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DETERMINATION OF Cu(II) IN BHEEMA RIVER WATER AND THEIR SEDIMENT SAMPLES OBTAINED FROM KALABURAGI, KARNATAKA, INDIA USING 2-HYDROXY ACETOPHENONE PHENYLHYDRAZONE DERIVATIVES BY SPECTROPHOTOMETRIC METHOD

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ABSTRACT

Two chromogenic reagents5-Chloro-2-hydroxy acetophenone phenylhydrazone (CHAPH) and5-Bromo-2-hydroxy acetophenone phenylhydrazone (BHAPH) were used for determination Cu(II) by spectrophotometric method. Both the reagents produce pale yellowish Cu(II) complexes at p^H range 7.0-9.0 and obeyed Beer's law in the concentration range of 0.13–1.4 and 0.42–1.25 µg/mL, respectively, for both Cu(II)– (CHAPH) and Cu(II)– (BHAPH). The molar absorptivity was 5.2×10^4 lit/mol cm at 380 nm, and 2.5×10^4 lit/mol cm at 350 nm, respectively, while the Sandell's sensitivity was found that 0.00384 and 0.00222 µg/cm^2 for both Cu(II)– (CHAPH) and Cu(II)– (BHAPH). The correlation coefficient was calculated from standard curves of Cu(II)– (CHAPH) and Cu(II)– (BHAPH) were 0.890 and 0.958, respectively. This method was usedfor Cu(II) determination in Bheema river water and its sediment samples, the results obtained were compared with the standard method using a flame atomic absorption spectrophotometer by using 2-acetylpyridinethiosemicarbazone[2-ATP] for Cu(II) determination.The stability is constant of the Cu(II) complexes with (CHAPH) and (BHAPH) reagent found to be 3.4×10^4 and 1.8×10^4, respectively, by Jobs method.

Keywords: Spectrophotometric, Sediment, Bheema River Water, Stability Constant, Complexes, Chromogenic.

INTRODUCTION

The deficiency of copper decreases the activity of many metalloenzymes, because copper is a trace metal and essential for several metalloenzymes activities.[1] Anemia, hair kinky and jaundice are different health issues due todeficiency of copper.[2] A serious threat to human health and the environment due to contamination by heavy metal ions, theseheavy metals ions are accumulating in living organisms throughout their lifetime, therefore these metals are considered toxic. Copper, iron and cobalt are certain essential trace elements to organisms, which are required per day in few milligrams; however, due to excessive intake of these trace elements can be harmful to humans, animals and plants. Especially copper can cause hemolytic crisis and neurological disturbances due to excessive intake of copper.[3]Among the total world'sproduction of copper, the major portion of copper is used in electrical equipment, apart from the biological activity of copper[2]and also finds its applications in agriculture as micronutrient fertilizers, fungicides, and insecticides, which causes for the contamination of various environmental samples, therefore the determination of copper in various environmental samples is becoming a challenging task.Copper plays a substantial role in the environment, can be considered either essential or hazardous to life.[4]Several instrumental techniques have been used for the determination of copper.[5,6]However, one of the inexpensive instrument that is spectrophotometric methods are often preferred, provide comparable sensitivity when appropriate color developing reagents are available.[7,8]

Copper is the third most essential trace element widely distributed[9] and it plays an important role in biological systems during cell respiration in the blood in vertebrate animals[10]. Copper has good

electricalproperties, therefore it is used in the electrical industry as fine wires, semiconductors, commuter bars, and high conductivity tubes.[12]Visible spectrophotometric determination ofcopper(II) ion was described with the influence of the structure of the molar absorptivity value of complex in aqueous solution with biruate.[13-14] A new reagent 2,5-dimercapto-1,3,4-thiazol[15] had been used forthe determination of copper(II) at a trace level bya simple spectrophotometric method.

Many spectrophotometric methods have been aromatic carboxylic acids as an amount of copper(II) ions. These acids are 1,4,8,11-tetrabenzyl-1,4,8,11 tetraazacyclodecane[16], 3-hydroxy-2-naphthoic acid[17], nitrilotriacetic acid[18], 3,8,13,18-tetramethyl-21H,23H-prophine-2,7,12,17-tetrapropionic acid.[19]The method involves several steps for the development of color, requires heating and waiting period for full-color development and also has a narrow pH range. Because of their biological and structural importance oxime compounds have been extensively used as spectrophotometric reagents for copper(II) ion. These reagents are 3-{2-[2-hydroxyimine-1-methylpropylideneamino]-ethylamineethyl-imino}-butane-2-one oxime, 3,3'-(1,3-propanediyldimine)bis-[3methyl-2-butane]dioxime[20], di(2-ethylhexyl)phosphoric acid and 5-dodecyl salicyldoxime.[21]These methods are selective and sensitive.Zincon (2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene) is an excellent colorimetric reagentused for the determination of copper(II) ion in aqueous solution. Zincon and it's complex with copper(II) were used in the presence of guanidine hydrochloride and urea used to labialized metal ions in proteins and also partial least square method [22] and solid phase spectrophotometric method.

