

## Determination of Cu(II) with 1-Nitroso-2-naphthol in Micellar Medium by Derivative Spectrophotometry

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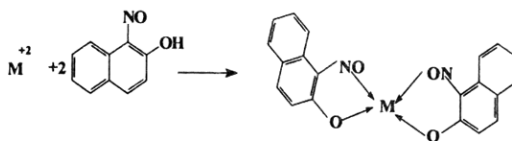
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**Summary:** A spectrophotometric and first derivative spectrophotometric determination of copper(II) is carried out with 1-nitroso-2-naphthol as complexing reagent in aqueous phase using non-ionic surfactant Tween 40. The copper is determined in the range 1.7–120 ng ml<sup>-1</sup> with detection limit (2 $\sigma$ ) of 1.7 ng ml<sup>-1</sup>. The molar absorptivity and Sandell's sensitivity are 1.90  $\times$  (10<sup>4</sup> mol<sup>-1</sup>cm<sup>-1</sup>) and 7.9 ng cm<sup>-2</sup> at 483.5 nm. The optimum pH of the complex is 9. The critical micelle concentration (cmc) of Tween 40 is 5%. Absorption studies in the first derivative mode is carried out to determine the absorption maximum of the complex for higher sensitivity and to overcome interference due to the presence of certain metal ions. The present method is compared with that of AAS and no significant difference is noted between the two methods at 95% confidence level. The method has been applied for the determination of Cu(II) in industrial waste samples.

### Introduction

Copper is a nutritionally essential metal and is widely distributed in nature [1]. In chemical analysis, metal chelation followed by solvent extraction and spectrophotometric detection is the preferred mode of analysis for a number of metal ions [2, 3] due to rapidity, simplicity and wide applications. Several spectrophotometric methods have been developed in which the solvent extraction step is conveniently replaced by the use of a surfactant [4, 5]. Due to the solubility of several compounds in micelles (aggregates of surfactants), many analytical techniques for the determination of metal ions in aqueous system, have been developed and modified [6-14]. Micellar media is mainly used to enhance the absorption sensitivities, thus simplifying the system by replacing the toxic organic solvents. The use of polyoxyethylene sorbitan mono-oleate (Tween 40) is reported for the determination of metal ions using 1-nitroso-2-naphthol as a complexing agent [15]. The determination of metal complexes of 1-(2-pyridylazo)-2-naphthol in micellar media has been reported earlier [16]. Tween series surfactants are very soluble in aqueous systems than other non-ionic surfactants. 1-nitroso-2-naphthol forms coloured water-insoluble complexes with a large number of metal ions and the use of surface-active reagent increase the solubility of 1-nitroso-2-naphthol has been reported [17]. Derivative mode spectrophotometry is recently shown to be more useful than classical spectrophotometry for solving several analytical problem [18]. The use of derivative mode spectrophotometry offers a useful

means of enhancing the sensitivity and selectivity of the method besides convenient solution to well defined analytical problems such as resolution of multi component systems, overcoming interference due to sample turbidity, matrix back ground and enhancement of spectral details [19, 20]. The scale of this increase depends on the shape of the normal absorption spectra of the analyte and the interfering substances, as well as on instrumental parameters and the measurement technique (e.g. peak-to-trough or zero-crossing), chosen by the analyst in a given analytical procedure. In the present work, determination of Cu(II) as 1-nitroso-2-naphthol complex, in a non-ionic surfactant Tween 40 using first derivative mode spectrophotometric method is reported. The method was successfully applied for the determination of Cu(II) in industrial waste samples.



Suggested reaction of metal(II)-1-nitroso-2-naphthol to form bis[1-nitroso-2-naphthol]metal(II) complex

### Results and Discussion

Fig. 1 shows absorption spectra in first derivative mode spectroscopy of Cu(II)-1-nitroso-2-naphthol complex at 450 nm (i.e. a shift from 483.5 nm). It can be seen in the Fig. 1 the height of the peak at

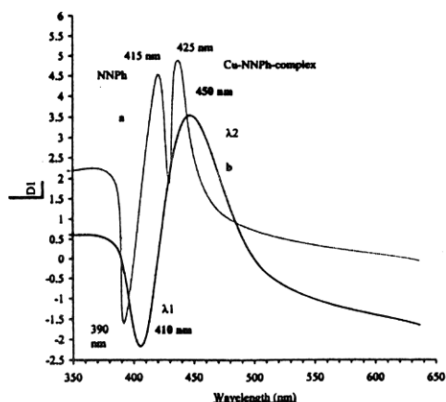


Fig. 1: First derivative spectra (a) 1-nitroso-2-naphthol and (b) copper (II)-1-nitroso-2-naphthol complex in 5% Tween 40 at pH 9.

