross Ref DOI: 10.30574/ijsra
Journal homepage: https://ijsra.net/

(RESEARCH ARTICLE)

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Application of [2-((Z)-(4-hydroxy-3-methoxy-5-((E)-thiazol-5-yldiazenyl) benzenylidene) amino) benzoic acid] (MThBABA) in Extractive Spectrophotometric Determination of Copper (II)

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International Journal of Science and Research Archive, 2024, 12(02), 629–635

Publication history: Received on 27 May 2024; revised on 09 July 2024; accepted on 12 July 2024

Article DOI: https://doi.org/10.30574/ijsra.2024.12.2.1250

Abstract

For estimation of copper at the trace level a simple, sensitive and rapid spectrophotometric method has been developed using MTHBABA reagent. Elemental and spectral analysis techniques were used for characterization of MTHBABA reagent. Solvent chloroform was used for quantitative (99.61 %) extraction of Copper (II) with the help of MTHBABA at pH range 5.6 to 6.7 from aqueous solution. An intense peak of λ max (540 nm) was observed from chloroform extract. Concentration range for Beers law observed between 2.5 to 30 µg/ml for Copper (II). For Copper complex MTHBABA molar absorptivity and sandell's sensitivity was found to be 39524 L $mole^{-1}cm^{-1}$ and 0.0243 μgcm^{-2} respectively. Job's Continuous Variation as well as the Mole Ratio Method confirm complex nature 1:1 (Copper: MTHBABA). During MTHBABA present study interference of various ions is also discussed. The proposed method has been successfully applied for determination of Copper (II) in alloy and pharmaceutical samples

Keywords: MTHBABA; Copper (II); Spectrophotometry; Solvent Extraction; Alloy; Pharmaceutical

1. Introduction

Copper is a transition metal. It has atomic number 29. Copper occurs in nature in elemental state, in sulfides, arsenites, chlorides, and carbonates. At the trace level copper plays a significant role in many biological systems. Copper is also present in the blood of invertebrate animals in the form. of hemocyanin. Copper is also a potentially dangerous toxin exploited by immune cells and that Copper dysregulation causes human disease, the homeostasis of this metal ion must be under exquisite regulatory control. Various analytical methods are developed to determine copper at micro level. Among these methods. The spectrophotometry coupled with the solvent extraction method is extensively used for estimation of metal at trace level [1,7] These methods are of great significance in the pharmaceutical science [3]

Spectrophotometric determination of Copper (II) is done by various reported methods [2,4,5,6,8,9]. In present communication we report the spectrophotometric determination of Copper (II) by using [2-((Z)-(4-hydroxy--3-methoxy-5-((E)-thiazol-5-yldiazenyl) benzenylidene) amino) benzoic acid] (MThBABA).

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2. Materials and methods

2.1. Conventional method of synthesis of ligand [2-((Z)-(4-hydroxy-3-methoxy-5-((E)-thiazol-5-yldiazenyl) benzylidene) amino) benzoic acid

2.1.1. Preparation of azo compound

2-Aminothiazol (0.005 moles) solution was diazotised by adding sodium nitrite solution (0.005 moles) in instalment of 2 ml at a time and maintaining the temperature below 5 ˚C for 30 min. Then the cold diazonium salt was poured into this vanillin solution (25 cm^3 of 10 % sodium hydroxide) (0.005 moles) very slowly to this solution and stirring it till red crystals separates out. After an hour, filtered it in a Buchner funnel with suction. The product was washed with a saturated solution of sodium chloride.

2.1.2. Preparation of Schiff's base by conventional method:

In a round bottom flask containing a few porcelain pieces using 50 ml of ethyl alcohol as solvent 0.01 moles of azo compound is taken along with 0.01 moles of 2-aminobenzoic acid. It is attached to water condenser and refluxed for 3 hours. After that mixture is poured into a beaker and kept in the fridge overnight. The product was filtered and dry. Brown crystals of Schiff's base, 2-(((Z)-4-hydroxy-3-methoxy-5-((E)-thiazol-5-yldiazenyl) benzylidene) amino) benzoic acid Figure 1. It has been recrystallized [12] and is characterized by elemental and spectral analysis Table 1&2. The full name of Schiff's base is used as MTHBABA in the entire paper.

