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## Determination of Cu (II) in water and alloy samples with 2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol) using extractive spectrophotometric method

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### ABSTRACT

A simple, sensitive and selective extractive spectrophotometric method was developed for the determination of Cu (II) in various water and alloy samples using newly synthesized reagent 2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol). Cu (II) forms a green colored complex with 2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol) in acetate buffer medium (pH 6) which increases the sensitivity and complex was extracted into chloroform. Under optimum conditions the maximum absorption of the chloroform extracts were measured at 602nm. Beer's law was obeyed in the range of 0.4 to 5.0  $\mu\text{g mL}^{-1}$  of Copper. The molar absorptivity and Sandell's sensitivity of the complex were as  $0.12 \times 10^2 \text{ l mol}^{-1} \text{ cm}^{-1}$  and  $2.438 \mu\text{g cm}^{-2}$  respectively. The detection limit was found to be  $0.044 \mu\text{g mL}^{-1}$ . The detailed study of various interfering ions made the method more sensitive. The method was successfully applied for the determination of Cu (II) in water and alloy samples. © 2010 Trade Science Inc. - INDIA

### KEYWORDS

Cu (II), 2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol); Spectrophotometry; Water; Alloy samples.

### INTRODUCTION

Metal works, semiconductor, copper industries and mining industrial wastewater streams, contain heavy metals, which are of great environmental concern and must be removed prior to water discharge or water recycling<sup>[1-2]</sup>. Copper is both vital and toxic for many biological systems depending on its concentration<sup>[3,4]</sup>. Thus, the determination of trace amounts of copper is becoming increasingly important because of the increased interest in environmental pollution<sup>[5]</sup>. Flame and graphite furnace atomic absorption spectrometry and

spectrophotometric methods provide accurate and rapid determination of copper in natural water and waste water<sup>[6]</sup>. Several analytical techniques have been monitored for the determination of copper (II), they include atomic absorptionspectrometry<sup>[7-14]</sup> voltammetry<sup>[15,17]</sup> spectrophotometry<sup>[18-20]</sup> inductive coupled plasma-atomic emission spectrometry<sup>[21-23]</sup> and inductive coupled plasma-mass spectrometry<sup>[24]</sup>. Spectrophotometry still represents an attractive technique for the determination of metal ions in aqueous media because of its simplicity, being inexpensive and is readily available<sup>[25]</sup>. Therefore, Extractive spectrophotometry<sup>[26-30]</sup>

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was chosen for this investigation.

The aim of the present work is provided facile, sensitive and selective extractive spectrophotometric method for the determination of trace amounts of Cu (II) in water and alloy samples of significant importance. Here authors successfully synthesised new analytical reagent 2,2'-(ethane-1,2-diylbis[nitrilo-methylidene])bis(4-bromophenol) for the determination of Cu (II) in water and alloy samples.

### EXPERIMENTAL

#### Reagents

All reagent used were of analytical reagent grade. Double distilled water was used throughout the experiment. A stock solution of Cu (II) ( $1 \times 10^{-2}$  M) was prepared by dissolving 3.9295 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (E-Merck, Germany) in double distilled water containing a few drops of concentrated sulfuric acid in 1000 mL standard flask. Cu (II) working standard stock solutions was prepared freshly by appropriate dilution of the standard stock solution with double distilled water. 0.1 M of 2,2'-(ethane-1,2-diylbis[nitrilo-methylidene])bis(4-bromophenol) was prepared by dissolving 4.261 g of 2,2'-(ethane-1,2-diylbis[nitrilo-methylidene])bis(4-bromophenol) in 100 mL of methanol. This solution is further diluted, when ever necessary required concentration with double distilled water.

#### Buffer solutions

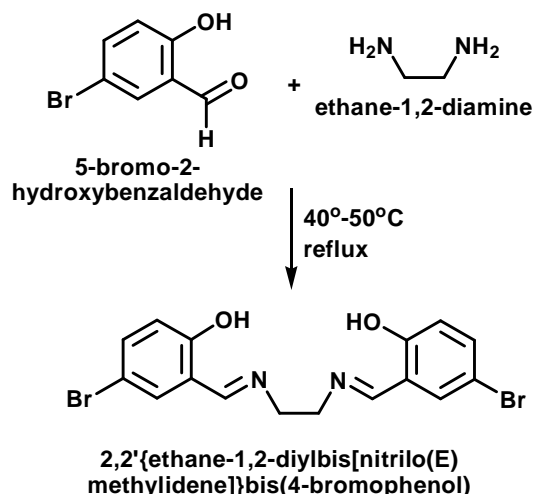
Buffer solutions of pH 3-6 and 6-10 were prepared by mixing appropriate ratios of a 0.50 M acetic acid and 0.50 mol  $\text{L}^{-1}$  of sodium acetate solution and 0.10 mol  $\text{L}^{-1}$  sodium dihydrogen phosphate solution and 0.10 mol  $\text{L}^{-1}$  dipotassium hydrogen phosphate solution respectively.