In this present work, authors were developed two chromogenic reagents 5-Chloro-2-hydroxy acetophenone phenylhydrazone (CHAPH) and 5-Bromo-2-hydroxy acetophenone phenylhydrazone (BHAPH) for determination Cu(II) in Bheema river water and its sediments by spectrophotometric method. P^H and concentration ranges of applicability of Beer's law and many other factors influencing the sensitivity of the proposed method forthe determination of Cu(II) was also studied. The method was successfully applied to Bheema river water and its sediment samples as well and compared to the standard method.

EXPERIMENTAL

The chemicals used wereethanol, 99 % acetic acid, ammonium hydroxide, 65 % nitric acid, 35 % hydrochloric acid, 30 % hydrogen peroxide, ammonium chloride, 98 % sulphuric acid, sodium acetate98 % copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$). All these chemicals were A Rgrade. 10 % HNO_3 was used for cleaning all the glasswares.

Sample Collection

Samples of water were obtained from the river called the Bheema river located at kalaburagi district Karnataka and sediment samples are also collected from the same place. Topsediment composite samples were collected and dried by keeping in the sunlight, foreign objects and stones being separated by hand. They were stored into the plastic bags, dried in the oven, then ground to make fine powder, sieved to < 2 mm and stored in polyethylene bottles beforeuse for analysis.

Instrumentation

UV–Vis absorption spectra were recorded at 800–200 nm range by using Shimadzu 2450 double beam spectrophotometer.The pH measurement was carried out by using An ELICO digital pH meter (Model LI-120) with a combined glass electrode.The IR spectrum of the synthesized reagent was recorded using Perkin-Elmer (spectrum 100) IR spectrophotometer as KBr discs in the 4000–200 cm^{-1} range. The ^{1}HNMR spectra of the synthesized reagents were recorded by usingJEOL GSX-400 high-resolution spectrometer at room temperature using tetramethylsilane as the internal standard. Varian AA 240FS fast sequential atomic absorption spectrometer was used for the determination of copper concentration.

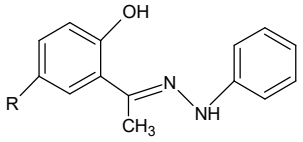
Preparation of Cu(II) and Buffer Solutions

A standard copper sulphate solution was prepared by dissolving 3.93 g of $CuSO_4 \cdot 5H_2O$ in 25ml of distilled water then add a few drops of conc. H_2SO_4 in 1 liter volumetric flask, then add distilled water up to the mark and this solution was standardized by iodometry.[23]To get the desired pH the different buffer solutions were prepared by mixing strong acids with its salts, weak acids with its salts, strong base with its salts and weak base with its salts.

Synthesis ofReagents

Procedure for the Preparation of Phenyl Hydrazones[24]

To a solution of the appropriatephenylhydrazine (24 mmol) in 40 ml methanol, 2-hydroxyacetophenone derivatives (24 mmol)was added and refluxed for three hours. After cooling the reaction mixture the phenyl hydrazone derivatives were crystallized and filtered, the yield was 91-94 %.



R= Cl, Br

Synthesis of Metal Complexes

$CuSO_4 \cdot 5H_2O$ salt (1 mmol) is dissolved in 25 ml of ethanol solution, mixed to 1 ml of ligands (2 mmol) in 25 ml ethanol solution and this reaction mixture was refluxed for 5.5 hours at 60 °C. A pale yellow solid was obtained after cooling the reaction mixture to room temperature. This was filtered and washed with distilled water and ethanol.

Absorption Spectra of Reagent Solutions and Metal Complexes

A 10 ml of buffer solution mixed to 1 ml of 0.01M reagent in a 25-ml volumetric flask, and then add distilled water up to the mark. The absorbance of this reagent solution was recorded against different wavelengths at constant pH. A 10 ml of buffer solution mixed to $CuSO_4 \cdot 5H_2O$ salt (1 mmol) and 1 ml of ligands (10 mmol) in a 25-ml volumetric flask and then add distilled water up to the mark and the absorbance of this metal complexes solution was recorded against different wavelength at constant pH.

