

Spectrophotometric Determination of Copper (II) With Diethyldithiocarbamate in Polyoxyethylenedodecylether (Brij-35) Media

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Summary: A spectrophotometric determination of copper(II)-diethyldithiocarbamate (DDTC) complex in aqueous phase in the presence of polyoxyethylenedodecylether (Brij-35), a nonionic surfactant is reported here. The method obeys Beer's law in the concentration range of 1.5×10^{-3} to 7.0×10^{-3} mol.dm⁻³. The detection limit of copper(II) is 3×10^{-6} mol.dm⁻³. The molar absorption, sensitivity, critical micelle concentration, and DDTC metal ion concentration have been studied and discussed. The method has been applied to the determination of copper in goat liver and fly ash samples. The present method was compared with that of Flame Atomic Absorption Spectroscopy (FAAS). No significant difference was noted between the two methods at 95% confidence interval.

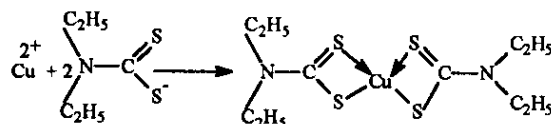
Introduction

The use of DDTC 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]. Gracia *et al.* 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 [14]. Agnihotri *et al.* developed a photometric determination of copper(II) in a Triton X-100 in normal and derivative modes [15]. Recently cobalt has been reported to be selectivity determined by complexation with 1-nitroso-2-naphthol in the presence of Triton X-100 as a neutral surfactant [16]. Sodium dodecylsulphate anionic surfactant has also been used for the trace analysis of Cu (II) in water with DDTC as a complexing reagent [17]. In continuation to our previous report on the determination of Zn²⁺-dithizone complex in presence of a cationic surfactant [18], the present work describes a procedure to determine Cu (II) as a complex of diethyldithiocarbamate in the presence of an inexpensive nonionic micelles the polyoxyethylenedodecylether (Brij-35). The method has been applied for the analysis of Cu (II) in the fly ash and goat liver samples.

Results and Discussion

Complexation of diethyldithiocarbamate, with several metal ions is well established. A reaction of

copper with diethyldithiocarbamate to produce copper-diethyldithiocarbamate complex is shown as follows:



Reaction of copper (II) with diethyldithiocarbamate to form copper (II) diethyldithiocarbamate complex

Fig. (1) shows the spectra for a diethyldithiocarbamate solution 5×10^{-4} mol.dm⁻³ and for a copper (II) diethyldithiocarbamate complex with an absorbance maxima at 348 nm and 440 nm respectively. Comparison of the analytical wavelengths of micellar media with λ_{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) diethyldithiocarbamate. On increasing pH to 8.5, the peak at 436 nm shifts hyperchromically and bathochromically to 440 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.(2) This plot shows a maximum at pH 8, which has been taken as the pH of maximum complex formation throughout this work.

As shown in Fig.(3) the absorbance spectra of solutions showed an increase in absorbance with an

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Table-1: Experimental conditions for copper metal ion determination by complexation with diethyldithiocarbamate in (a) aqueous nonionic micellar medium and (b) by solvent extraction in CCl_4

Solvent	Method	pH	λ_{max} (nm)	Conc. of Brij-35 (mol.dm^{-3})	Conc. of DDTC (mol.dm^{-3})	ϵ_{max} $\text{mol}^{-1} \cdot \text{cm}^{-1} (10^4)$
Aqueous	Micellar	8	440	6×10^{-3}	5×10^{-4}	2.3
CCl_4	Solvent Extraction	4-11	436	—	0.02 %	1.49

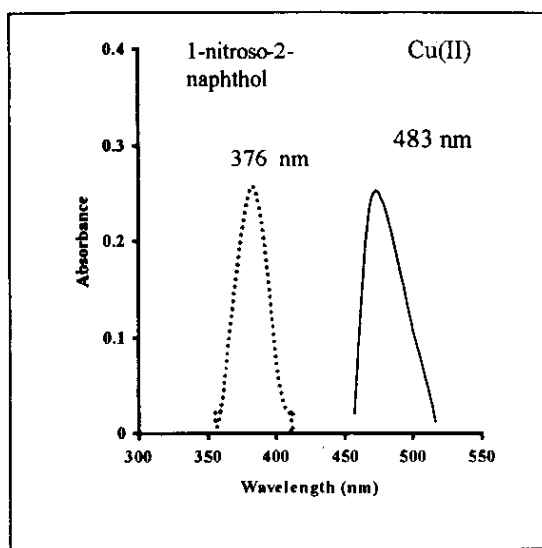


Fig. 1: Absorption spectra of diethyldithiocarbamate (λ_{max} 348 nm) and copper (II) diethyldithiocarbamate complex in Brij-35 at pH 8 (λ_{max} 440 nm).

