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# SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN VARIOUS ENVIRONMENTAL SAMPLES USING GREEN REAGENT

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## ABSTRACT

p-dimethyl amino benzyl ethylene diamine reagent has been successfully synthesized by the author under ordinary laboratory conditions and this reagent was used for the determination of copper metal ions in various environmental samples. Various parameters like effect of pH, reagent concentration; choice of solvent, foreign ions interferences was studied. The molar absorptivity of the complex was calculated and reported as $2.3x10^4$ lit $mol^{-1}$ $cm^{-1}$ and the Sandell's sensitivity of the complex was found to be $2.4283x\ 10^{-3}$ µg $cm^{-2}$.

**Key words:** copper ion, leaf samples, p-dimethyl amino benzyl ethylene diamine, spectrophotometry, water samples, etc.

## 1. INTRODUCTION

Copper is a very common substance that occurs naturally in the environment. Humans widely use copper. Copper can be released into the environment by both natural sources and human activities. Copper is often found near mines, industrial settings, landfills and waste disposals. Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhea. Intentionally high uptakes of copper may cause liver and kidney damage and even death. Whether copper is carcinogenic or not is yet to be established. Industrial exposure to copper fumes, dusts, or mists may result in metal fume fever with atrophic changes in nasal mucous membranes. Chronic copper poisoning results in Wilson's disease, characterized by a hepatic cirrhosis, brain damage,

ISSN: 2348-4098
VOLUME 02 ISSUE 04 APRIL-MAY 2014

demyelization, renal disease, and copper deposition in the cornea.

Turkoglu et al [1] reported a simple spectrophotometric determination of copper in natural waters and pharmaceutical samples with chloro(phenyl) glyoxime. Copper is quantitatively retained with 1,5-diphenylcarbazone (DPC) on microcrystalline naphthalene in the pH range 6.5 - 8.0 from a large volume of aqueous solutions of various samples as reported by Shishehborea et al [2]. The liquid-liquid extraction of $Cu^{2+}$ ions with organic solutions containing different chelating agents was reported by Marczenko [3] and Eaton [4]. Spectrophotometric determination of copper in environmental water samples by solvent extraction of an ion association complex of the dichlorocuprate(I) ion with ethylviolet has been developed by Yamamoto and Kumamaru [5]. Yamamoto [6] reported Spectrophotometric determination of copper in steel, stainless steel and aluminium alloys by the solvent extraction of an ion associate of dichlorocopper(I) ion with ethyl violet. A new solvent extraction spectrophotometric determination of copper with 2-nitroso-5-dimethyl aminophenol and zephiramine was developed by Cheng [7]. Akaiwa [8] developed a novel method of preconcentration of copper with 4,7-diphenyl-1,10-phenanthroline disulfonic acid-loaded resin. Jun-Ichi [9] reported a method for the interference of organic material with chelating resin preconcentration of trace copper in environmental water and its elimination by photochemical decomposition. Shishehborea et al [10] developed a spectrophotometric method for the determination of trace copper after preconcentration with 1,5-Diphenylcarbazone on microcrystalline naphthalene. The liquid-liquid extraction of $Cu^{2+}$ ions is reported with organic solutions containing different chelating agents [11, 12]. A very simple, highly sensitive and selective spectrophotometric procedure was developed by Ghazy et al [13] for the determination of copper (II) in natural waters, vitamins and certified steel scrap samples. It is based on the reaction at pH 4-9 between the synthesized acetophenone-*p*-chlorophenylthiosemicarbazone (A-*p*-ClPT) and Cu (II) forming a green complex, Cu (II): A-*p*-ClPT (1:2) that floats

