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1-Nitroso-2-naphthol and Its Position Isomer as Photometric Reagent for Copper Determination in Aqueous Phase

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Complexation reactions of copper(II) with 1-nitroso-2-naphthol and its position isomer 2-nitroso-1-naphthol have been studied in aqueous phase in presence of Triton X-100 and spectrophotometric methods of determining copper(II) developed. Molar absorption coefficient (ϵ), specific absorptivity (a), Sandell's sensitivity (S) and conditional stability constant of the two complexes at 490 nm and 505 nm (the respective absorption maxima) at pH 6.0 and 6.5 (the corresponding optimum pH) have been found to be 1.013×10^4 l mol^{-1} cm^{-1} and 1.298 l mol^{-1} cm^{-1}; 0.159 ml g^{-1} cm^{-1} and 0.204 ml g^{-1} cm^{-1}; 6.273 ng cm^{-1} and 4.895 ng cm^{-1}; 5.907×10^7 l^2 mol^{-2} and 5.240×10^7 l^2 mol^{-2} respectively. Beer's law is obeyed from 4 to 24 μM and 8 to 32 μM of copper(II) respectively. Interference of common cations, anions and ligands have been investigated and the method applied successfully to determine copper content in a number of alcoholic beverages.

INTRODUCTION

A large number of methods exist for spectrophotometric determination of copper[1-11]. Some of the sensitive and selective methods are those using dithizone[1-3], dithiocarbamate[4-6], cuproin[7,8] and cuprizone[9-11]. All, except cuprizone, involve extraction steps. Cuprizone forms a blue coloured water-soluble complex in the basic medium. Under these conditions, interference due to cations is the main problem. Besides, the method is not sensitive. It was observed that copper forms a red coloured water insoluble complex with cobaltone (1-nitroso-2-naphthol) and its position isomer (2-nitroso-1-naphthol) in alcoholic medium. However, when a micellar solution[12,13] of the reagent was taken, a water soluble pink coloured complex instead of a precipitate was obtained. In the present work these reactions have been investigated with a view to develop a sensitive and selective spectrophotometric method devoid of the cumbersome extraction step. Of the cationic (CTMAB, CPC, DTAB), anionic (SDS) and neutral (Triton X-100) surfactants investigated, those belonging to the last category were found to be the most suitable.

EXPERIMENTAL

All reagents used were of analytical grade purity. Aqueous solution of Cu^{2+}. (4.0×10^{-4} M) was prepared from $CuSO_4 \cdot 5H_2O$. 4.0×10^{-4}M solution each of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol were prepared by stirring 0.006927 gm each of the compounds in 5 ml Triton X-100 at 60°C and diluting the solution with water to 100 ml.

Shimadzu UV–260 recording spectrophotometer with 1 nm bandwidth and 10 mm matched silica cells was used for recording the absorption spectra. First and second order derivative spectra were recórded from the digitalized spectra with $\Delta\lambda = 2$ and 4 nm respectively. An ECIL digital pH meter with combined glass electrode was used for pH measurement. Perkin Elmer Atomic Absorption Spectrophotometer Model-5000 was also used.

Preparation of Working Solution

Effect of H^+ concentration on complex formation was investigated by preparing two sets of solutions covering the pH range 1.0–9.0. The first set contained 2.0×10^{-4} M ligand and 2.5% m/v Triton X-100, while the second contained 4.0×10^{-5} M Cu^{2+} in addition to the same amount of ligand and Triton.

Effect of varying ligand concentration on the absorbance of the system was investigated by preparing a set of solutions containing 8.0×10^{-6} M metal ion and increasing amounts (4.0×10^{-6} to 2.0×10^{-4} M) of ligands at optimum pH.

Effect of varying metal ion concentration on absorbance has been ascertained (i) by varying metal ion concentration at a fixed ligand concentration and (ii) keeping a fixed metal to ligand ratio.

Effect of foreign ions on the determination of copper(II) was studied by adding the ion/ligand to the solution of the complex and recording the change in absorbance.

RESULTS AND DISCUSSION

Effect of pH on Absorbance

Absorption spectra, against water, of copper 1-nitroso-2-naphthol complex shows two maxima at 400 nm and 490 nm which shift batho-hyperchromically with increase in pH. Copper 2-nitroso-1-naphthol complex absorbs at 350 nm, 430 nm and 505 nm, among which the last one shows batho-hyperchromic shift with increase in pH. The complexation starts at pH 3.0 and 4.0 in the two cases respectively and the absorbance remains practically constant between pH 5.0 to 7.0 in both the systems. Plot of pH versus absorbance shows maxima at 6.0 and 6.5 for the respective systems which have been taken as the optimum pH in all subsequent studies.

