

## Spectrophotometric Determination of Copper(II) with 1-Nitroso-2-naphthol in Tween 40

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**Summary:** A spectrophotometric determination of copper(II)-1-nitroso-2-naphthol complex in aqueous phase in the presence of Tween 40, nonionic surfactant is reported here. The method obeys Beer's law in the concentration range of 0.25-2.0  $\mu\text{g ml}^{-1}$ . The detection limit of copper (II) is 0.25  $\mu\text{g ml}^{-1}$ . The molar absorption, sensitivity, critical micelle concentration, and 1-nitroso-2-naphthol metal ion concentration have been studied and discussed. The method has been applied to the determination of copper in industrial waste samples. The present method was compared with Flame Atomic Absorption Spectroscopy (FAAS), and no significant difference was noted between the two methods at 95% confidence interval.

### Introduction

The use of 1-nitroso-2-naphthol as complexing reagent with several metal ions followed by their solvent extraction and spectrophotometric determination is well reported in the literature [1-5]. However, in recent years ionic as well as non-ionic surfactants have been used to replace the solvent extraction process in these determinations [6-13]. Surfactant aggregates called micelles have an excellent solubilizing property for several organic molecules or their complexes. Consequently many analytical techniques have been developed over the years [14-19]. Gracia *et al.* [20] have reported the use of Triton X-100 a nonionic surfactant for the spectrophotometric determination of Cu(II), Hg(II) and Ag (II) in water. Agnihotri *et al.* [21] developed a photometric determination of copper(II) in a Triton X-100 in normal and derivative modes. Cobalt has been reported to be selectively determined by complexation with 1-nitroso-2-naphthol in the presence of Triton X-100 as a neutral surfactant [22]. Sodium dodecylsulphate an-anionic surfactant has also been used for the trace analysis of Cu (II) in water with DDTC as a complexing reagent [23]. Recently polyoxyethylene sorbitan mono-oleate (Tween 80) has reported in the determination of metal ion using 1-nitroso-2-naphthol as complexing agent [24]. Tween series surfactants are very soluble in aqueous systems than other non-ionic surfactant. Therefore in the present work sorbitan monopalmitate (Tween 40) has been utilized as micellar media for the determination of copper (II) using 1-nitroso-2-naphthol. The work described here is in continuation to our previous report on the determination of  $\text{Zn}^{2+}$ -dithizone complex in presence

of a cationic surfactant [25]. The method has been applied for the analysis of Cu (II) in the industrial waste samples.

### Results and Discussion

Complexation of 1-nitroso-2-naphthol, with several metal ions is well established. Fig. (1) shows a reaction of copper with 1-nitroso-2-naphthol to produce copper- 1-nitroso-2-naphthol complex.

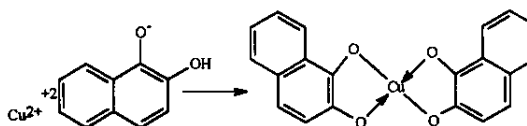


Fig. 1: Reaction of copper (II) 1-nitroso-2-naphthol to form Bis[1-nitroso-2-naphthol] copper (II) complex

Fig. (2) shows the spectra for a 1-nitroso-2-naphthol 185  $\mu\text{g ml}^{-1}$  and for a copper(II) 1-nitroso-2-naphthol complex with an absorbance maxima at 376 nm and 483 nm, respectively.

Comparison of the analytical wavelengths of micellar media with  $\lambda_{\text{max}}$  of solvent extraction are given in Table-1. The pH of the solution also had a marked effect on the absorbance of the copper(II) 1-nitroso-2-naphthol. On increasing pH to 9.5, the peak at 483 nm shifts hyperchromically and bathochromically to 485 nm. As the ligand absorbs significantly at the absorption maxima of the complex relative increase in absorbance of the complex was calculated and plotted against pH as shown in Fig. (3) This plot shows a maximum at pH

9, which has been taken as the pH of maximum complex formation throughout this work.