ISSN: 2348-4098
VOLUME 02 ISSUE 04 APRIL-MAY 2014

quantitatively with oleic acid (HOL) surfactant. A facile, sensitive and selective extractive spectrophotometric method was developed by Rekha et al [14] for the determination of copper (II) in various water and alloy samples using a newly synthesized reagent, 3-methoxy-4-hydroxy benzaldehyde 4-bromophenyl hydrazone (3,4-MHBBPH). Jankiewicz et al [15] developed a spectrophotometric determination of copper (II) in soil samples from selected allotment gardens in Lodz. A simple, rapid and sensitive ultraviolet-visible spectrophotometric technique was developed by Liao et al [16] for the determination of ultra-trace copper based on injection-ultrasound-assisted dispersive liquid-liquid microextraction. Spectrophotometric measurement of $Cu(DDTC)_2$ for the simultaneous determination of zinc and copper by Uddin etal [17]. In the present study, the author synthesized *p*-dimethyl amino benzyl ethylene diamine reagent in the laboratory and this reagent was used for the determination of copper metal ions in various environmental samples.

## 2. EXPERIMENTAL

All the chemicals and solvents used were of analytical reagent grade procured from Sigma – Aldrich Company and double-distilled water was used to prepare all solutions in the experiments. A pH meter (Elico, Model LI-129, India) with combined glass electrode was used for pH measurements. A single pan analytical balance (Dhona, Model 100 DS, India) was employed for weighing the samples. A Systronics UV- Vis Spectrophotometer 118 model with 1 cm matched quartz cells was used for all absorbance measurements.

### 2.1 Synthesis of *p*-dimethyl amino benzyl ethylene diamine

Equi-molar ratio *of* p-dimethyl amino benzaldehyde and ethylene diamine (1:1) mixture was refluxed at room temperature for 3 h and allowed to stand at room temperature for two hours. Light yellow color crystals were obtained and these crystals were washed with double distilled water and recrystalized from methanol. The melting point of the reagent is $145^{o}$ C .

### 2.2 General Procedure for the extraction of *p*-dimethyl amino benzyl ethylene diamine-copper complex

ISSN: 2348-4098
VOLUME 02 ISSUE 04 APRIL-MAY 2014

Transfer a sample aliquot, 1-10 mL of solution containing up to 50 µg copper, to a 125 mL separatory funnel. Add 1.0 mL of 2.0 M sulfuric acid and make the solution with double distilled water to reach a final volume of about 20 mL. To this add 20 mL of ethyl acetate. Cool the funnel and its contents in an ice water bath at 10$^{o}$C for 30 min. All reagents added beyond this point are also cooled to 10$^{o}$C. Add 3.0 mL of 3.0 % hydrogen peroxide. Shake the funnel vigorously for 30 s, allow for layer separation, and discard the aqueous phase. Add 10 mL 0.01% *p*-dimethyl amino benzyl ethylene diamine. Again extract for 30 s, allow for layer separation, and discard the aqueous phase. Transfer the organic phase to a 25 mL volumetric flask, warm to room temperature, and add sufficient additional ethyl acetate to achieve a volume of exactly 25 mL. Measure the absorbance of this solution at 480 nm against a reagent blank prepared in the same manner but containing no metal ion.

## 3 RESULTS AND DISCUSSION

*p*-dimethyl amino benzyl ethylene diamine yields a yellow colored complex with copper metal solution in acetate buffer of pH 5.0. This complex has maximum absorption at 480 nm and is stable for eight hours. Effects of pH, reagent concentration, choice of the solvent, interference of foreign ions were investigated in order to develop a sensitive spectrophotometric method for the determination of copper ion in various environmental samples.

### 3.1 Absorption spectrum of the *p*-dimethyl amino benzyl ethylene diamine- copper complex

An aliquot of 1.0 mL of copper solution was transfered into a 25 mL separating funnel. To it, 1.0 mL of *p*-dimethyl amino benzyl ethylene diamine in ethyl acetate solution and 3.0 mL of acetate buffer of pH 5.0 were added. The yellow colored complex was transferred into a 25 mL standard flask and made up to the mark. The reagent blank was prepared by using the same solutions without copper and extracted similarly. The absorption spectrum of the complex is recorded against the reagent blank. The absorption spectrum of the reagent and the complex is shown in Figure 1. The spectrum reveals that the *p*-dimethyl amino benzyl ethylene diamine-copper complex has maximum absorbance at

ISSN: 2348-4098
VOLUME 02 ISSUE 04 APRIL-MAY 2014

480 nm. Hence, further absorbance measurements of the complex were made at 480 nm.