Effect of Reagent Concentration on the Absorbance of the System

Absorbance of solutions containing copper(II) and increasing amounts of 1-nitroso-2-naphthol/2-nitroso-1-naphthol increases due to significant absorption of ligand at 490 nm and 505 nm, the λ_{max} of the two complexes. Absorbance values were therefore corrected and plotted against molar ratio (L : M) of the reagent. A sharp increase in absorbance upto 4-fold excess of ligand [3.2×10^{-5} M] was observed. Absorption became practically constant above this molar ratio. In all subsequent studies, a fixed concentration of ligand between 4–20 fold excess of copper(II) was maintained.

Effect of Copper(II) Ion Concentration on the Absorbance of Cu-1-Nitroso-2-Naphthol Complex

In order to investigate the effect of copper ion concentration on absorbance of the complex, a set of solutions containing increasing metal ion concentration at a fixed metal to ligand ratio was prepared and its normal as well as derivative spectra recorded against water (Fig. 1). Absorption spectra in the region 300–600 nm of the complex shows a

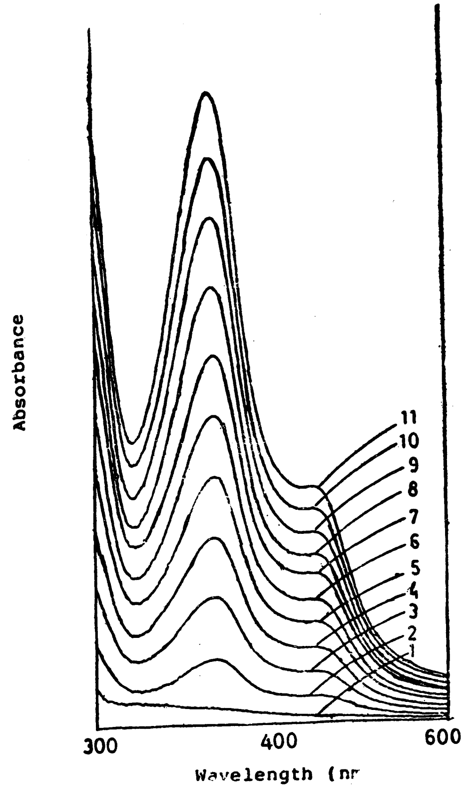

Fig. 1 Spectra of Cu-1-nitroso-2-naphthol-Triton X-100 system: 1, reagent blank, 2-11, increasing Cu(II) concentration.

peak at 400 nm and a shoulder around 490 nm; peak of 1-nitroso-2-naphthol at 390 nm shifts to 400 nm on complexation with the metal ion. Absorbance values at 400 nm and 490 nm of the solutions containing increasing metal [ligand : metal = 4 : 1] were linearly proportional to the metal ion concentration. Linear regression of absorbance on concentration shows following relationship with regression coefficient 0.9997 and 0.9991 at 400 nm and 490 nm respectively.

$$C = 3.57\times10^{-5}\ A_{400} + 1.03\times10^{-2}$$

$$C = 9.664\times10^{-5}\ A_{490} - 1.009\times10^{-6}$$

where 'C' is concentration and 'A' the observed absorbance. From the values of the slope obtained above, though studies at 400 nm appear to be more sensitive to metal ion concentration these are not of much analytical use on account of proximity to λ_{max} of the ligand (390 nm). It is, however, not practicable to keep the metal-to-ligand ratio constant in the unknown samples and a suitable excess of ligand is normally employed for determining copper content of an unknown sample. The normal practice is to use a fixed amount of ligand and take such an aliquot of the sample which gives absorbance in linearity range. Following linear relationships between absorbance and metal ion concentration with residue square of 0.9995 and 0.9982 at 400 nm and 490 nm respectively are obtained for solution containing 4.0×10^{-6} to 4.0×10^{-5} M copper(II) and 2.0×10^{-4} M ligand.

$$C = 4.805\times10^{-5}\ A_{400} + 1.393\times10^{-7}$$

$$C = 1.370\times10^{-4}\ A_{470} - 1.43\times10^{-6}$$

Cu-1-nitroso-2-naphthol system obeys Beer's law from 4.0 to 24 μM of copper(II). Molar absorption coefficient (ϵ), specific absorptivity (a) and Sandell's sensitivity (S) of the complex at 490 nm have been found to be 1.013×10^{4} l mol^{-1} cm^{-1}, 0.159 ml g^{-1} cm^{-1} and 6.273 ng cm^{-2} respectively.

