Spectrophotometric Determination of Copper (II) by Used of New Hetero Cyclic azo Reagent 4-[(6-Methoxy-2-benzothiazolyl)azo] resorcinol (6-MBTAR)

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Abstract

The new azo reagent 4-[(6-Methoxy-2-benzothiazolyl) azo] resorcinol (6-MBTAR=LH₂) was prepared by coupling reaction between (6-methoxy-2-benzothiazolyl diazonium) chloride with resorcinol in alkaline alcoholic solution. The reagent was examined by using element analysis, UV-Vis. and infrared spectra. A sensitive and selective spectrophotometric method is proposed for the rapid determination of copper(II) using (6-MBTAR), as anew spectrophotometer reagent. The reaction between this reagent and copper(II) is instantaneous at 634 *nm* (λ_{max}) and pH=6.5 to form green complex having a mole ratio 1 : 2 (metal : ligand) and the absorbance remains stable for over 24 hr. Beer's law is obeyed in the rang of (1-30) µg.ml⁻¹ with molar absorptivity (€) = 0.1019×10⁴ L.mol⁻¹.cm⁻¹and a detection limit of 0.97 µg.ml⁻¹. The precision and accuracy were obtained to be R.S.D%=2.3%, Re%=101.2% and E_{rel}%= +1.2%. The method is successfully employed for the determination of copper(II) in soil samples. The most important interference were due to Ni⁺², Zn⁺², Co⁺², Cd⁺², Fe⁺³, and Cr⁺³ and suitable masking agents were used.

الخلاصة:

1.Introduction

A large number of thiazolyl azo phenols and its derivatives have been prepared and investigated for many purposes. These compounds are applied for dyeing fibers^(1,2), and have been used as sensitive chromogenic reagents⁽³⁻⁶⁾. In addition to used as reagents for spectrophotometeric and extraction-photometric determination of many metal ions^(7,8), some of these days useful as indicators in complexometric titration. These dyes have been useful in the spectrophotometric determination due to its good selectivity and sensitivity over a wide range of pH and because they are relatively easy to synthesized and purify⁽¹⁰⁻¹²⁾. Copper is an essential element for human body was important to establish its function in the body, oxygen and electrons transport constituent of enzymes to redox reactions involvement in the mobilization to hemoglobin synthesis⁽¹³⁾, and copper levels in serum is used as marker for many disease⁽¹⁴⁾. So copper determination is of great interest to analytical chemistry particularly to soil and environmental chemists.

In this work we describe here the synthesis of new heterocyclic azo reagent 4-[(6-methoxy-2-benzothiazolyl)azo] resorcinol (6-MBTAR=LH₂) and used it for spectrophotometric determination of copper(II).

2. Experimental

2.1. Apparatus and materials

Absorption spectra were recorded with a model (UV – 1650) Shimadzu analyzer while absorption measurements were obtained with spectrophotometer(RSP – 721) Triup International corp, both with matched 1cm quartz cells and ethanol as solvent. Elemental analysis (C.H.N)were carried out by Perkin-Elmer 2400 Elemental analysis. I.R spectra were recorded with FTIR-8000 Shimadzu spectrophotometer, in the (4000 – 400) cm⁻¹ range using CsI disc. pH measurements were carried out using a Microprocessor 211 pH meter(pH ± 0.001),and 214 HANNA instruments conductivity meter was used . Melting points were taken in open capillaries on a Stuart melting point apparatus and are uncorrected.

All chemicals and solvents were of highest purity and used as supplied by Fluke, BDH and riedel-dehaën except of 2-amino-6-methoxybenzothiazole was prepared by reported procedure⁽¹⁵⁾. All solutions were prepared using d-ionized water.

2.2. Synthesis and characterization of the reagent (6-MBTAR)

synthesis of (6-MBTAR) Fig.1, was followed using the general procedure⁽¹⁶⁾ (with some modification). 2-amino-6-methoxybenzothiazole (1.84gm, 0.01mol) was dissolved in 50 ml of distilled water and 6 ml of concentrated hydrochloric acid and diazotized below 5 °C with (0.75gm, 0.01mol) of sodium nitrite. The resulting diazonium chloride solution was added drop wise with cooling to solution of (1.1gm, 0.01 mol) of resorcinol dissolved in100 ml alkaline ethanol. After leaving in the refrigerator over night. The mixture was neutralized with dilute hydrochloric acid to (pH=6.0) The solid product was filtered off, washed with 500 ml cold distilled water and crystallized twice from hot ethanol and dried over CaCl₂. The yield was 52% of dark red crystals, melting at 168 °C, which is in soluble in water, but soluble in most organic solvents. The structure of (6-MBTAR) was confirmed by I.R spectrometry . Analysis,C₁₄H₁₁N₃O₃S required;55.81% C,3.65% H and 13.95% N. Found , 55.48% C , 3.51 %H and 13.74% N.