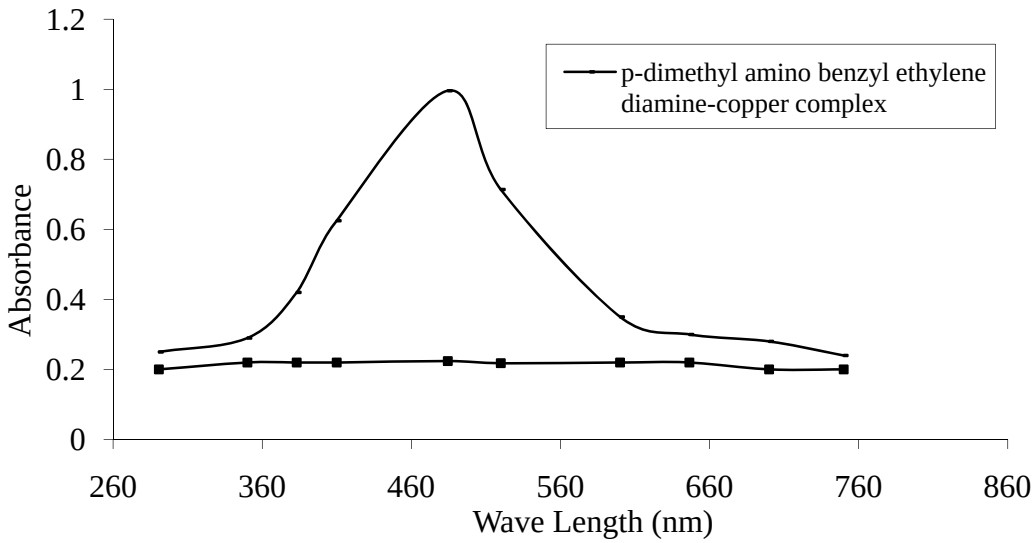


Figure 1. Absorption spectrum of p-dimethyl amino benzyl ethylene diamine-copper complex

### 3.2 Choice of solvent

Various organic solvents such as chloroform, n-butanol, carbontetrachloride, ethyl acetate, MIBK, benzene, etc, were used for the extraction of *p*-dimethyl amino benzyl ethylene diamine-copper complex. The results show that maximum absorbance was obtained in ethyl acetate medium. Hence, ethyl acetate solvent was chosen for further investigations.

### 3.3 Effect of pH

A mixture containing 5.0 µg of copper, 3.0 mL of the suitable buffer and 1.0 mL of reagent solution was taken and the volume was adjusted to 10.0 mL with double distilled water. The experiment was repeated with acetate buffer at different pH values from 3.0 to 9.0. The values obtained were shown in Figure 2. It is observed that the extraction of the metal ion gives maximum abosorbance at pH 5.0. Hence pH 5.0 is selected for further investigations.

ISSN: 2348-4098
VOLUME 02 ISSUE 04 APRIL-MAY 2014

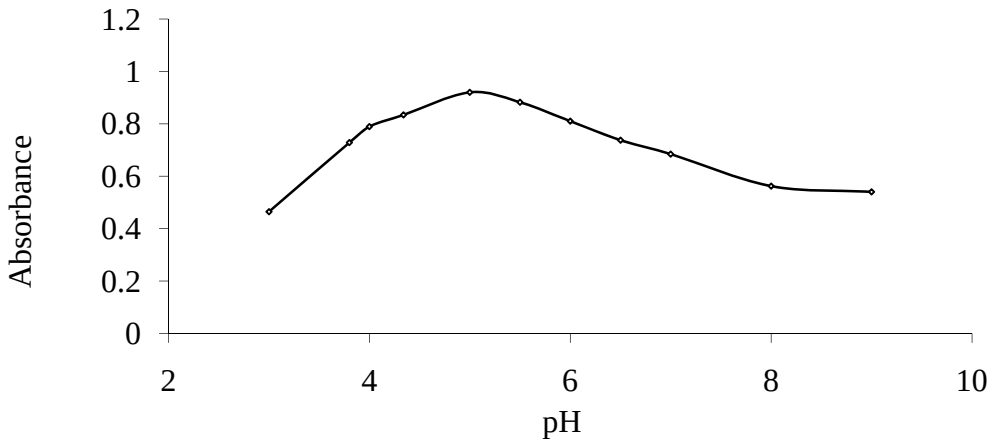


Figure 2. Variation of absorbance with pH for p-dimethyl amino benzyl ethylene diamine- copper complex