(PH) 450 nm and the depth of the trough (TD) at 410 nm were linearly related to the metal ion concentration. It can be seen by comparing Fig. 1 that the first derivative spectra are more resolved than those obtained for the normal mode. It can be seen that the first derivative spectra are more resolved than those obtained for the normal mode. However, even higher derivative orders yield sensitive but irreproducible signal, so this possibility was discarded. As derivative spectroscopy provides additional possibilities because it enhances the detectability of minor spectral features, this technique was adapted. The first order derivative spectrum is of great significance as it exhibits the  $\lambda_{max}$  of the complex which is otherwise difficult to ascertain due to several absorbing species and only a shoulder appears in the normal absorption spectrum due to the desired component. Weak and broad peaks give higher sharpest peak; other close peaks were changed from normal mode wavelength to new ones length showing no close ness to other neighbour peaks. The micelle of non-ionic surfactant with polyoxyethylene group comprises two parts. One is the hydrocarbon tail directed to the interior core of micelle and the other is the hydrated polyoxyethylene group located at outer sphere. Organic compounds and metal chelates having large affinity towards polyoxy-ethylene group may be incorporated. 1-nitroso-2-naphthol could be dissolved by this phenomenon, because this species has a hydroxyl group, which interacts with the ether oxygen of polyoxyethylene group, by hydrogen bonding. It seems that micelle in solution was formed because 5% Tween 40 solution was above (0.0013 %, w/v) concentration [21].

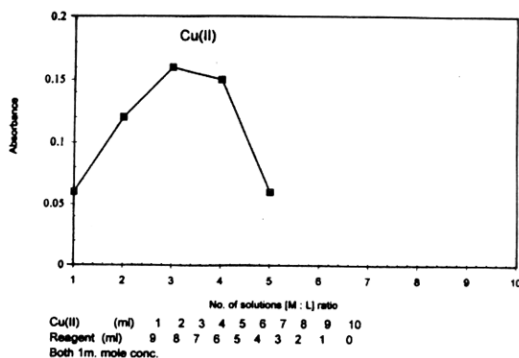


Fig. 2: Job's plot of metal : ligand ratio

### Composition

Composition of the complex formed under experimental conditions was investigated by Job's method of continuous variations. Fig. 2 plot of absorbance versus mole fraction of the metal ion shows at maximum which corresponds to 1: 2 (M: L) ratio for metal ion in the complex.

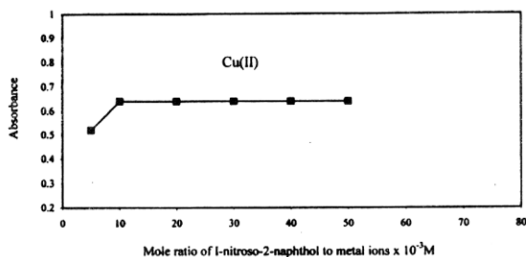


Fig. 3: Effect of amounts of I-nitroso-2-naphthol on the absorbance of Cu(II)

Fig. 3 shows increase in the absorption with increase in the concentration of 1-nitroso-2-naphthol solution from  $10\text{-}50 \times 10^{-3}$  M in presence of constant Cu(II) concentration: Fig. 4 shows the optimum pH 9.0 for Cu(II) 1-nitroso-2-naphthol complex formation. Fig. 5 shows the calibration graph of Cu(II)-1-nitroso-2-naphthol complex in the range of 1.7-120  $\text{ng ml}^{-1}$  at 450 nm with increasing concentration of copper (II). In normal mode detection limit is 3.3  $\text{ng ml}^{-1}$  while in first derivative mode lowered significantly from 3.3 to 1.7  $\text{ng ml}^{-1}$  which is the great success of the present method. All other experimental conditions are same as in normal mode spectroscopy, molar absorptivity is  $1.90 \times (10^4 \text{ mol}^{-1}\text{cm}^{-1})$ , Sandell's sensitivity ( $3.3 \text{ ng cm}^{-2}$ ) and Beer's law linear range is  $0.25\text{-}2.0 \mu\text{g ml}^{-1}$  already given in Table-1 and

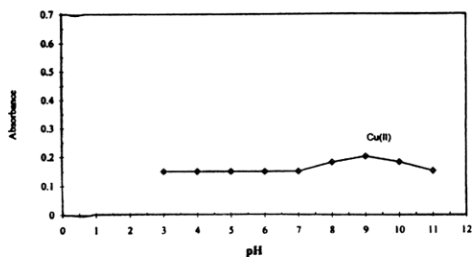


Fig 4: Effect of pH on the absorbance of metal-1-nitroso-2-naphthol complexes.