#### Apparatus

A HITACHI U 2001 spectrophotometer with 1.0 cm matched quartz cells were used for all absorbance measurements. An Elico Li-129 model pH meter with combined glass electrode was used for all pH measurements.

#### Synthesis of 2,2'-(ethane-1,2-diylbis[nitrilo-methylidene])bis(4-bromophenol)

5-bromo-2-hydroxybenzaldehyde and ethane-1,2-



**Scheme 1 : Synthesis of 2,2'-(ethane-1,2-diylbis[nitrilo-methylidene])bis(4-bromophenol)**

diamine take equimolar ratio added methanol were refluxed for 1 h, and the contents were cooled to room temperature for separating the formed yellow solid product was filtered, washed with water, dried and recrystallized from hot aqueous methanol (m.p. 174°C-178°C, 89% yield as shown in Scheme 1). The band at  $3490\text{cm}^{-1}$  is due to the -OH group and absorption bands at  $1593\text{cm}^{-1}$  are due to the C=N group of reagent.

#### Procedure

To an aliquot of working standard solution containing 1-100  $\mu\text{L}$  is taken in to 50 mL separating funnel, 5 mL of acetate buffer solution (pH 6.0), 2 mL of reagent solution and salting out agent 0.1 M magnesium sulphate were added. The mixture was shaken with 5.0 mL portions of chloroform for 30 s and allowed to stand for few minutes. The organic phases are collected and made up to 25 mL with chloroform and absorbance was measured at 602 nm against the corresponding reagent blank and the calibration graph was constructed.

#### Procedure for the determination of Cu (II) in natural water samples

Different water samples (tap water, river water, spring water) were collected from various places in and around Tirupati, A.P., and India. The samples (150 mL) were stored at 0-5°C in metal free polyethylene bottles. Water samples were filtered through Whatman filter paper no.41 and clean solution is collected into 250 mL beaker. The contents are diluted up to the mark with

TABLE 1 : Comparison of the present method with other spectrophotometric methods for the determination of copper

Reagent	$\lambda_{\text{Max}}$ / nm	Optimum pH range	Beer's law validity range, ppm	Molar absorptivity/l $\text{mol}^{-1} \text{cm}^{-1}$	M:L	Remarks	Ref
4-Chloroisoinitroso-acetophenone thiosemicarbazone	400	7.5-8.5	0.2-20	2518	1:2	Ag(II), Ni(II), Co(II), Pb(II), Cd(II), Cyanide, Tartarate and EDTA interfere, less sensitive	26
2-Carboxybenzaldehyde thiosemicarbazone	346	-	0.5-5.0	12000	1:1	Less sensitive	27
8-Methoxy-2-chloroquinolin-3-carbaldehyde Thiosemicarbazone	410	5.0	3.0	0.0026768	1:1	Interference no. of metal ions and poor sensitivity and selectivity	10
2,4-Dihydroxy benzophenone isonicotinoyl hydrazone	-	2.0	0.063-2.550	0.0165	1:1	Less sensitive more reagent consumption	29
2,4-Dihydroxy benzophenone benzoic hydrazone	-	4.0	0.31-2.20	0.0155	-	Less sensitive	28
2,2'-(ethane-1,2-diylbis[nitrilo-ethylidene])bis(4-bromophenol)	602	6.0	0.4-5.0	$0.12 \times 10^2$	-	Selective and Inexpensive reagent	Present method