Effect of pH on the Absorbance of the Metal Complexes

In a set of 25-ml volumetric flasks, prepare series of the solution by adding 10 ml of a buffer solution with different pH (pH3.0–10.0), constant amount of metal ion solution and reagents (1:10) and by adding distilled water make up to the mark each flask.The absorbance of each solution was recorded against the corresponding reagent blank at respective λmax (380 and 350 nm, for (CHAPH) and (BHAPH) respectively.

Determination of Copper in Bheema River Water Samples

One liter Bheema river water sample was filtered by using Whatman No.40 filter paper andit is evaporated by boiling nearto dryness by adding a mixture of 2ml of conc. H_2SO_4 and 5ml ofconc. HNO_3 to sulfur trioxide fumes in a fuming cupboard. Then cool the content and add 5 ml of concentrated HNO_3 was repeatedly heating to a dense fume continued to discharge until the solution becomescolorless and then it was cooled and neutralized with dilute NH_4OH and 1-2ml of tartrate solution. Thenthe solution was then filtered and poured into a 25mlcalibrated flask and dilute with distilled water up to the mark. Pipette out sample 2 ml this sample into 25 ml calibrated flask and the amount of copper content was determined by using spectrophotometric method with the standard calibration curve (Table-2).

Determination of Copper in SedimentSamples

A sediment sample of 0.2 g was dissolved in the 6 ml of HNO_3–HCl aqua regia solution in a conical flask and it was heated at 100 °C on a hot plate for 4 hours for the digestion of sediment samples[25,26]. Thecontent solutions were diluted to 25 ml with distilled water and it was used determination of Cu(II) by spectrophotometric method with the standard calibration curve[27]. The calibration of solutions wasmade and it is within the recommended linear ranges from 1g/L certified standards. The regression values were calculated (R^2) of the calibration curve was >0.85. The Cu content in the digested samples was determined at a wavelength of 380 and 350 nm, for (CHAPH) and (BHAPH) reagents, respectively. The analyses were carried out in triplicate and the results presented as mean ± SD, are given in Table-3.

Table-1: Physico-chemical and Analytical Characteristics of Cu(II)- CHAPH and Cu(II)- BHAPH

Characteristics	Results	
	Cu(II)- CHAPH	Cu(II)- BHAPH
λ max (nm)	380	350
pH range (Optimum)	7-8	8-9
Molar Absoptivity ($Lmol^{-1}cm^{-1}$)	$5.2x10^4$	$2.5x10^4$
Sandell'sSensitivity(µg/cm2)	0.0038	0.0022
Standard Deviation in the Determination of Cu(II) for ten determinations.	0.000324	0.000265
RSD	0.025%	0.032%
Regression Coefficient	0.890	0.958
Regression Equation	$A_{380} = 0.125\ C + 0.0521$	$A_{350} = 0.0932\ C + 0.0615$
Beer's Law Validity Range(µg/ml)	0.13–1.4	0.42–1.25
Composition of the Complex (M:L) Obtained in Job's and Mole Ratio Method. 1:2 Stability Constant	3.4×10^4	$1.8x10^4$

Statistical Analysis

The data reported in this work were calculated by Excel 2007 (Microsoft Office) and Origin Pro 8.5.0 SR1 (Origin Lab Corporation, USA) for mathematical and statistical computations. Data were reported as mean ± SD. The student t test was used for comparison of the developed method with the standard method.

RESULTS AND DISCUSSION

The determination of copper by the spectrophotometric method by using investigated reagents form the yellow-coloredCu(II)– (CHAPH) and Cu(II)– (BHAPH) complexes and both complexes were having a maximum absorbance at 380 and 350 nm respectively (Fig.-1). The effect of the pH on the formation of Cu(II) complexes was studied in the range from 1.0 to 10.0 for both (CHAPH) and(BHAPH) reagents. These results suggested that the complexes formation required alkaline medium (7.0–9.0pH) condition and hence pH of 9.0 was maintained as the optimal condition for experiments (Fig.-3). The effects of concentration of reagents on the absorbance of the complexes were studied at λmax. The obtained results suggested that tenfold molar excess of reagents was required for full color development. At least tenfold molar excess of a reagent to Cu(II) was required for further studies.