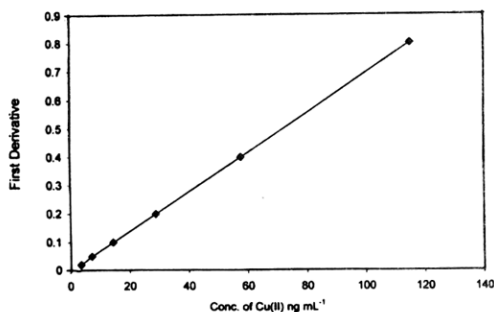


Fig 5: Calibration graph of Fe(III)-1-nitroso-2-naphthol complex in 5% Tween 40 at pH 1 at ( $I_{\max}$  430 nm and 400 nm) in first derivative mode spectroscopy

Beer's law linear range in first derivative mode spectroscopy is 1.7-120  $\text{ng ml}^{-1}$ .

#### Study of interference's by foreign ions

In the Cu(II) determination with 1-nitroso-2-naphthol in presence of 5 % Tween 40 were studied results are shown in the Table-2, these interference's can be avoided in general by the addition of complexing agent like EDTA which forms stable complexes with many metal ions so that in this medium Cu(II) reaction with 1-nitroso-2-naphthol is highly selective with  $\text{NH}_4^+/\text{NH}_3$  buffer at pH 9. Cd(II), Ni(II), Fe(III) and Pb(II) interfere at low trace level as given in Table-2. The interference due to absorption by Fe and Ni (II)-1-nitroso-2-naphthol complex in normal mode spectroscopy is thus removed by the use of first derivative mode spectroscopy.

#### Validation of method

Proposed method was verified by % recovery test by standard addition method, results were

Table-1: Tolerance limits for interference's of metal ions and salts with 1-nitroso-2-naphthol in Tween 40 in normal mode spectroscopy Tolerance limits  $\mu\text{g ml}^{-1}$

Ion / salt	Cu(II)
KSCN	1000
NaF	600
$\text{Na}_2\text{C}_2\text{O}_4$	500
$\text{KClO}_3$	1000
$\text{Na}_2\text{tartarate}$	1000
$\text{Na}_2\text{citrate}$	300
KCN	50
Mg(II)	800
Al(III)	10
Cd(II)	2
Co (II)	10
Cr (III)	50
Cr (VI)	8
Fe (III)	5
Mn(II)	300
Ni(II)	5
Pb (II)	3
Zn (II)	50
Cu (II)	-

The conc. of metal ions is  $2\mu\text{g ml}^{-1}$

Table-2: Percent recovery of known amount added to tap water.

Metal ions	Amount added	Amount found	Recovery (%)
Cu(II)	1.70 $\text{ng ml}^{-1}$	1.69 $\text{ng ml}^{-1}$	99 $\pm$ 1
	0.50 ( $\mu\text{g ml}^{-1}$ )	0.49 ( $\mu\text{g ml}^{-1}$ )	99 $\pm$ 1

compared with AAS, which are in good agreement with (AAS) given in Table-2.

#### Experimental

A UV/Vis spectrophotometer Perkin Elmer model Lambda 2 was used for recording normal as well as derivative spectra. Atomic absorption spectrophotometer, model Spectra AA. 20 Varian was used for metal ion determination. The following analytical parameters were used: photomultiplier voltage 349.9 volts, wavelength 324.8 (nm), slit width 0.5 nm, flame air-acetylene, acetylene flow rate 1.5 L/min. The Pye Model 292 pH meter was used.

#### Reagents

All chemicals used were analytical grade reagents (Merck and Fluka A.G) unless otherwise stated. Standard Cu(II) stock solutions of ( $100\mu\text{g ml}^{-1}$ ) were prepared dissolving their nitrate salt. Other metal ions solutions were prepared from their nitrate or chloride salts. 5% Tween 40 solution was prepared by dissolving that in a 100 ml volumetric flask, and was diluting to the mark with double distilled water.

Buffer solution of pH 9 was prepared by taking 0.025 M sodium borate (50 ml) and 0.1M hydrochloric acid (4.6 ml) mixtures and adjusting the volume to 100 ml according to Perrin and Dempsey [22].

### Procedure

Absorption spectra (normal and derivative) of the following solutions were recorded, taking reagent blank as reference, in order to determine photometric characteristics of the 1-nitroso-2-naphthol-Cu(II) complex.