First derivative spectra (dA/dλ) of the complex shows a peak at 375 nm with two sharp troughs at 420 nm and 510 nm. As the concentration of the complex increases, peak height and trough depth both increase simultaneously with two crossover points at 400 nm and 490 nm. Position of λ_{max} of the complex is not very close in normal spectra as only a shoulder is observed. This, however is clearly depicted by the crossover point in the first derivative spectra (Fig. 2). Peak height (PH) and trough depth (TD) are proportional to metal/complex concentration. Linear regression on concentration of PH at 375 nm, TD_1 at 420 nm and TD_2 at 510 nm give a good linear fit with a residue square of 0.997, 0.999 and 0.998 respectively.

$$C = 6.489\times10^{-6}\ PH - 6.489\times10^{-7}$$

$$C = 4.165 \times 10^{-6}\,TD_1 + 7.358 \times 10^{-7}$$
$$C = 1.225 \times 10^{-5}\,TD_2 - 2.451 \times 10^{-7}$$

As peak height/trough depth are linearly proportional to metal ion concentration over a wide range, depth measurement at 510 nm in Cu-1-nitroso-2-naphthol system is recommended. Second derivative ($d^2A/d\lambda^2$) spectra is not found to be useful due to signal to noise ratio.

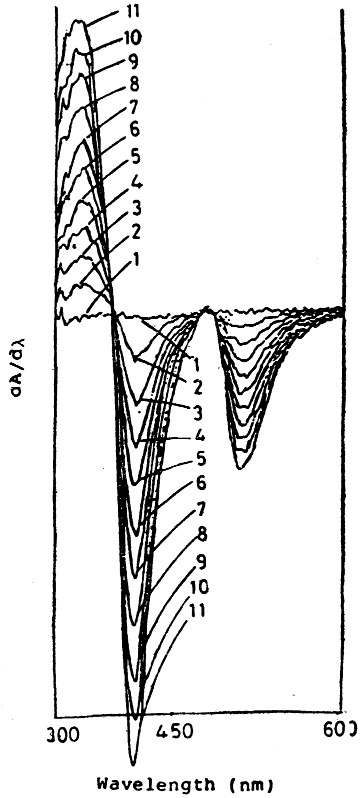

Fig. 2 First order derivative of spectra in Fig. 1.

Effect of Copper Concentration on Absorbance of Cu-2-nitroso-1-naphthol System

Absorption spectra of the solution containing 2-nitroso-1-naphthol and its copper complex (Fig. 3) show a sharp peak at 350 nm and broad peaks at 430 nm and 505 nm. Exact positions of the broad peaks could be ascertained from the first derivative spectra. Absorption of the solutions at 350 nm and 505 nm have been found to be proportional to copper concentration. Linear regression gives following relationships

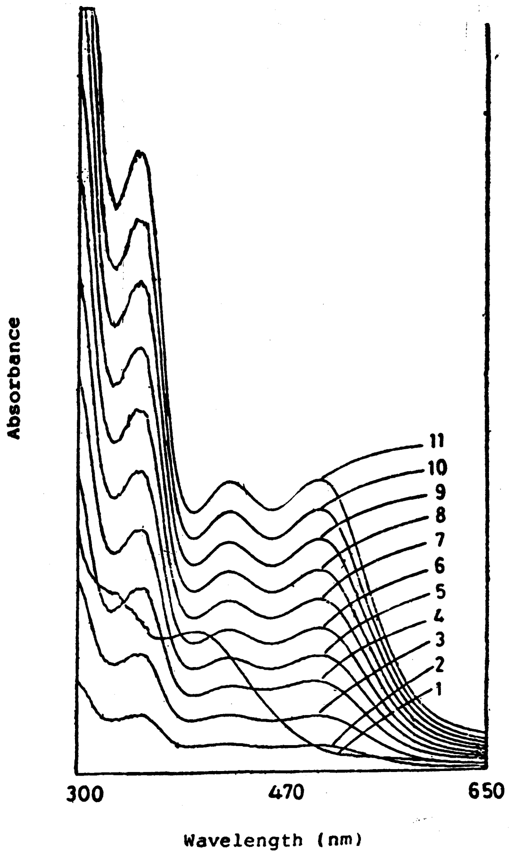

Fig. 3 Spectra of Cu-2-nitroso-1-naphthol-Triton X-100 system.
1, reagent blank, 2-11 increasing Cu(II) concentration.