Table-2: Determination of Cu(II)(mean ± SD, n=3) in Bheema River Water Samples

Location of the River Water Samples	Amount of Cu(II) Found µg/ml		
	F-ASS Method by Using(2-ATP)*	Spectrophotometric Method	
		CHAPH Method	BHAPH Method
GhattargaAfzalpur Kalabuaragi	0.15 ± 0.01	0.19 ± 0.01	0.19 ± 0.01
Deval Ghanagapur, AfzalpurKalabuaragi	0.88 ± 0.05	1.02 ± 0.07	1.02 ± 0.09
KattiSangavi, Jewargi, Kalaburagi	2.01 ± 0.08	2.40 ± 0.10	2.11 ± 0.01

*2-acetylpyridinethiosemicarbazone

Beer's Law and Sensitivity of Cu(II)– (CHAPH) and Cu(II)– (BHAPH) Complexes

For the determination of coppera calibration graph was prepared under the optimum experimental conditions. The concentration range of 0.13–1.4 µg/ml with the equation $A_{380} = 0.125C + 0.0521$, obeys Beer's law for the Cu(II)– (CHAPH) complex. TheCu(II)– (CHAPH) complex, Sandell's sensitivity and molar absorptivity values were 0.0038 µg/cm^2 and 5.2×10^4 lit/mol cm respectively.A solution containing 1.0 µg/mL of Cu(II) was 1.08 ± 0.0123 (%RSD = 0.025 %) obtained by the replicate (n = 10) analyses. The concentration range of 0.44–1.25 µg/ml with the equation $A_{380} = 0.0932C + 0.0615$, obeys Beer's law for the Cu(II)– (BHAPH) complex. The Cu(II)– (BHAPH) complex, Sandell's sensitivity and molar absorptivity values were 0.0022 µg/cm^2 and 2.5×10^4 lit/mol cm respectively. A solution

containing 1.0 µg/mL of Cu(II) was 1.028 ± 0.0134 (%RSD = 0.032 %) obtained by the replicate (n = 10) analyses. The correlation coefficient values of the standard curves were found to be 0.890 and 0.958, for Cu(II)– (CHAPH) and Cu(II)– (BHAPH) complexes respectively, showing excellent linearity of the investigated methods. Both investigated reagents for the determination of copper, detection limit [expressed as 3 × standard deviations of blank (n = 10) divided by the slope of the calibration line] were found to be 0.053 and 0.147 µg/mL respectively. Comparing the two reagents, (CHAPH)is more sensitive than BHAPH) for Cu(II) determination.

Stoichiometry of Cu(II)– (CHAPH) and Cu(II)– (BHAPH) Complexes

The spectrophotometric method for the determination of copper by using the reagents (CHAPH) and (BHAPH), color complexes were formed with copper. Hence, to determine the composition of the complexes Job's continuous variation method has been used. The application of Job's method of continuous variation and mole ratio methods showed that 1:2 molar ratio is found in the complex between Cu(II) and (CHAPH) and (BHAPH) reagents.[28-29] Moreover, from Jobs method of continuous variation the stability constant of the complexes found to be 3.4×10^4 and 1.8×10^4, respectively.

