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Determination of Cu(II) in Amarja Dam water and their sediment samples obtained from Aland, Kalaburagi, Karnataka, india using 2-[4-(hydroxymethyl)-1-phenyl-1*H*-pyrazol-3-yl]phenol derivatives by spectrophotometric method.

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ABSTRACT:
Chromogenic reagents such as 2-[4-(hydroxymethyl)-1-phenyl-1H-pyrazol-3-yl]phenol $[H_2L^1]$ *and :4-Chloro-2-[4-(hydroxymethyl)-1-phenyl-1H-pyrazol-3-yl]phenol* $[H_2L^2]$ *were used for determination Cu(II) by spectrophotometric method. Both the reagents produce brown Cu(II) complexes at pH range 8.0-9.0 and obeyed Beer's law in the concentration range of 0.14–1.5 and 0.32–1.20µg/ml for both Cu(II)–* $[H_2L^1]$ *and Cu(II)–* $[H_2L^2]$ *respectively. The molar absorptivity was* $4.6x10^4$ *lit/mol cm at 520nm, and* $3.2x10^4$*lit/mol cm at 480 nm, while the Sandell's sensitivity was found that 0.0033 and 0.0018* $\mu g/cm^2$ *for both Cu(II)–* $[H_2L^1]$ *and Cu(II)–* $[H_2L^2]$ *respectively. The correlation coefficient was calculated from standard curves of Cu(II)–* $[H_2L^1]$ *and Cu(II)–* $[H_2L^2]$ *were 0.870 and 0.898 respectively. This method was used for Cu(II) determination in Amarja dam water and its sediments samples, the results obtained were compared with the standard method using a flame atomic absorption spectrophotometer for Cu(II) determination. The stability constant of the Cu(II) complexes with* $[H_2L^1]$ *and* $[H_2L^2]$ *reagents found to be* 4.2×10^4 *and* 3.5×10^4*respectively by Jobs method.*

KEYWORDS: *Amarja dam Water, Chromogenic, Complexes., Sediment, Spectrophotometric, Stability Constant,*

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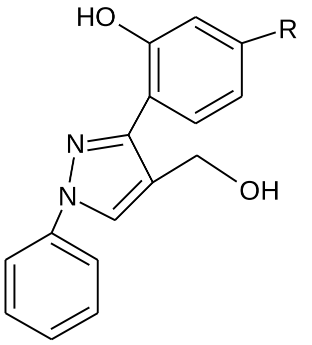
I. INTRODUCTION:

Copper is the third most essential trace element widely distributed[1] and it plays an important role in biological systems during cell respiration in the blood in vertebrate animals[2]. A serious threat to human health and the environment due to contamination by heavy metal ions, these heavy 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's production of copper, the major portion of copper is used in electrical equipment, apart from the biological activity of copper[4] 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. The deficiency of copper decreases the activity of many metalloenzymes, because copper is a trace metal and essential for several metalloenzymes activities[5].

Compounds of pyrazolone and azopyrazolone are widely used as analytical reagents capable of forming chelates with a variety of metal cations[6,7], followed by changes in spectra of colour, p^H, conductance and absorption[8]. Due to its applicability as possible ligands for a huge number of metal ions, azo derivatives have increasingly gained attention[6]. The pyrazoline-5-one complex is strongly reactive in 4th positions and undergoes a coupling reaction to provide 4-ary-lazo derivatives with diazonium salts[9]. The 5-pyra-zolone azo-derivatives and their metal complexes currently used in the colouring industries as well as quantitative reagents for trace metal determination and some biological and medical applications were also expected[10,11]. They have been studies of different methods of synthesising azopyrazolone derivatives[12-13].

In this present work, authors were developed two chromogenic reagents 2-[4-(hydroxymethyl)-1-phenyl-1*H*-pyrazol-3-yl]phenol $[H_2L^1]$ and :4-Chloro- 2-[4-(hydroxymethyl)-1-phenyl-1*H*-pyrazol-3-yl]phenol $[H_2L^2]$ for determination Cu(II) in Amarja dam 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 for the determination of Cu(II) was also studied. The method was successfully applied to Amarja dam water and its sediments samples as well and compared to the standard method.



R = H : 2-[4-(hydroxymethyl)-1-phenyl-1*H*-pyrazol-3-yl]phenol [H_2L^1]
R = Cl :4-Chloro- 2-[4-(hydroxymethyl)-1-phenyl-1*H*-pyrazol-3-yl]phenol [H_2L^1]

II. EXPERIMENTAL:

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

2.1. Sample Collection:

Samples of water were obtained from the Amarja dam water located at Koralli village, Aland taluka, Kalaburagi district, Karnataka and sediment samples are also collected from the same place. Top sediment 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 before use for analysis.