between absorbance (at 350 & 505 nm) and Cu(II) concentration with correlation coefficients of 0.9998 and 0.9996 respectively.

$$C = 3.173\times10^{-5} \quad A_{350} + 1.536\times10^{-7}$$

$$C = 2.411\times10^{-4} \quad A_{505} + 6.190\times10^{-7}$$

Correction for the absorption of ligand at λ_{max} of complex were also applied but were not found to be of much practical use as their regression coefficients were lower, then system obeys Beer's law from 8.0 to 32.0 μM of copper at 505 nm. Spectrophotometric parameters, i.e. molar absorption coefficient (ε), specific absorptivity (a) and Sandell's sensitivity (S) of the complex have been found to be 2.432×10^4 l mol^{-1} cm^{-1} and 1.298×10^4 l mol^{-1} cm^{-1}; 0.382 ml g^{-1} cm^{-1} and 0.204 ml g^{-1}cm^{-1} and 2.613 ng cm^{-1} and 4.895 ng cm^{-1} at 350 nm and 505 nm respectively.

First derivative spectra (Fig. 4A) of these solutions were found to be of great use as position of maximum of the submerged complex peak (in normal spectra), could be easily envisaged from the crossover points. The complex has troughs at 375 nm, 450 nm and 540 nm with four crossover points at 365 nm, 400 nm, 430 nm and 505 nm respectively. The two peaks at 415 nm and 485 nm are too small to be of any significance. Trough depths of complex gradually increases with metal ion concentration. Linear regression of trough depth at 375 nm (TD_1) and 540 nm (TD_2) on concentration gives good linear fit with residue squares of 0.9995 and 0.9991 respectively.

$$C = 3.248\times10^{-6}\,(TD_1) + 2.815\times10^{-7}$$

$$C = 1.271\times10^{-5}\,(TD_2) + 1.144\times10^{-6}$$

The second-order derivative spectra ($d^2A/d\lambda^2$) of Cu-2-nitroso-1-naphthol (Fig. 4B) system shows only one clear peak at 380 nm, which is proportional to the metal ion concentration. Regression analysis gives following linear relationship between concentration and absorbance with correla-

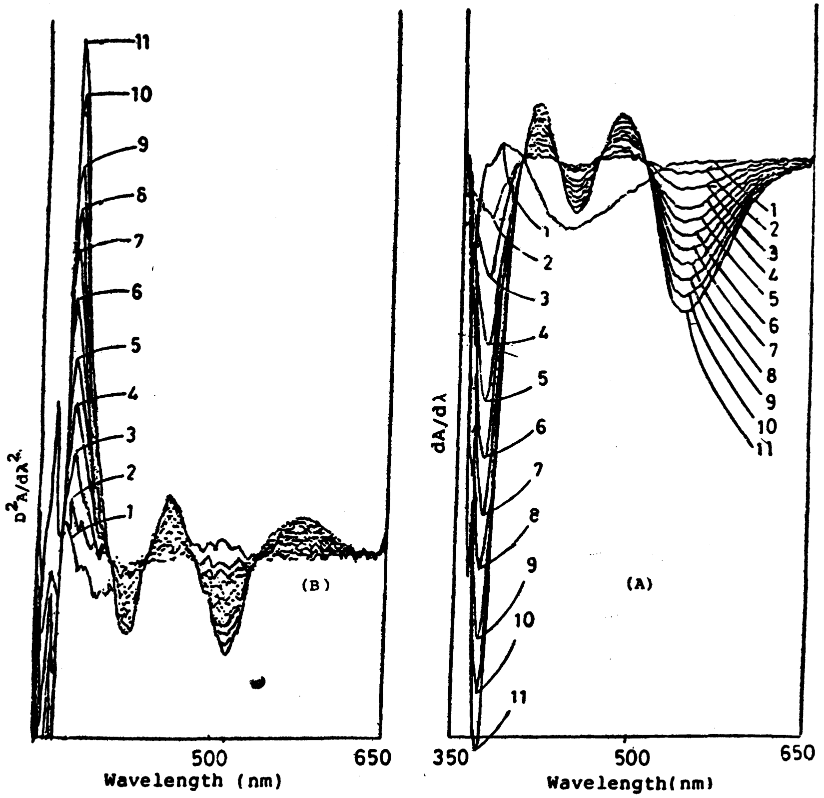

Fig. 4 First order (A) and second order (B) derivatives of spectra in Fig. 3.

tion coefficient of 0.9982.

$$C = 3.854 \times 10^{-6}\ PH + 1.246 \times 10^{-6}$$

where PH is the peak height.