Two sets of solutions, one containing 3.0  $\mu\text{g ml}^{-1}$  metal ion and other without it, and each containing fixed amount of the reagent (185  $\mu\text{g ml}^{-1}$ ) and Tween 40 (5 %) in the pH range 2.0 –11.0, were prepared to determine the optimum pH range of the complexation reaction.

To study the impact of varying surfactant concentration on the absorbance of the 1-nitroso-2-naphthol-Cu(II) complex, a set of solutions containing increasing amounts of Tween 40 (2%-10%), and 3.0  $\mu\text{g ml}^{-1}$  Cu(II) and 185  $\mu\text{g ml}^{-1}$  1-nitroso-2-naphthol, at the pH of the maximum complex formation was prepared.

Effect of varying ligand concentration on the absorbance of the system was investigated by preparing a set of solutions containing  $10 \times 10^{-3}$  to  $80 \times 10^{-3}$  M of the reagent at the optimum pH.

Range of linear proportionality of absorbance of the system with Cu(II) ion concentration has been ascertained based on a set of solutions containing varying amount of the metal ions (1.0-120  $\text{ng ml}^{-1}$  and 0.06 to 3.0  $\mu\text{g ml}^{-1}$ ), 185  $\mu\text{g ml}^{-1}$  1-nitroso-2-naphthol, and 5% Tween 40 at pH 9 condition of maximum complex formation.

### Spectrophotometric metal ion determination in micellar solution.

Appropriate volumes of stock solutions of metal ions, 1-nitroso-2-naphthol, and surfactant Tween 40 were added and made up to 25 ml volume with distilled water having metal ions concentration of 1.0-120  $\text{ng ml}^{-1}$  and 0.06-3.0  $\mu\text{g ml}^{-1}$ , 1-nitroso-2-naphthol 185  $\mu\text{g ml}^{-1}$  and 5 % Tween 40. Absorption spectra were recorded against reagent as reference to generate analytical calibration curves in normal mode ( $\lambda_{\text{max}}$  483.5 nm) or in first derivative mode (peak

height (PH) at 450 nm) or (trough depth (TD) at 410 nm). Copper content of the standard and the sample was determined using AAS equipped with an air acetylene flame. The pH and wavelength used are listed in Table-3.

Table-3: Analytical characteristics of Cu(II)-1-nitroso-2-naphthol in presence of Tween 40 in normal mode spectroscopy

Characteristics	Cu(II)
Beer's law range ( $\mu\text{g ml}^{-1}$ )	0.25 –2.0
Absorption maxima	
( $\lambda_{\text{max}}$ , nm): (a) micellar	483.5
(b) $\text{CCl}_4$	449.2
Molar absorptivity ( $10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ )	1.9
Sandell's sensitivity $\text{ng cm}^{-2}$	7.9
Detection limit ( $\text{ng ml}^{-1}$ )	3.3
pH range	9
Conc. of Tween 40	5%
Conc. of 1-nitroso-2 naphthol ( $\mu\text{g ml}^{-1}$ )	185
RSD $\pm$	8.03

At 95% confidence limit, n=6

Table-4: Determination of Cu(II) ions in industrial waste samples

Sample	Amount of Cu(II) determined ( $\mu\text{g}$ )		
	Present method	AAS method	C.V. %
*Industrial waste	$0.99 \pm 0.32$	1.00	2.57

At 95%, n=6, \*Kotri SITE area

### The determination of Cu(II) in industrial waste samples.

#### The industrial waste

Industrial waste water sample, 1L obtained from industrial effluent collected from Kotri site area was filtered using Whatman filter paper. Concentrated nitric acid 4 ml and 30 % hydrogen peroxide 2 ml were added to the filtrate. The resulting solution was preconcentrated in an oven at 110  $^{\circ}\text{C}$  to a final volume of 25 ml. Appropriate amounts of Tween 40 and 1-nitroso-2-naphthol was added to a 25 ml calibrated flask to obtain final concentration of 5 % in Tween 40 and 185  $\mu\text{g ml}^{-1}$  in 1-nitroso-2-naphthol. Then 5 ml of the sample was added and the absorbance was measured against reagent blank. The same sample, 5 ml was diluted to 25 ml with double distilled water for AAS analysis. The following analytical parameters were used: photomultiplier voltage 349.9 volts, wavelength 324.8 (nm), slit width 0.5 nm, flame air-acetylene, acetylene flow rate 1.5 l/min.

### Acknowledgment

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