2.2. 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 LI120) 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 1HNMR spectra of the synthesized reagents were recorded by using JEOL 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.

2.3. Preparation of reagents:

2 . 3 . 1 . 3-aryl-1-phenyl-1H-pyrazole-4- carbaldehyde:

The derivatives of 2-hydroxyacetophenone phenylhydrazone(0.01 mol) was dissolved in DMF (15 ml) and then $POCl_3$ (0.03 mol) was added drop wise at 0^oC. After a complete addition of $POCl_3$, the reaction mixture warmed at room temperature and heated at 60-70 ^oC for 2.5-3h.The reaction was poured onto crushed ice and then neutralized with 10% aqueous NaOH solution. The precipitate was filtered, strongly washed with water and crystallized from ethanol[14], yielding 84- 88%.

2.3.2. 2-(4-(hydroxymethyl)-1-phenyl-1H- pyrazol-3-yl)phenol [H_2L^1] / 4-Chloro- 2-[4-(hydroxymethyl)-1-phenyl-1H-pyrazol-3-yl]phenol [H_2L^2]:

To a solution of 3-aryl-1-phenyl-1H-pyrazole-4-carbaldehyde (1.2 m mol) in methanol (30 ml), $NaBH_4$ (3.6 m mol) was added at 0^oC slowly. Then the mixture of reaction was removed to room temperature for 2 h. Then the reaction mixture was poured onto crushed ice and neutralized by hydrochloric acid. The 2-(4-(hydroxymethyl)-1-phenyl-1H-pyrazol-3-yl)phenols was precipitated and filtered. The crud compounds were crystallized from ethanol[15].

2.4. Synthesis of Metal Complexes:

In 25 ml of ethanol solution dissolve 1mmol $CuSO_4 \cdot 5H_2O$ salt then add 4ml of ligands (2 mmol) and this reaction mixture was refluxed for 5.5 hours at 55 °C. A brown colour solid was obtained after cooling the reaction mixture to room temperature. This was filtered and washed with distilled water and ethanol.

2.5. Absorption Spectra of Reagent Solutions and Metal Complexes:

1 ml of 0.01M reagent solution mixed to 10 ml of buffer solution in a 25-ml volumetric flask, and then adds 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.

2.6. Effect of pH on the Absorbance of the Metal Complexes:

Prepare series of the solutions by adding 10 ml of a buffer solution with different pH (pH 3.0–10.0) in a set of 25-ml volumetric flasks, constant amount of metal ion solution and reagents (1:5) 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 (520 and 480 nm, for $[H_2L^1]$ and $(H_2L^2]$ reagents respectively.

2.7. Determination of Copper in Amarja dam water Samples:

Collect one liter of Amarja dam water sample, was filtered by using Whatman No.40 filter paper and it is evaporated by boiling near to dryness by adding a mixture of 2ml of conc. H_2SO_4 and 5ml of conc. 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 becomes colorless and then it was cooled and neutralized with dilute NH_4OH and 1-2ml of acetic acid solution. Then the solution was filtered and poured into a 25ml calibrated 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).

2.8. Determination of Copper in Sediment Samples:

0.2 g of sediment sample 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[16,17]. The content 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[18]. The calibration of solutions was made 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 520 and 480 nm, for $[H_2L^1]$ and $(H_2L^2])$ reagents, respectively. The analyses were carried out in triplicate and the results presented as mean ± SD, are given in Table-3.

2.9. 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.

Table-1: Physico-chemical data of Cu(II)- $[H_2L^1]$ and Cu(II)- $[H_2L^2]$

Characteristics	Results	
	Cu(II)- $[H_2L^1]$	Cu(II)- $[H_2L^2]$
λ max (nm)	520	480
P^H range (optimum)	7.5-8	8
Molar absoptivity (Lmol^{-1}cm $^{-1}$)	$4.6x10^4$	$3.2x10^4$
Sandell's sensitivity(μg/cm2)	0.0033	0.0018
Standard deviation in the determination of Cu(II) for ten determinations.	0.000316	0.000132
RSD	0.023%	0.028%
Regression Coefficient	0.870	0.898
Regression equation	A_{520} = 0.135 C + 0.0472	A_{480} = 0.0823 C + 0.0510
Beer's law validity range(μg/ml)	0.14–1.5	0.32–1.20
Composition of the complex (M:L) obtained in job's and mole ratio method.	1:2	1:2
Stability constant	4.2×10^4	3.5×10^4