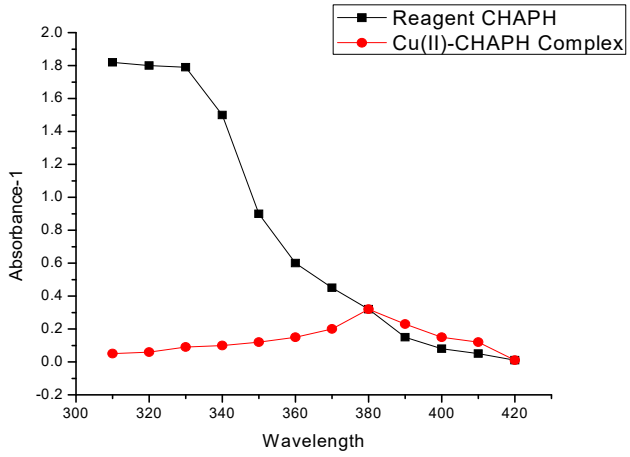


Fig.-1: Absorption Spectra of Reagent CHAPH and Cu(II)-CHAPH Complex

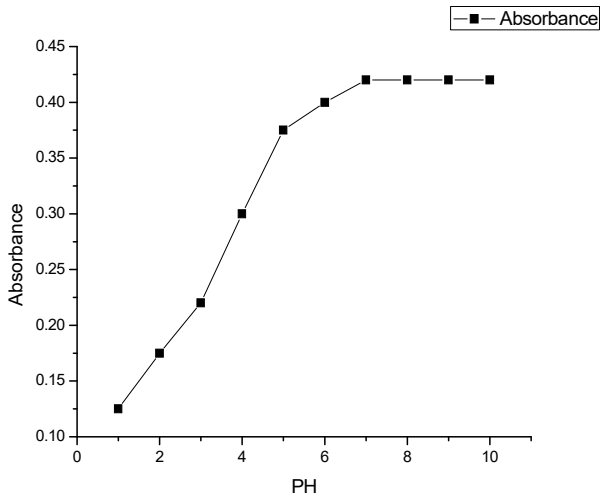


Fig.-2: Effect of pH on the Absorbance of C(II)-CHAPH Complex

Table-3. Determination of Cu(II)(mean ± SD, n=3) in Bhima River Water Sediment Samples

Location of the Sediment Samples	Amount of Cu(II) Found µg (/ml)		
	F-ASS Method by Using (2-ATP)*	Spectrophotometric Method	
		CHAPH method	BHAPH method
GhattargaAfzalpur Kalabuaragi	10.00	9.95	9.92
Deval Ghanagapur, AfzalpurKalabuaragi	15.00	14.96	14.94
KattiSangavi, Jewargi, Kalaburagi	20.00	19.74	19.80

*2-acetylpyridinethiosemicarbazone

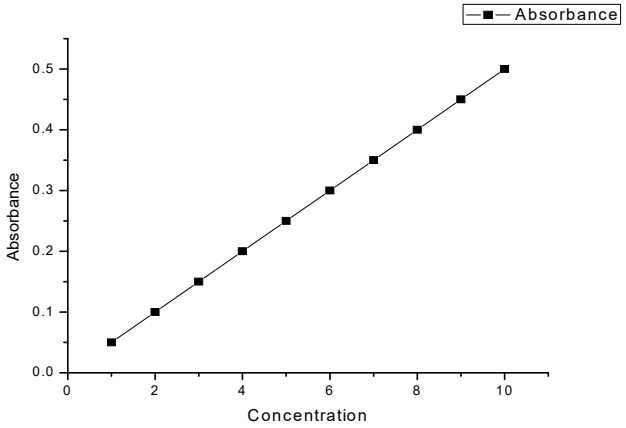


Fig.-3:Validity of Beer's Law for Cu(II)-CHAPH Complex

The method described in this paper is applicable for the rapid, precise and reliable determination of trace amounts of copper in water and sediment sample of water. The present method is compared with other spectrophotometric methods for the estimation of copper.

Table-4:Comparison of the Present Method with other Spectrophotometric Methods for the Determination of Copper

Reagent	λ_{max}	Optimum pH range	Beer's Law Validity Range ppm	Molar Absorptivity $Lmol^{-1}cm^{-1}$	M:L[a]	Remarks	Ref
2,7-Dichloroquinoline-3carbaldehyde thiosemicarbazone	406	6	0.003	1843.5	--	Many metal ions interfere and poor sensivity	30
5,5′-Dimethyl-1,2,3cyclohexanetrione-1,2dioxime	383	---	0-11.2	4600	1:3	Less sensitive	31
2,4-Dihydroxy-5bromoacetophenone thiosemicarbazide	420	6	12.7	1459	1:1	Poor sensitive	30
Benzaldehyde-4-(2-hydroxy -5sulphonyl 3-thiosemicarbazone	325	4.5	7.62	744	1:2	Very poor sensitive	31
5-Chloro-2-hydroxy acetophenonephenylhydrazone (CHAPH)	380	7-8	0.13–1.4	$5.2x10^4$	1:2	Highly sensitive	P.M[b]
5-Bromo-2-hydroxy acetophenonephenylhydrazone (BHAPH)	350	8-9	0.42–1.25	$2.5x10^4$	1:2	Highly sensitive	P.M[b]

a.Metal: ligand. b. Present method

CONCLUSION

Two complexing agents(CHAPH) and (BHAPH) have been used as a reagents to determine Cu(II) from Bheema river water and sediment samples using spectrophotometric method. The investigated methods were practical and valuable for the determination of copper. The results showed good agreement with the results obtained by other reported spectrophotometric methods for the estimation of copper. The methods described in this paper are applicable for the rapid, precise and reliable determination of trace amounts of copper in water and sediment samples of water.

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