Composition and Stability Constant of the Complex

Molar composition of the complexes, Cu-1-nitroso-2-naphthol and Cu-2-nitroso-1-naphthol have been determined by Job's method of continuous variations. The plot of absorbance versus mole fraction of the metal ion gives a maximum at 0.33 which corresponds to 1 : 2 Cu^{2+} to ligand ratio in the complexes. The complex can, therefore, be represented as $Cu(ORNO)_2$ where ORNO represents deprotonated ligand. This composition is in agreement with the reported composition in organic phase (14, 15).

Conditional stability constants (16, 17) were calculated on the basis of the following chemical equilibrium.

$$Cu^{2+} + 2ORNO^- \rightleftharpoons [Cu(ORNO)_2]$$

$$K' = \frac{[Cu(ORNO)_2]}{[Cu^{2+}][ORNO^-]^2}$$

Concentration of the species have been taken instead of the activities in the calculation as the solutions are dilute and a neutral surfactant has been used. The values of K′ thus calculated have been found to be $5.907 \times 10^7\ l^2\ mol^{-2}$ and $5.244 \times 10^7\ l^2\ mol^{-2}$ at pH 6.0 and 6.5 respectively for Cu-1-nitroso-2-naphthol and Cu-2-nitroso-1-naphthol.

Effect of Diverse Ions on the Absorbance of the System

Interference due to the presence of foreign ions in microgram determination of copper(II) with 1-nitroso-2-naphthol and 2-nitroso-1-naphthol was studied in normal as well as derivative mode at 25 and 125 fold excess of the interfering species. Fe^{2+}, Fe^{3+}, Co^{2+}, Hg^{2+}, Ni^{2+}, Mn^{2+} and Pb^{2+} at 25 fold excess interfered in both the systems but Be^{2+}, Tl^{2+}, Al^{3+}, Ca^{2+} and Zn^{2+} interfered only at 125 fold excess.

Anions/ligands tested were citrate, ascorbate, tartrate, EDTA, SCN^-, acetate, bromate, Cl^-, Br^- and I^-. Only EDTA interfered seriously, masking upto 46% and 60% complexation respectively, at 25 fold excess. Presence of 125 fold excess of ascorbic and tartaric acid interfered significantly in Cu-1-nitroso-2-naphthol system, and citrate and chloride in like amount in case of Cu-2-nitroso-1-naphthol system.

Determination of Copper in Beverages

Copper content of a number of commercially available alcoholic

TABLE 1

COPPER CONTENT OF BEVERAGES AS DETERMINED BY THE DEVELOPED METHODS AND AAS

S. No.	Sample* labelled Cu^{2+}	Copper content (ppm)				
		AAS*	Cu-1-nitroso-2-naphthol	Error (%) w.r.t. AAS results	Cu-2-nitroso-1-naphthol	Error (%) w.r.t. AAS results
1.	Rum (10 ppm)	9.27	9.30	+0.323	9.28	+0.107
			9.26	−0.107	9.25	−0.215
			9.29	+0.215	9.23	−0.431
			9.24	−0.323	9.26	−0.107
2.	Gin (10 ppm)	9.15	9.18	+0.327	9.12	−0.327
			9.16	+0.109	9.19	+0.437
			9.10	−0.546	9.15	+0.000
			9.13	−0.219	9.18	+0.546
3.	Whisky (5 ppm)	4.21	4.25	+0.950	4.23	+0.47
			4.20	−0.327	4.26	+1.187
			4.23	+0.475	4.20	−0.237
			4.18	−0.712	4.17	−0.950
4.	Brandies (5 ppm)	3.95	3.93	−0.506	3.98	+0.759
			3.94	−0.253	3.91	−1.017
			3.92	−0.759	3.94	−0.253
			3.98	−0.759	3.97	+0.506

*Sample manufactured by Ajudhia Distillery, Moradabad, India.

beverages have been determined by the developed method to evaluate its practical applicability. To determine copper content of a sample, it is digested with nitric acid and residue taken in H_2SO_4 and content made upto suitable volume with distilled water. Absorption spectra recorded against water and copper content calculated from the regression equation obtained with standard copper solution. The results obtained were compared with those obtained by atomic absorption spectrophotometry (AAS).

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