III. RESULTS AND DISCUSSION:

The maximum absorbance at 520 and 480 nm was measured for determination of copper by the spectrophotometric method by using investigated reagents form the brown-colored Cu(II)– $[H_2L^1]$ and Cu(II)–$[H_2L^2]$ complexes respectively(fig. 1). The impact of the pH on the formation of Cu(II) complexes with the $[H_2L^1]$ and $[H_2L^2]$ was studied in the pH range from 1.0 to 10.0 for both $[H_2L^1]$ and $[H_2L^2]$ reagents. These results suggested that the complexes formation required alkaline medium (7.5–8.0 pH) condition and hence pH of 8.0 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 Amarja dam water samples

Location of the Amarja dam water samples	Amount of Cu(II) found µg/ml		
	F-ASS method by using(2-ATP)*	Spectrophotometric Method	
		$[H_2L^1]$ Reagent	$[H_2L^2]$ Reagent
East side sample	0.22 ± 0.04	0.20 ± 0.03	0.21 ± 0.05
West side sample	0.75 ± 0.07	0.78 ± 0.05	0.80 ± 0.06
North side sample	1.95 ± 0.06	1.85 ± 0.13	1.90 ± 0.03
South side sample	1.02± 0.08	1.20± 0.10	1.10± 0.04

* 2-acetylpyridinethiosemicarbazone

3.1 Beer's Law and sensitivity of Cu(II)– $[H_2L^1]$ and Cu(II)– $[H_2L^2]$ complexes:

A calibration graph was prepared under the optimum experimental conditions for the determination of copper. The concentration range of 0.14–1.5 µg/ml with the equation $A_{520} = 0.135\ C + 0.0472$ obeys Beer's law for the Cu(II)–$[H_2L^1]$ complex. For the Cu(II)– $[H_2L^1]$ complex, Sandell's sensitivity and molar absorptivity values were 0.0033 µg/cm^2 and 4.6×10^4 lit/mol cm respectively. A solution containing 1.0 µg/ml of Cu(II) was 1.06 ± 0.0123 (%RSD = 0.023 %) obtained by the replicate (n = 10) analyses. The concentration range of 0.32–1.20 µg/ml with the equation $A_{480} = 0.0823\ C + 0.0510$, obeys Beer's law for the Cu(II)–$[H_2L^2]$ complex. The Cu(II)–$[H_2L^2]$ complex, Sandell's sensitivity and molar absorptivity values were 0.0018µg/cm^2 and 3.2×10^4 lit/mol cm respectively. A solution containing 1.0 µg/ml of Cu(II) was 1.018 ± 0.0134 (%RSD = 0.028 %) obtained by the replicate (n = 10) analyses. The correlation coefficient values of the standard curves were found to be 0.870 and 0.898, for Cu(II)–$[H_2L^1]$ and Cu(II)–$[H_2L^2]$ 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 0.043 and 0.132 µg/ml respectively. Comparing the two reagents, $[H_2L^1]$ is more sensitive than $[H_2L^2]$ for Cu(II) determination.

3.2 Stability of Cu(II)–$[H_2L^1]$ and Cu(II)–$[H_2L^2]$ complexes:

The spectrophotometric method for the determination of copper by using the reagents Cu(II)–$[H_2L^1]$ and Cu(II)–$[H_2L^2]$, 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 $[H_2L^1]$ and $[H_2L^2]$ reagents[19-20]. Moreover, from Jobs method of continuous variation the stability constant of the complexes found to be 4.2×10^4 and 3.5×10^4, respectively.

Table-3. Determination of Cu(II)(mean ± SD, n=3) in Amarja dam water sediment samples

Location of the sediment samples	Amount of Cu(II) found µg (/ml)		
	F-ASS method by using (2-ATP)*	Spectrophotometric method	
		$[H_2L^1]$ Reagent	$[H_2L^2]$ Reagent
East side sample	12.50	12.90	12.92
West side sample	14.42	14.93	14.94
North side sample	18.56	18.74	18.80
South side sample	15.30	14.69	14.75