Fig. 1: The structure of reagent (6-MBTAR=LH₂) 4-[(6-Methoxy-2-benzothiazolyl)azo] resorcinol

2.3. Standard copper solution

A stock solution of copper 100 ppm (μ g.ml⁻¹), prepared by dissolving (0.0251 gm) of CuCl₂.2H₂O in 100 ml of distilled water, working solutions were prepared freshly by appropriate dilution of the stock solution.

2.4. Standard reagent solution

A solution of 1.75×10^{-4} M was prepared by dissolving (0.0131 gm) of reagent (6-MBTAR) in 250 ml of absolute ethanol.

2.5. General procedure

One ml of solution containing less than 100 μ g.ml⁻¹ of copper (II) was transferred to a 10 ml calibrated flask and adjust the pH to 6.5 with ammonium acetate buffer solution, added 2.5 ml 1.75×10^{-4} M ethanolic (6-MBTAR) solution and diluted to the mark with distilled water. The absorbance of the resultant solution was measured after 10 min at 634 *nm* at 25 °C against a reagent blank prepared in a similar way but with out of copper(II).

3. Results and Discussion

3.1. Infrared spectra

The infrared spectroscopic data of reagent (6-MBTAR) and 6-MBTAR-Cu(II) chelat have been studied. The comparison between spectra of reagent with the coordination Cu(II)-complex have revealed certain characteristic differences some of these main shifts along with conclusions are given below:-

- 1-The spectrum of free reagent shows a broad and weak absorption band around 3350 cm⁻¹ due to v (O-H). This suggests a strong inter-molecular hydrogen bonding^(17,18). In the spectrum of Cu(II)-Complex the very broad and week absorption band around 3300 cm⁻¹ due to meta hydroxyl group v (O-H).
- 2-Two weak bands had been observed at 3100 cm⁻¹ and 2940 cm⁻¹ in the spectrum of the free reagent are due to v (C-H) aromatic and aliphatic respectively. These bands are stable in position as well as in intensity for both reagent and Cu(II)-Complex ⁽¹⁹⁾.
- 3-The ν (C=N) of thiazole ring⁽¹⁹⁾ appear at 1605 cm⁻¹ in the spectrum of reagent. This band shifts to lower frequency at 1590 cm⁻¹ with a little change in shape . These differences suggest a linkage of copper ion with nitrogen of hetero cyclic thiazole ring⁽²⁰⁾.
- 4-The spectrum of reagent shows two absorption bands at 1495 cm⁻¹ and 1480 cm⁻¹ due to azo group ν (N=N).The position of these bands in the spectrum of Cu(II)-complex is shifted to alower frequencies at 1435 cm⁻¹ and 1420 cm⁻¹ with decreased in intensity. This may indicates that it has been effected on coordination with copper ion^(20,21).
- 5- Two bands at 1270 cm⁻¹ and 840 cm⁻¹ in the spectrum of reagent , these bands are due to v (C-S) of thiazole ring⁽²²⁾. The unchanged of these band in copper complex means that the sulpher atom of the heterocyclic ring does not participate in coordination^(20,23).
- 6-New weak bands in the region(560-470) cm⁻¹ occurring in the spectrum of copper complex .These bands did not present in the spectrum of free reagent may be attributed to v (M-O) and v (M-N)^(24,25).

Thus, the above IR spectra data lead to suggest that the reagent (6-MBTAR) behaves as a tridentate chelating reagent coordinating through the position of phenolic oxygen (ortho OH),nitrogen of azo group and thiazole ring nitrogen. Fig.2 shows the spectra of $[Cu(LH)_2]$ and reagent (LH₂).



Fig. 2: FTIR Spectra of ;(a) the reagent (6-MBTAR = LH₂) and (b) [Cu(LH)₂]

3.2. Absorption spectra and characteristics of the complex

The absorption spectra UV-Vis of the reagent (6-MBTAR) and(6-MBTAR)-Cu(II) complex are shown in fig.3. The maximum absorbance (λ_{max}) of the reagent occurs at 429 *nm* and copper complex maximum absorbance (λ_{max}) at 634*nm*, hence the wavelength difference ($\Delta \lambda_{max}$) is 205 nm. The reagent reacts immediately with copper(II) forming an violet complex in aqueous medium at pH = 6.5 and the absorbance reached its maximum with 10 min, and remained stable, for at least, 24 hr, at room temperature.