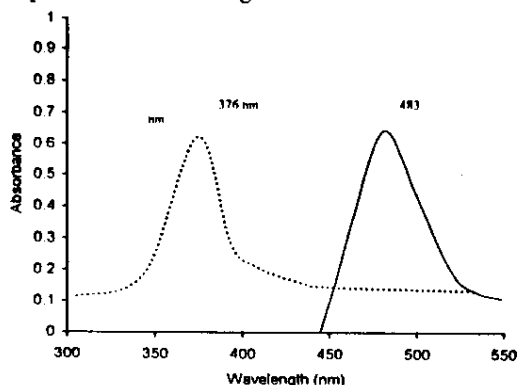


Fig. 2: Absorption spectrum of 1-nitroso-2-naphthol at (376 nm), and Cu(II) 1-nitroso-2-naphthol (483 nm) in 5% Tween 40 at pH 9 (II) conc. Of Cu(II)  $7 \mu\text{g ml}^{-1}$  (II) 1-nitroso-2-naphthol conc.  $185 \mu\text{g ml}^{-1}$

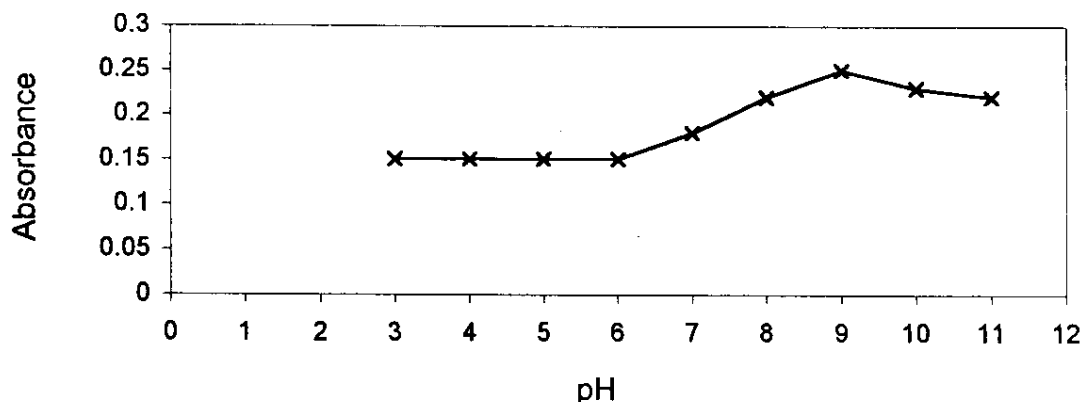


Fig. 3: Effect of pH on the absorbance of 1-nitroso-2-naphthol complex. The conc. Of Cu(II) ion was  $2.0 \mu\text{g ml}^{-1}$

Table-1: Experimental conditions for copper metal ion determination by complexation with 1-nitroso-2-naphthol in (a) aqueous nonionic micellar medium and (b) by solvent extraction in  $\text{CCl}_4$

Solvent	Method	pH	$\lambda_{\text{max}}$ (nm)	Conc. of Tween 40	Conc. of 1-nitroso-2-naphthol	$\epsilon_{\text{max}} \text{ ml}^{-1} \text{ cm}^{-1}$ ( $10^4$ )
Aqueous	Micellar	9.0	483.5	5%	$185 \mu\text{g ml}^{-1}$	0.6
$\text{CCl}_4$	Solvent Extraction	9.0	449.2	—	0.003 g	$2.82^a$

<sup>a</sup>These values were obtained assuming metal ions were completely extracted.

As shown in Fig.(4) the absorbance spectra of solutions showed an increase in absorbance with an increase in Tween 40 concentration up to 5 % of the complex and the ligand. A slight decrease, however, was observed above this concentration. The surfactant concentration was maintained at 5 %

during subsequent studies. The absorption maximum at ( $\lambda_{\text{max}}$  of 483 nm) of the solution containing varying amounts of 1-nitroso-2-naphthol in presence of constant copper(II) concentration  $2 \mu\text{g ml}^{-1}$  increased with increase in 1-nitroso-2-naphthol concentration up to  $185 \mu\text{g ml}^{-1}$  as shown Fig. (5).

Higher ligand concentration posed dissolution problem besides introducing error in the absorbance correction due to higher ratio of ligand to complex absorptivity. Metal to ligand ratio in the complex is 1 : 2 (M : L), found by job's method and the complex remained stable for at least 2 h. Fig. (6) shows a calibration graph of copper concentration against the absorbance at 483 nm. Linear regression was carried out from which the regression coefficient was calculated as 0.999. The relative standard deviation for a  $1.5 \times 10^{-4} \text{ M}$  standard ( $n=8$ ) was 1.2%. The lowest detection limit for this metal was found to be  $0.25 \mu\text{g ml}^{-1}$ .

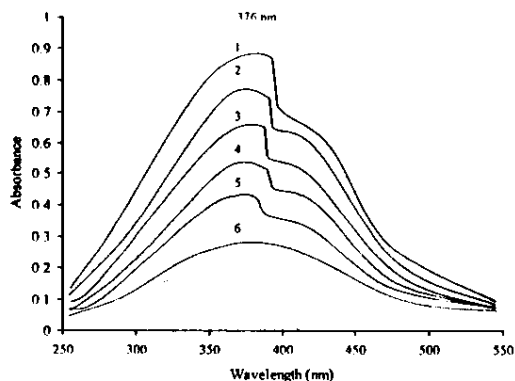


Fig. 4: Absorption spectra of saturated 1-nitroso-2-naphthol in various percent conc. Of Tween 40 solution. The conc. Of Tween 40 in (1) 10%, (2) 8%, (3) 6%, (4) 5%, (5) 4% and (6) 2%.