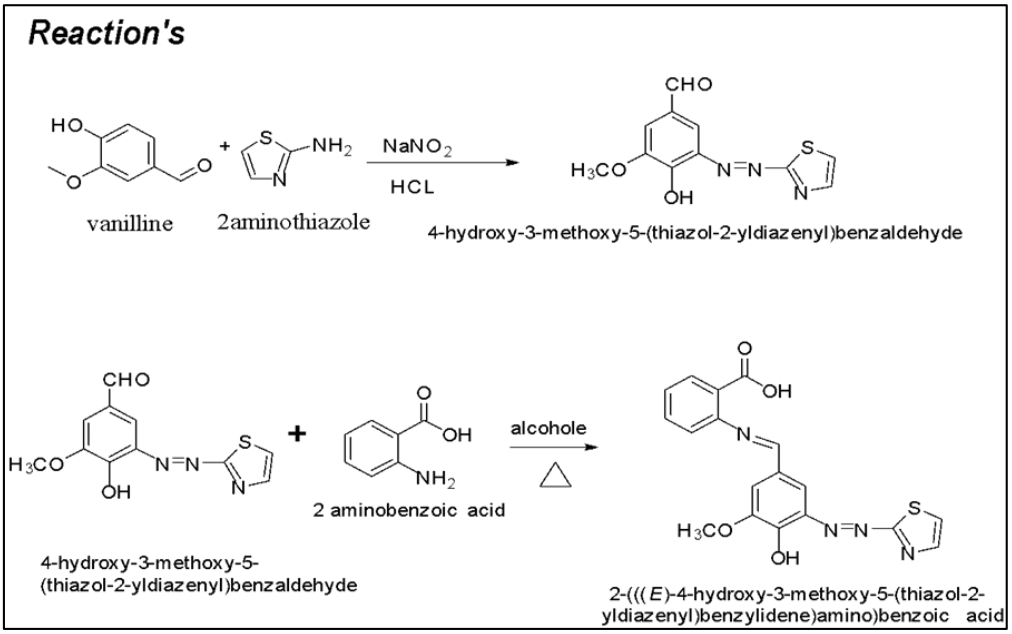

Figure 1 Preparation of Schiff's base

Table 1 The Analytical and physical data of ligand

Compound (Colour)	Molecular Weight	Reaction period & %yield	Reaction period % Yield	M.P.	% Elemental Analysis Found (Calculated)				
		Conventional methods	Micro synthesis		C	H	O	S	N
Ligand (greenish brown)	382.39	4 hours 79%	0.4 Minutes 92%	244	56.53 (56.54)	3.70 (3.69)	16.78 (16.79)	8.40 (8.39)	14.67 (14.65)

Table 2 The Important IR bands of Ligand

Compound	υ phenolic (-OH) cm^{-1}	υ(C-O) stretching cm^{-1}	υ(C=O) stretching cm^{-1}	υ(C=N) stretching cm^{-1}
Ligand	3376	1272	1683	1629

2.1.3. Green synthesis: Preparation of Schiff's base by microwave method: -

0.005 moles of azo compound and 0.005 moles of 2-aminobenzoic acid along with few drops of pure alcohol were taken in a beaker which was then irradiated in the microwave oven at 180^0 for 2 minutes. The reaction was completed in a short time (2 min) with higher yields. Greenish brown crystals of Schiff's base are obtained.

2.2. Stock Solution Preparation: -

A stock solution of copper was prepared by dissolving accurately weighed copper sulphate in water containing sulphuric acid and it was standardized gravimetrically [10, 11]. Working solutions of Copper (II) were made by diluting the stock solution to an appropriate volume. All other reagents used were of AR grade and all the solutions were prepared in doubly distilled water.

2.2.1. Procedure for the extractive spectrophotometric determination of Copper (II)

2 mL of buffer solution of pH 6.0 and 2 mL of 1% solution of MThBABA prepared in DMF were added to an aliquot of aqueous solution containing 1-50 µg of Copper (II). The volume of solution was made up to 10 mL by using distilled water. The phases were then allowed to separate after the aqueous solution had been equilibrated for one minute with 10 mL of organic solvent. The organic solvent (chloroform) extract was collected in a 10 mL standard measuring flask and made up to mark with chloroform. At 540 nm the absorbance of chloroform extract was measured against a reagent blank prepared with similar conditions. Using a preset calibration curve, the observed absorbance was used to calculate the quantity of Copper (II) contained in the sample solution.

Prior to extraction and pH adjustment, the appropriate foreign ions were introduced to the aqueous phase to evaluate the effects of other ions.

2.2.2. Procedure for the determination of Copper (II) in alloy sample

The aluminum alloy sample weighing 0.1 -- 0.2 g was dissolved in 10 mL of aqua regia by heating it to dryness. The residue was dissolved in 10 ml of diluted hydrochloric acid & filtered. The resultant solution was diluted to 250 mL with distilled water. By using the previously mentioned approach, a 1 ml aliquot of this solution was examined for Copper (II).