TABLE 2 : Determination of Cu (II) in water samples

Sample	Proposed method		
	Copper added $\mu\text{g mL}^{-1}$	Found <sup>a</sup> $\mu\text{g mL}^{-1}$	Recovery (%) <sup>a</sup>
Lake water <sup>b</sup>	-	0.59	-
	1.0	1.59	98.0±0.23
River water <sup>b</sup>	1.40	1.99	99.2±0.07
	-	0.19	-
Spring water <sup>b</sup>	0.60	0.79	98.3±0.07
	1.0	1.19	98.0±0.27
Sea Water <sup>c</sup>	-	0.38	-
	0.60	0.98	98.3±0.09
Upper level	0.80	1.18	98.7±0.06
	1.20	2.39	99.1±0.06
Lower level	-	0.59	-
	1.0	1.59	99.0 ±0.18
Polluted water <sup>b</sup>	1.40	1.99	99.2±0.51
	-	0.58	-
Polluted water <sup>b</sup>	0.90	1.48	98.8± 0.16
	1.20	1.78	98.3±0.07

<sup>a</sup>n=5, <sup>b</sup> Collected around Tirupati area, <sup>c</sup> Collected form Bay of Bengal

double distilled water. 15mL of this solution is further diluted to get working solution for determination of Cu (II) as described in above procedure. The results were summarized in TABLE 2.

### Procedure for the determination of Cu (II) in sea water samples

100mL of sea water was taken from Bay of Bengal near Sullurpet, Nellore dist, A.P., India and spiked with known amounts of metal ion. The pH of the sample was adjusted to pH 6 with acetate buffer as reported in

literature. The metal ion present in the sea water was analyzed from aforesaid procedure. The analytical data was presented in TABLE 2.

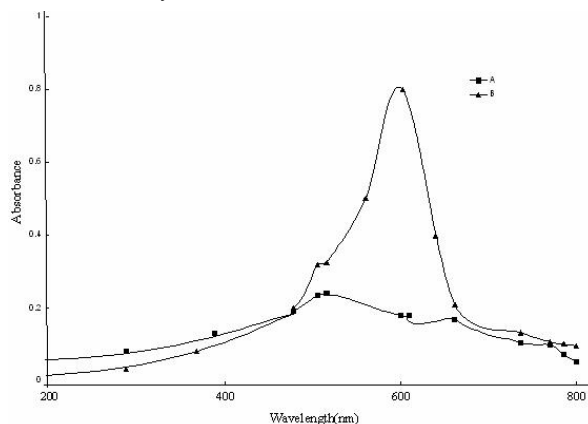
### Procedure for the determination of Cu (II) in alloys samples

The proposed method is applied for the determination of Cu(II) in standard alloys such as Aluminium Alloy (BCS 19e) and Copper Base Alloys (BCS 207 and 179). About 0.1g of alloy sample was dried(110°C)and dissolved in a 15mL of aqua regia, They are heated to near dryness and the nitrate is expelled from the residue, using 5mL of concentrated HCl. Each residue is twice extracted in to double distilled water and made up to 100mL separately. Suitable volumes of these solutions are taken and, using the recommended general procedure, are analysed for Cu (II). The process is repeated four times with each sample, and the average value obtained is noted. They are presented in TABLE 3.

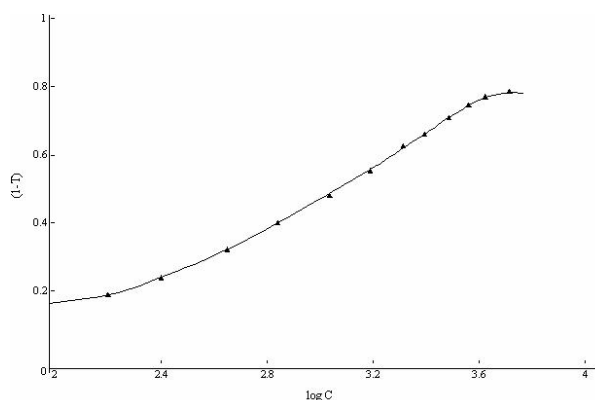
## RESULTS AND DISCUSSION

Cu(II) reacts with 2,2'-(ethane-1,2-diylbis[nitrilo-methylidene])bis(4-bromophenol) to form a green colored complex in buffer of pH 6.0 and complex was extracted in to chloroform. The organic extract shows a maximum absorption at 602nm, the formation of the complex and it's extraction in to chloroform is instantaneous. The complex is stable for more than 6 days the conditions for effective extraction are improved by studying the effect of various factors such as pH,

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**Figure 1 :** (A) Absorption spectra of Cu(II)- 2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol) complex vs Reagent blank, (B) absorption spectra of 2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol) chloroform blank