### 3.4 Effect of reagent concentration

The effect of reagent concentration has been studied by taking constant 2 mL of copper solution and 3.0 mL of pH 5.0 buffer solution. The reagent concentration varied between 1 µg $mL^{-1}$ and 9 µg $mL^{-1}$ to obtain maximum color formation. The total volume of aqueous phases was brought to 10.0 mL with double distilled water. The absorbance of these phases was measured at 480 nm, against their corresponding reagent blanks. Maximum color development of the complex is absorbed at 3 µg $mL^{-1}$. Hence, 3 µg $mL^{-1}$ of the reagent is maintained for all further studies.

### 3.5 Stability of the color reaction

The absorbance values of *p*-dimethyl amino benzyl ethylene diamine- copper complex were noted at different intervals of time at 480 nm. It was observed that the absorbance remained constant upto 8 hours, thereby indicating that the complex is stable for at least 8 hours.

### 3.6 Sensitivity and molar absorptivity

The molar absorptivity of the complex was calculated and reported as $2.3x10^4$ lit $mol^{-1}$ $cm^{-1}$ and the Sandell's sensitivity of the complex was found to be $2.4283x\ 10^{-3}$ µg $cm^{-2}$.

### 3.7 Effect of foreign ions

The effect of diverse ions on the extraction of copper ion was studied by taking known amount of copper in the solution. The results are presented in Table 1.

ISSN: 2348-4098
VOLUME 02 ISSUE 04 APRIL-MAY 2014

**Table No. 1 Effect of foreign species**

| **Species** | **Tolerance limit [µg $mL^{-1}$]** |
|---|---|
| $Na^+$, $Mg^{2+}$,$Cl^-$, $NO_3^-$, $F^-$, $CHCOO^-$, $CO_3^{2-}$, $K^+$ | <2130 |
| $Ba^{2+}$, $SO_4^{2-}$, $CN^-$, $SCN^-$, Tartarate | <1000 |
| $PO_4^{3-}$, $Al^{3+}$, $Cd^{2+}$, $NO_2^{-}$ [(a)] | 800 |
| $Fe^{3+}$ [(b)], $Ni^{2+}$, $Co^{2+}$, $Ca^{2+}$ | 84 |
| $Zn^{2+}$, $Pb^{2+}$, $SO_3^{2-}$, $NO_3^-$, $Cr^{3+}$, $As^{5+}$ | 50 |
| $Fe^{2+}$, $S^{2-}$ | 36 |

[a]Can be masked up to 750 µg $mL^{-1}$ by the addition of 2 mL of 1 % sulfamic acid.

[b]Can be masked up to 43 µg $mL^{-1}$ by the addition of 1 mL of 5% EDTA.

In this study, it is noticed that there is no interference due to presence of ions such as Ca(II), Mg(II), V(V), Mn(II), Ti(IV), Mo(VI), Sr(II), Bi(III), Sb(III), W(VI), iodide, chloride, bromide, thiourea, nitrate, acetate, citrate, tartrate, phosphate and oxalate up to 2500 µg or more. Cations like Ag(I), Hg(II) and Be(II) can be tolerable up to 1250 µg. The metal ions like Ni(II), Co(II), Fe(III), Zn(II), Cd(II) and Pd(II) and anions interferences was suppressed by adding 1.0 mL of 0.3% oxalate, Ni(II), Zn(II) were suppressed by using 1.0 mL of 0.4% thiourea as masking agents and Cd(II) interference was suppressed by using 1.0 mL 0.3% citrate solution.