2.2.3. Procedure for the determination of Copper (II) in pharmaceutical sample

The pharmaceutical sample weighing 0.5-1.0 g was dissolved in boiling 10 mL of aqua regia. After evaporating the solution to dryness and the residue was obtained which was dissolved. in 5 mL of diluted hydrochloric acid. The resulting solution was then diluted to 100 mL with distilled water.

Using the method previously described, a 1 mL aliquot of this solution was tested for Copper (II) using a 1 mL 0.5 M solution of Triethanolamine to mask Iron (III). The results of the analysis of the samples were equivalent to those obtained by the diethyldithiocarbamate method [12] for Copper (II) (Table 4).

3. Results and discussion

(MTHBABA) was able to extract Copper (II) quantitatively (99.61%) into chloroform from an aqueous solution of pH 5.6 to 6.7.

Extraction of Copper (II) was done by using various organic solvents. The values of extraction coefficient were in the order chloroform > carbon tetrachloride > n amyl alcohol > n-butanol > ethyl acetate> chlorobenzene > bromobenzene > benzene > xylene is depicted in figure 3 Due to the highest extraction coefficient, chloroform was used as solvent for extraction.

An intense peak at 540 nm was shown by chloroform extract of Copper: MTHBABA complex (Figure-3) The absorbance due to the reagent is negligible at this wavelength, (wavelength for reagent = 400) Hence the entire experiment was done at wavelength 540 nm.

Calibration curve was plotted as shown in Figure-5 between absorbance values and concentration of copper complex. Calibration curve is linear over a concentration range of 2.5 to 30.0 µg/ml. The molar absorptivity observed to be 39524 L mol^{-1} cm^{-1} and Sandel's sensitivity was 0.0243 µgcm^{-2} respectively.

1.0 % Dimethyl formamide solution (2 ml) of MTHBABA was optimum to extract 30 µg of Copper (II). It was found that color of the chloroform extract was stable for at least 24 hours at room temperature.