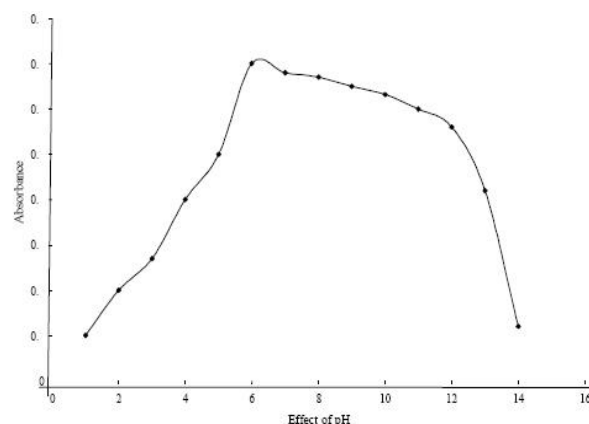


**Figure 3 :** Ringbom plot of Cu (II) - 2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol) complex

reagent concentration, choice of solvent and salting out agent, influence of diverse ions in order to enhance the sensitive and rapid extraction spectrophotometric method for the determination of Cu(II) in  $\mu\text{g}$  level. The complex formation reaction between Cu(II) with 2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol) has been studied in detailed.

### Absorption spectra

Under experimental condition, the absorption spectra of the 2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol) and Cu (II) -2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol) complex were scanned against the reagent blank. Similarly, the absorption spectrum of the reagent is recorded against the solvent as blank. The absorption spectra of both the reagent and the complex are shown in figure 1. The spectra obtained reveal that the



**Figure 2 :** Effect of pH on the absorbance of Cu (II) - 2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol) complex

[Cu (II) 2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol)] complex gave an absorbances at 602nm respectively.

### Analytical parameters

Beer's law was obeyed in the concentration range 0.4 to  $5.0\mu\text{g mL}^{-1}$  of Cu (II). The molar absorptivity and Sandell's sensitivity of complex at pH 6.0 was calculated as  $1.24 \times 10^{-4}$  M and  $2.438\mu\text{g cm}^{-2}$  respectively. The correlation coefficient (r) for the experimental data is 0.9996.

### Effect of reagent concentration

To a series of 25mL separating funnels, each containing 1mL of Cu(II) solution ( $0.01\text{M}$ ), 5mL of buffer solution (pH 6.0) were added different volume of the reagent solution and extracted with chloroform to obtain the maximum color formation. The absorbance of each solution was measured at 602nm against a reagent blank. From the experimental observation it was found that beyond a ten-fold excess of the reagent, the absorbance remained almost constant. Hence, for further studies, 2mL of the reagent was recommended for complete color development.

### Effect of solvent

Extraction for Cu(II)- 2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol) complex is tested in various organic solvents such as toluene, benzene, xylene, n-butanol, 1-amylalcohol, dimethyl formaldehyde,  $\text{CCl}_4$ , chlorobenzene, cyclohexane and chloroform. Among the various solvent studies chloroform was selected as the suitable solvent

TABLE 3 : Determination of Cu (II) in standard alloy samples

Alloy composition, %	Amount of Cu(II) <sup>a</sup> found, %	
	Certified value	Found <sup>*</sup>
Aluminium Alloy (BCS 78)Cu, 4.53; <sup>b</sup> Zn,19; Fe, 0.28; Mn,0.69; Si, 0.73; Mg, 0.75.	4.53	4.49
Copper base alloy (BCS 207)Cu, 86.84; Sn, 9.8; <sup>b</sup> Zn, 2.53; <sup>c</sup> Pb, 0.4.	86.84	86.60
Copper base alloy(CS 174) Cu, 58.8; <sup>b</sup> Zn,33.9; Sn,1.75; Al,1.62; Mn, 1.03; <sup>b</sup> Ni, 1.01; Fe,0.91.	58.8	58.62

<sup>a</sup>Average of four determinations. <sup>b</sup>Masked with thiocyanate.

<sup>c</sup>Masked with citrate

for the extraction of Cu(II)- 2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol) complex, because of it's maximum absorbance and greater extraction ability due to polarity.

### Physico chemical properties of 2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol)

2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol) being a yellow color solid, easily soluble in Methanol. The spectra of 2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol) in different pH are shown in figure 2. At phosphate buffer, dark orange, instability and maximum absorption at 480 nm, corresponding to the protonation appears and disappears. According to the absorbance of the reagent at 528nm, the dissociation constant of 2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol) was measured to be  $1.11 \times 10^{-8}$  by potentiometric titration.