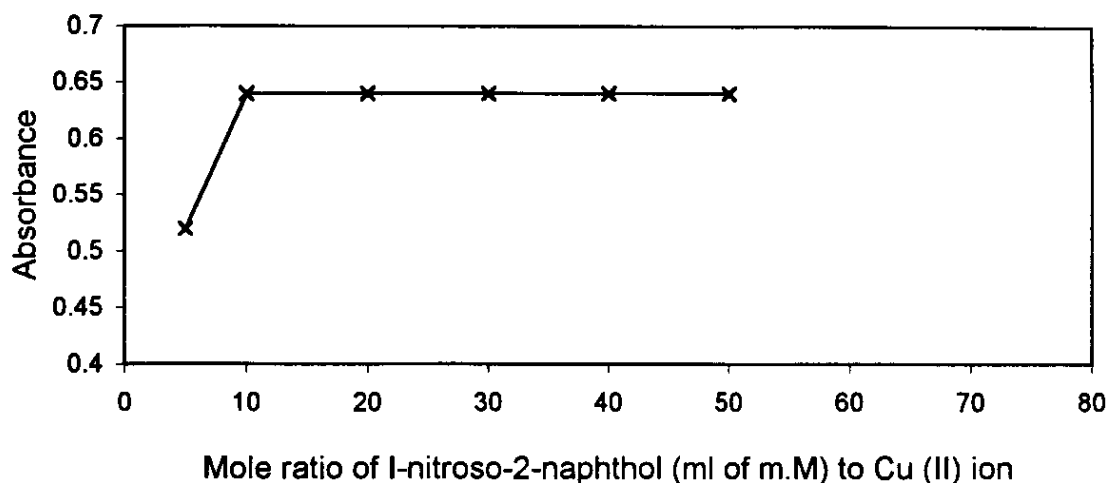


Fig. 5: Effect of amount of 1-nitroso-2-naphthol (ml of m.M) on the absorbance to Cu(II) (1 m.M) ion.

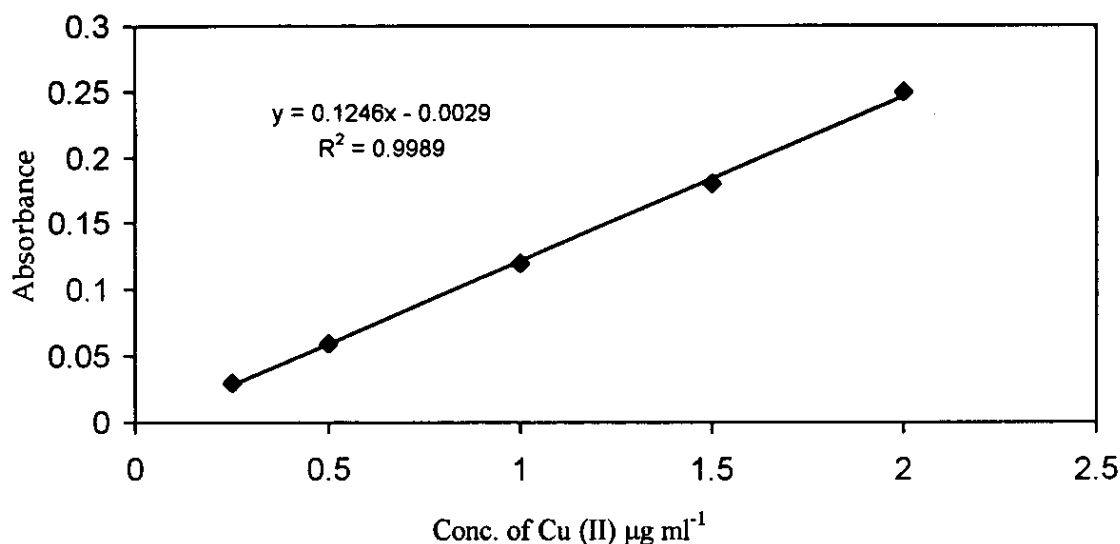


Fig. 6: Calibration graph of Cu(II) 1-nitroso-2-naphthol in 5% Tween 40

The interfering effects of foreign ions, in the determination of Cu (II) with 1-nitroso-2-naphthol in presence of Tween 40 have been studied. For Cu ions, KSCN, KClO<sub>3</sub>, and sodium tartarate did not interfere until their amount reached 1000  $\mu\text{g ml}^{-1}$ . The Mn (II) and Mg (II) does not interfere till (1000  $\mu\text{g ml}^{-1}$ ). Co, Cd, Ni, Fe strongly interfere when given concentration exceeds those given in Table 2. Oxalate is masking agent of Co (II). These interferences can be avoided in general by the addition of a complexing agent, like EDTA, which forms stable complexes with many metal ions, so