## 4 APPLICATIONS OF THE DEVELOPED METHOD

The procedure developed for the determination of copper was successfully employed to determine the content of copper in various water and industrial effluent samples.

### 4.1 Application of method to natural water samples

ISSN: 2348-4098
VOLUME 02 ISSUE 04 APRIL-MAY 2014

The proposed procedure was applied for the preconcentration and determination of copper metal ion in natural water samples. The natural water samples were collected in and around Tirupati, India. Analysis of copper in natural water samples was carried out as described in general procedure section. The results are presented in Table.2.

**Table.2. Determination of copper in various water samples with proposed method**

| **Sample** | **Cu added (µg $mL^{-1}$)** | **Found[a]** | **Recovery (%)[a]** |
|---|---|---|---|
| Polluted water[b] | - | 0.29 ± 0.05 | - |
| | - | 0.37 ± 0.03 | - |
| | - | 0.42 ± 0.06 | - |
| | - | 0.51 ± 0.03 | - |
| Natural water[c] | 0.3 | 0.28 ± 0.04 | 93.33 |
| | 1.0 | 0.98 ± 0.03 | 98.00 |
| | 1.3 | 1.58 ± 0.06 | 99.30 |
| Bore well water[d] | - | 1.0 ± 0.04 | - |
| | - | 1.20 ± 0.03 | - |
| Drinking water[e] | 0.3 | 0.38 ± 0.05 | 97.50 |
| | 0.6 | 0.98 ± 0.02 | 99.00 |
| | 1.0 | 1.38 ± 0.04 | 99.20 |
| | 1.3 | 1.58 ± 0.02 | 98.80 |

a) Mean ± standard deviation (n=6),

b) Collected from near Gajulamanyam Industrial area, A.P., India

c) Collected from Swarnamukhi river, Srikalahasti, A.P, India.

ISSN: 2348-4098
VOLUME 02 ISSUE 04 APRIL-MAY 2014

d) Collected from in and around Tirupati,

e) Collected from municipal water supply, Tirupati.

### 4.2 Determination of copper in leaf samples

The proposed procedure was applied for the pre concentration and determination of copper in leaf samples following spectrometric method. First 0.1 g of powdered leaf sample was taken in a 100 mL beaker; to this 5 mL of 1:1 molar ratio of conc. $HNO_3$ and $HClO_4$ is added and then heated gently until the entire leaf sample becomes digested. After digestion the volume was made upto 25 mL with double distilled water and the copper contents were analyzed following general procedure. The values are recorded and shown in Table 3.

**Table.3. Determination of copper in various leaf samples**

| Leaf sample | Amount of Cu(II) found ($\mu g\ mL^{-1}$) | | CV (%) |
|---|---|---|---|
| | Standard Reagent [b] | Synthesized Reagent | |
| Amaranthus gangeticus (Totakura) | 0.82 | 0.80±0.03 | 3.8 |
| Hibiscus rosasinensis (Mandara) | 0.78 | 0.78±0.02 | 2.6 |
| Azadirachta indica (Neem) | 1.20 | 1.16±0.02 | 1.7 |
| Murraya koenigii(L) Spr. (Karivepaku) | 0.64 | 0.62±0.02 | 3.2 |
| Oscimum sanctum (Tulsi) | 0.86 | 0.84±0.03 | 3.6 |

a- average mean for five determination, b- 4-Amino-3-hydroxy naphthalene-1-sulphonic acid regent procured from local market.

ISSN: 2348-4098
VOLUME 02 ISSUE 04 APRIL-MAY 2014

## 5 CONCLUSIONS

The proposed method is sensitive, accurate, and tolerant to many foreign substances, and the reagent used is stable under laboratory conditions. The presented procedure has some advantages over the other spectrophotometric procedures for copper, with high molar absorptivity value, low detection limit, and easy application to the real samples. The method is easily applied for the determination of copper contents of different environmental samples.

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ISSN: 2348-4098
VOLUME 02 ISSUE 04 APRIL-MAY 2014

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ISSN: 2348-4098
VOLUME 02 ISSUE 04 APRIL-MAY 2014

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