* 2-acetylpyridinethiosemicarbazone

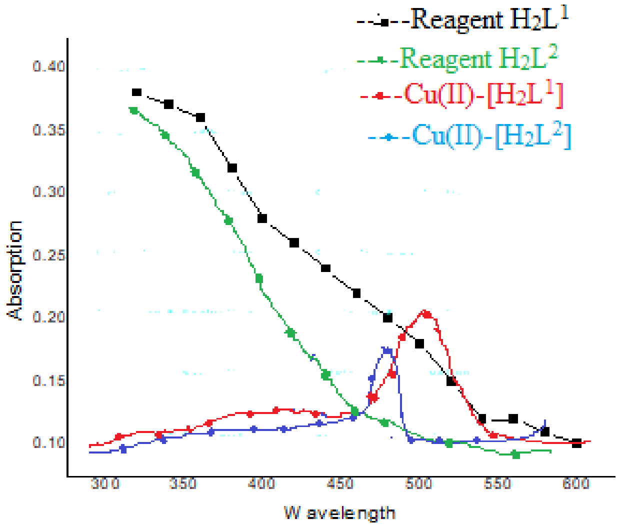


Fig: 1. Absorption spectra of a. Reagent CHAPH and Cu(II)-CHAPH complex.

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

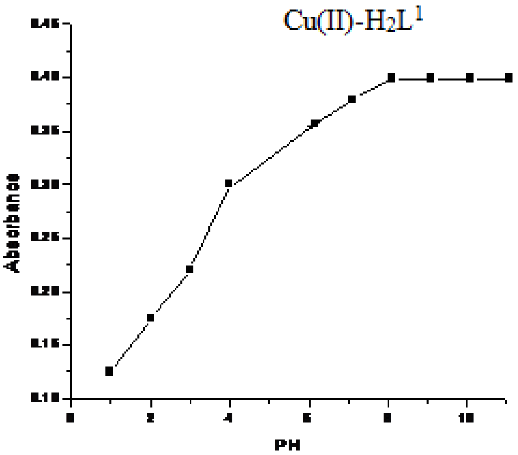


Fig: 2. Effect of P^H on the absorbance of C(II)-CHAPH complex

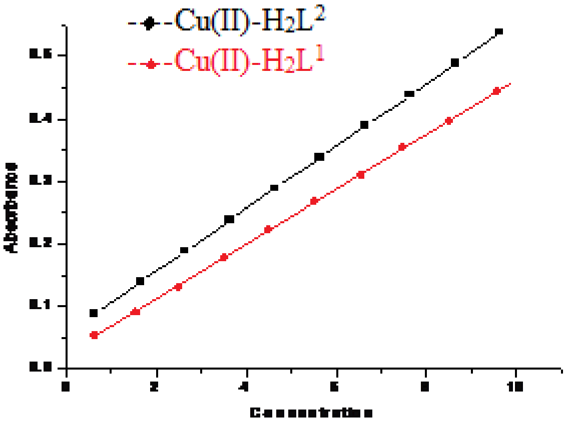


Fig: 3. Validity of Beer’s law for Cu(II)-CHAPH Complex

Table 4: Comparison of the other spectrophotometric methods with present investigated method for the determination of copper

Reagents	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	[21]
5,5′-Dimethyl-1,2,3cyclohexanetrione-1,2dioxime	383	---	0-11.2	4600	1:3	Less sensitive	[22]
2,4-Dihydroxy-5bromoacetophenone thiosemicarbazide	420	6	12.7	1459	1:1	Poor sensitive	[21]
Benzaldehyde-4-(2-hydroxy -5sulphonyl 3-thiosemicarbazone	325	4.5	7.62	744	1:2	Very poor sensitive	[22]
5-Chloro-2-hydroxy acetophenonephenylhydrazone (CHAPH)	380	7-8	0.13–1.4	$5.2x10^4$	1:2	Highly sensitive	[23]
2-[4-(hydroxymethyl)-1-phenyl-1*H*-pyrazol-3-yl]phenol [H_2L^1]	520	7.5-8	0.14–1.5	$4.6x10^4$	1.2	Highly sensitive	P.M[b]
4-Chloro-2-[4-(hydroxymethyl)-1-phenyl-1*H*-pyrazol-3-yl]phenol [H_2L^2]	480	8	0.32–1.20	$3.2x10^4$	1.2	Highly sensitive	P.M[b]

M:L[a]: Stochiometry of the complexes, P.M[b]. Present method

IV. CONCLUSION

Two bidentate ligands 2-[4-(hydroxymethyl)-1-phenyl-1*H*-pyrazol-3-yl]phenol [H_2L^1]and 4-Chloro-2-[4-(hydroxymethyl)-1-phenyl-1*H*-pyrazol-3-yl]phenol [H_2L^2] have been used as a reagents to determine Cu(II) from Amarja dam 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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