### Detection limit, precision and accuracy

The precision and accuracy of the proposed method, determinations are carried out for a set of ten measurement of  $1.5 \mu\text{g mL}^{-1}$  of Cu(II), under optimum conditions. Calculations reveal that the standard deviation of the method is  $0.0023 \mu\text{g mL}^{-1}$  and standard error is 0.0026. these values indicate that this method has the highest accuracy and precision.

### Ring bom plot for [Cu (II)-2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol)] complex

Ringbom's plot is the established standard adopted to know the optimum range of concentration for a system that obeys Beer's law. The plot is drawn

TABLE 4 : Tolerance limits of foreign ions on the determination of  $50 \mu\text{g L}^{-1}$  Cu(II) ion

Tolerance limit ( $\mu\text{g L}^{-1}$ )	Foreign ions [Cu(II) 2,2'-{ethane-1,2-diylbis[nitrilo-methylylidene]}bis(4-bromophenol)]
50,00	Na <sup>+</sup>
1000 <sup>a</sup>	Ca <sup>2+</sup> , Sr <sup>2+</sup> , Ba <sup>2+</sup> , Br <sup>2+</sup> , Mn <sup>2+</sup>
500 <sup>b</sup>	SiO <sub>3</sub> <sup>2-</sup> , CO <sub>3</sub> <sup>2-</sup> , K <sup>+</sup> , Cr <sup>3+</sup> , Zn <sup>2+</sup>
200 <sup>c</sup>	Pb <sup>2+</sup> , Fe <sup>2+</sup> , Sn <sup>2+</sup>
100	Co <sup>2+</sup> , Fe <sup>3+</sup> , Pb <sup>2+</sup>
50	Ni <sup>2+</sup> , Co <sup>2+</sup> , I <sup>-</sup> , CN <sup>-</sup>

<sup>a</sup>Can be masked up to  $10.000 \mu\text{g l}^{-1}$  by the addition of 2mL of EDTA, thiosulfate, cyanide. <sup>b</sup>Can be masked up to  $5000 \mu\text{g l}^{-1}$  by the addition of 2mL of 2% citrate solution. <sup>c</sup>Can be masked up to  $800 \mu\text{g l}^{-1}$  by the addition of 1% thiocyanate

between log C of Cu(II) and (1-T) (where T is the transmittance). The plot has a sigmoid shape with a linear segment at intermediate absorbance values (0.3-0.8) and concentration values ( $2.0-3.6 \mu\text{g cm}^{-3}$ ). The slop of the Ringbom plot from figure 3 is 0.720. Hence, the ratio between the relative error in concentration and photometric error is 3.024, for a concentration of 0.03024, for the percent photometric error.

### Effect of salting out agent

Various salting out agents such as lithium nitrate, thorium sulphate, magnesium sulphate lithium chloride, and ammonium chloride and ammonium sulphate were used for the enhancement of the metal complex extraction into the organic phase in a single step. It is observed that the presence of 1.0mL of 0.1M magnesium sulphate solution ensure the complete extraction. The aqueous phases is tested for the complete extraction of Cu(II) by using chloroform, disclosing that there is no Cu(II) content in the aqueous phase. It is established that 1.0mL of 0.1 M magnesium sulphate as salting out agent and a ten-fold molar excess of the reagent quantitatively extracts Cu(II) in to organic phase.

### Effect of foreign species

Several anions and cations were studied in detail. TABLE 3 summarizes the tolerance limits of interfering ions in the determination of  $50 \mu\text{g l}^{-1}$  Cu (II). The tolerance limit was taken as the amount causing an error of  $\pm 2\%$  at the peak height. The results are shown in TABLE 4.

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### Application of the extractive spectrometric method for the determination of Cu (II) with present method

The proposed extractive spectrophotometric method for the determination of Cu (II) has been employed for water and alloy samples were presented in TABLE 2 the obtained the analytical data summarised in TABLE 3 suggest that the percentage recovery of Cu(II) from water and alloy samples range from 95.0% to 99.8% which is more reliable and sensitive method.

### CONCLUSIONS

The proposed extractive spectrophotometric method is simple, highly sensitive and selective for the determination of Cu (II) in water and alloy samples. The limit of detection of the proposed method is superior to other methods. Proposed method is highly sensitive due to the stabilization of colored complex for more than 12 h formed by interactions of the metal ion with newly synthesized reagent.

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