Fig. 5: The absorption spectra of free reagent (R) and Cu(II)-Complex in pH=6.5; Con.=2.25x10⁻⁴ M, in aqueous ethanolic solution 50%(V/V);R=(6-MBTAR)

3.3. Effect of pH

The influence of pH on the absorbance (6-MBTAR)-Cu(II) complex is shown in fig.4, where the maximum absorbance obtained in the range of pH= 5.0-8.5, at pH < 5 (λ_{max} =634 nm) a decreases in absorbance was observed due to complication between the hydrogen ion and copper(II) cat ion, with the increase of the hydrogen ion concentration the complication leads to a less favorable complex formation.



Fig. 4: Effect of pH on the absorbance of copper complex, $Cu(II) = 30 \ \mu g.ml^{-1}(\lambda max=634 \ nm)$

3.4. Effect of temperature

The effect of temperature on the absorbance of the 6-MBTAR-Cu(II) complex was studied. The study was performed at temperature between 10°C and 80°C fig.5. The maximum absorption was obtained when the temperature was varied between 20°C and 40°C, the absorbance gradually decreased with increasing temperature until it reaches 80°C which may be due to dissociation of the complex.



Fig. 5: Effect of temperature on the absorbance of copper complex (6-MBTAR-Cu(II)) (\lambda max=634 nm).

3.5. Effect of time

It was found that the absorbance of copper 6-MBTAR-Cu(II) complex chromogenic system reaches its maximum value with in 10 mint at room temperature and remains stable for at least 24 hr. Fig.6.



Fig. 6: Effect of time on the absorbance of copper complex, $Cu(II) = 50 \ \mu g.ml^{-1}(\lambda max=634 \ nm)$

3.6. Composition of the complex

The empirical formula of complex was determined by the spectrophotometric method of mole ratio at the pH = $6.5^{(26)}$. The curve indicated the formation a (1 : 2) metal : ligand (λ_{max} =634 nm) was obtained as shown in fig.7. The stability constant was found⁽²⁷⁾ to be $9.6 \times 10^7 \text{ L}^2$. The structural formula of the complex may be proposed in fig.8.



Fig. 7: Mole ratio(M:L) of 6-MBTAR-Cu(II) complex at pH = 6.5,Conc. Of reagent and Cu(II) =1.75 x10⁻⁴ m

3.7. Analytical characteristics

3.7.1. Linearity range

Linear calibration graph through the origin was obtained and showed that the complex obeyed Beer's law over the range $(1 - 30) \ \mu g.ml^{-1}$ of Cu(II). The molar absorptivity (C) was found to be $0.1019 \times 10^4 \ L.mol^{-1}.cm^{-1}$ and the Sandal's sensitivity⁽¹⁰⁾ was $0.0062 \ \mu g$ of Cu(II)/cm² and correlation coefficient (r) was 0.9997. The high value of (r) indicate the good linearity and correspondence to Beer's low.

3.7.2. Precision and Accuracy

Seven replicate determination of standard solution containing 15 μ g of Cu(II) was carried out under optimum conditions. The relative standard deviations (R.S.D) was 2.3%. The recovery and $E_{rel}\%$ for the complex solution containing 20 μ g.ml⁻¹ of Cu(II) were found to be 101.2%, and +1.2% respectively. The detection limit was found to be 0.97 μ g.ml⁻¹. these values indicate that this method has the highest accuracy and precision.

3.7.3. Interference studies

The effect of the ions Ni(II), Zn(II), Co(II), Cd(II), Fe(II), Fe(III) and Cr(III) which form complex with the reagent (6-MBTAR) during its reaction with Cu(II) was studied. The selectivity various masking agents are examined for eliminating the effect of the interfering seventh ions. These are ascorbic acid, 5-sulphosalicylic acid, sodium fluoride and 1,10-phenathroline. The result are shown in Table.1.

Cu (II) / ppm	Foreign ion	Amount added / ppm	Error%
30	Ni (II)	30	0.3
30	Zn (II)	20	0.5
30	Co (II)	20	0.6
20	Cd (II)	30	0.0
20	Fe (II)	20	0.8
20	Fe (III)	20	1.0
20	Cr (III)	30	0.1

Table.1: Effect of foreign ions on the determination of Cu(II)

3.7.4. Analytical application

The proposed spectra photometric method will be of invaluable for the determination of copper(II) in soil samples generator. The result obtained from the proposed method was compared with those given by atomic absorption spectroscopy (AAS), (standard additions method). The concentration of copper(II) analyzed by the proposed method was found be 0.817μ g.ml⁻¹ and that (AAS) was found to be $0.769 \ \mu$ g.ml⁻¹. the results show a good agreement of the results obtained by the two methods.



Fig. 8: The suggest structural formula of [(6-MBTAR)-Cu(II)] complex [(LH)₂Cu] complex

Conclusion

The preparation of reagent (6-MBTAR= LH_2) is very simple and the proposed method is more simple ,speed and sensitive to determination of copper .stability constants refer to the high stability of complex .The copper complex under optimum conditions are stable to more than 24 hr.

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