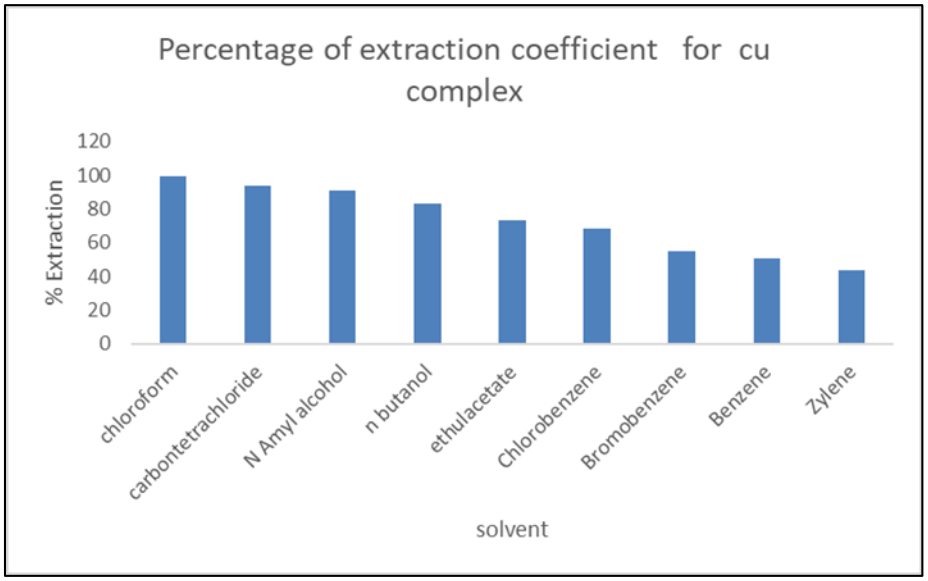

Figure 2 Chloroform as best solvent

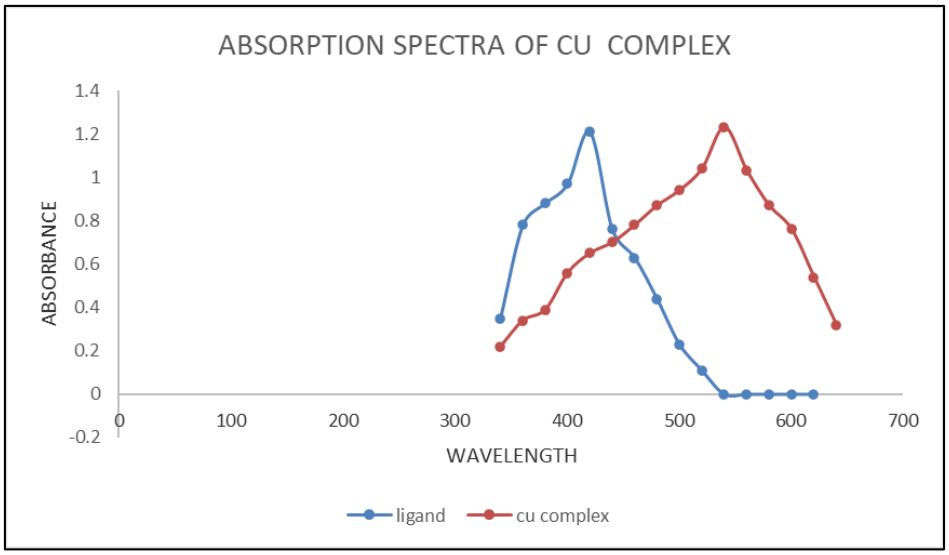

Figure 3 Absorbance Spectra of MTHBABA and Copper– MTHBABA Complex

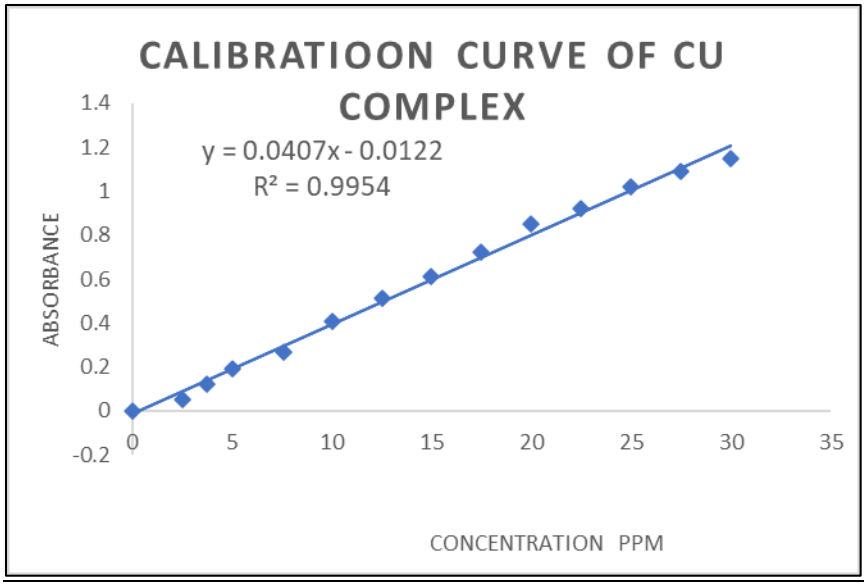

Figure 4 Calibration Curve of Cu–MThBABA Complex

3.1. Effect of other ions

Study of interference of ions was done. Copper (II) (20 µg) was used. It was found that following ion did not interfere in the study of study of Copper (II)

10 mg each of Lithium (I), Barium (II), Mercury (II), Tin (II), Strontium (II), Zirconium (II), Calcium (II), Zinc (II), Vanadium(V), Magnesium (II), Cadmium (II) and

5 mg each of Thorium (IV), Cerium (IV) and Tungsten (VI).

0.1 mg each of Ruthenium (III), Rhodium (III), Molybdenum (IV) and Platinum (IV)

20 mg each of sulphate, sulphide, nitrate, nitrite, chloride, bromide, iodide, fluoride, phosphate, citrate, triethanol amine, thiocyanate, acetate and 5-sulphosalicylic acid.

Appropriate masking agents were used to remove the interference by the various ions shown in table- 3.

Table 3 Interference by Various ions

Sr. No.	Interfering ion	Amount added in mg	Masking agent added 1 ml of 0.5 M solution
1	Manganese (II)	10	Potassium tartrate
2	Silver(I) & Palladium (II)	10	Potassium thiocyanate
3	Iron (III), Chromium (III) & Vanadium (II)	10	Triethanol amine
4	Nickel (II)	10	5-sulphosalicylic acid

3.2. Composition of the Extracted Complex:

Chloroform extract of Copper: MTHBABA complex was subjected to Job's continuous variation and Mole ratio method. It was found that composition of the extracted complex was 1:1 (Copper: MTHBABA).as shown in Figure 5 and 6.