that, in this medium the Cu (II) reaction with 1-nitroso-2-naphthol is highly selective with NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub> buffer at pH 9, using the surfactant Tween 40.

Copper by this method has been investigated by studying the absorption spectra. EDTA was added to mask interference from cobalt, nickel, chromium, manganese bismuth, lead and cadmium. Table-3 shows the results obtained with the above samples. These results correlate well with those obtained by atomic absorption spectrophotometry at 95% confidence level.

Table 2 :Foreign ion quantities below which interferences are not produced in the Cu(II) determination in a conc. of  $2.0 \mu\text{g ml}^{-1}$  in Tween 40

Ion / salt	Tolerance limits ( $\mu\text{g ml}^{-1}$ )
KSCN	1000
Na F	600
$\text{Na}_2\text{C}_2\text{O}_4$	500
$\text{KClO}_3$	1000
$\text{Na}_2\text{tartrate}$	1000
$\text{Na}_2\text{citrate}$	300
KCN	50
Mg(II)	800
Al(III)	1000
Cd(II)	2
Co(II)	10
Cr(III)	50
Cr(IV)	8
Fe(III)	5
Mn(II)	300
Ni(II)	5
Pb(II)	3
Zn(II)	100

Table- 3: Determination of Cu (II) in real samples

Sr. Sample No.	Amount of Cu(II) determined (mg)		
	Present method	FAAS	C.V %
1. Industrial waste (mg/L)	32.30	$32.50 \pm 0.13$	2.57

At 95% t-test, n=6

#### Application

The proposed spectroscopic method was applied to the determination of Cu (II) industrial waste samples. Results are given in table 3.

#### Experimental

All chemicals used were analytical grade reagents (Merck and Fluka) unless otherwise stated. Stock solution of copper was prepared from copper (II) nitrate salts. 1-nitroso-2-naphthol solutions were freshly prepared in distilled water just before use to avoid acid decomposition [26]. Tween 40 5% was prepared by dissolving 5.0 g/100 ml in freshly prepared double distilled water. Sodium acetate (0.2 M) buffer solution was prepared and adjusted to pH 9 with acetic acid (0.2 M). EDTA was added to mask interference. A UV / VIS Spectrometer Perkin Elmer model Lambda 2 was used throughout this study. Atomic absorption spectrometer, model Spectra AA. 20 Varian was used for comparative metal ion study. 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.

#### Spectrophotometric Metal Ion Determination in Micellar Solution.

Appropriate volumes of stock solutions of Cu (II) ion, 1-nitroso-2-naphthol and Tween 40 were added to a series of 25 ml calibrated flasks and made up to volume with distilled water. The following concentration was used Cu (II)  $1-10 \mu\text{g ml}^{-1}$ , 1-nitroso-2-naphthol  $185 \mu\text{g ml}^{-1}$  and Tween 40 5 %. The surfactant concentration, pH values and analytical wavelength used are listed in Table 1.

#### Spectrophotometric Metal Ion Determination after extraction with $\text{CCl}_4$

Appropriate volumes of stock metal and 1-nitroso-2-naphthol aqueous solutions were placed into a separating funnel and 10 ml of  $\text{CCl}_4$  was added. The organic layer was transferred to a 25 ml volumetric flask. In order to obtain complete extraction, the process was repeated twice, the first time with 10 ml and the second time with 5 ml of  $\text{CCl}_4$ . For the 25 ml total volume of the organic layer, absorbance was measured at the appropriate wavelength for metal ion [27].

#### Determination of Cu(II) in Real Samples

##### (a)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 water. The same sample, 5 ml was diluted to 25 ml with double distilled water for FAAS analysis.

#### Conclusion

Determination of trace amount of Cu (II) is carried out directly using 1-nitroso-2-naphthol in nonionic micellar media of Tween 40 in aqueous solutions. The method is simple and rapid with greater sensitivity, better selectivity, improved precision and replaces difficult step of extraction with toxic organic solvents. Cu (II) content in various matrixes can be determined by the present method.

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