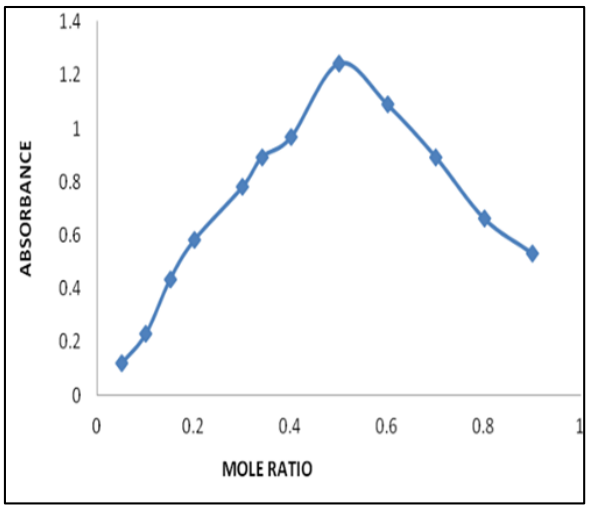

Figure 5 Composition of (Copper: MThBABA) Complex by Job's continuous Method

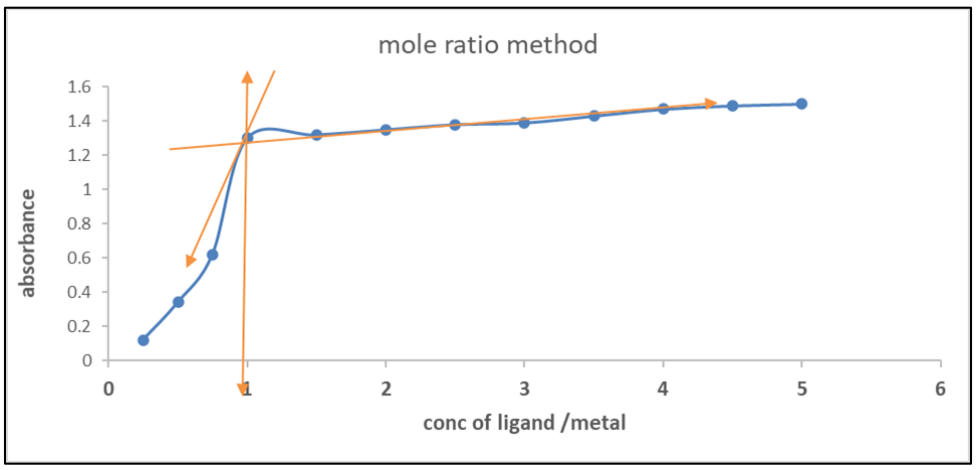

Figure 6 Composition Of (Copper: MThBABA) Complex by Mole Ratio Methods

3.3. Accuracy, Precision, Sensitivity and Applications of Method

To determine the accuracy and precision of the proposed method the experiment was repeated ten times. 20 µg of Copper (II) in 10 cm^3 solutions. The average of 10 determination of 20 µg of Copper (II) in 10 cm^3 solutions was 19.89 µg, which varied between 19.72 and 20.19 at 95 % confidence limit. Sandell's sensitivity and standard deviation is 0.0243 μgcm^{-2} and ± 0.368 respectively.

4. Application of the method

Table 4 Determination of Copper (II) In Alloy Sample and Pharmaceutical sample

Percentage of Copper (II)	**Alloy Sample and Pharmaceutical sample**	
	Aluminium alloy	**Revital capsule**
Proposed method	7.89*	0.44*
Diethyl-dithiocarbamate method [12]	8.02*	0.49
Reported method	7.92	0.50

* Average of three determination

The results of the analysis of the Alloy Sample and Pharmaceutical sample were comparable to those obtained by the diethyldithiocarbamate method [12] for Copper (II) (Table 4).

5. Conclusions

The reagent MThBABA forms complex with Copper (II) which was easily extracted into organic phase (chloroform). This method is feasible, sensitive and cost effective. The various factors for maximum extraction were optimized & this method is used as an analytical tool to find the amount of Copper (II) in alloys and pharmaceutical samples.

Compliance with ethical standards

Acknowledgement

The authors gratefully acknowledged the use of central instrumentation facilities at Vivekanand Education Society's College of Arts, Science and Commerce funded by FIST-DST (Department of Science & Technology, Government of India) and DBT Star college scheme. The Authors are also grateful to Dr. Anita Kanwar, Principal VES College of Arts Science and Commerce, for providing all the necessary facilities to complete the above research project.

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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