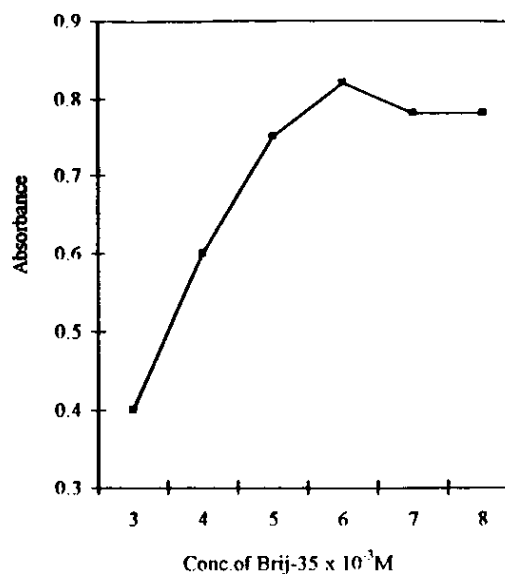


Fig. 3: Effect of Brij-35 conc. On the absorbance of Copper (II) diethyldithiocarbamate Complex at (λ_{max} 440nm)

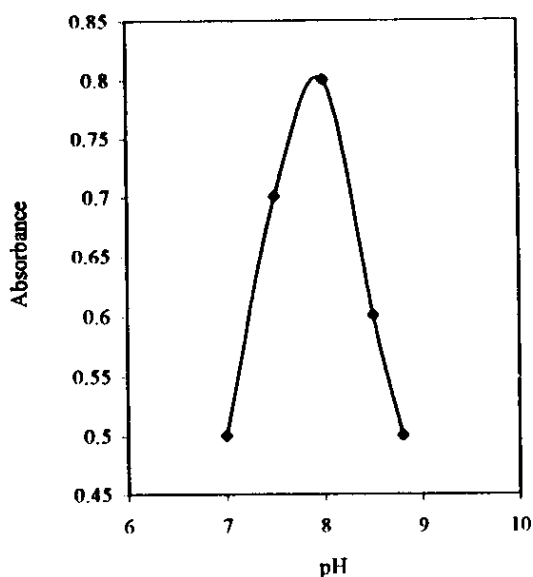


Fig. 2: Effect of pH on the Absorbance of Copper(II) Diethyldithiocarbamate Complex at (λ_{max} 440 nm)

increase in Brij-35 concentration up to $5 \times 10^{-3} \text{ mol.dm}^{-3}$ of the complex and the ligand. A slight decrease, however, was observed above this concentration. The surfactant concentration was maintained at $6 \times 10^{-3} \text{ mol.dm}^{-3}$ during subsequent studies. The absorption maximum at (λ_{max} of 436 nm) of the solution containing varying amounts of diethyldithiocarbamate in presence of constant copper(II) concentration ($4 \times 10^{-5} \text{ mol.dm}^{-3}$) increased with increase in diethyldithiocarbamate concentration up to $5 \times 10^{-4} \text{ mol.dm}^{-3}$ as shown Fig. (4).

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. (5) shows a calibration graph of copper concentration against the absorbance at 436 nm. Linear regression was carried out from which the regression coefficient was calculated as 0.999. The relative standard deviation

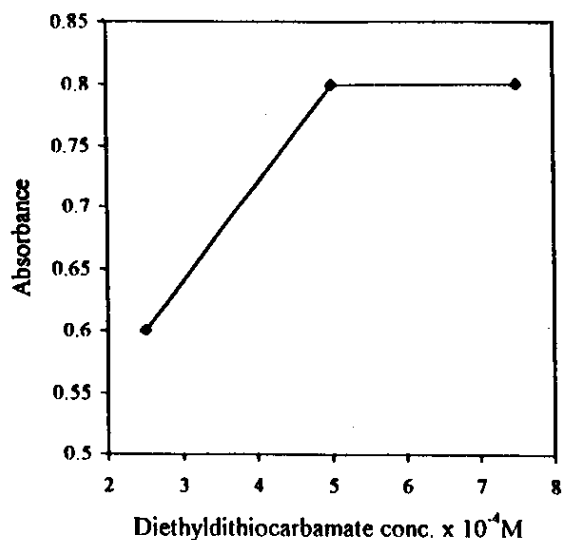


Fig. 4: Effect of Diethyldithiocarbamate Conc. On the Absorbance of Copper (II) Diethiocarbamate Complex at (λ_{\max} 440 nm).

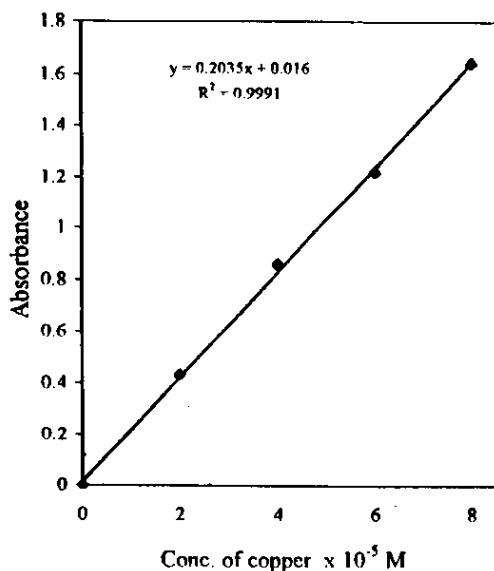


Fig. 5: Calibration Graph of Copper(II) Diethyldithiocarbamate Complex at (λ_{\max} 440 nm)

for a 1.5×10^{-4} mol.dm⁻³ standard (n=8) was 1.2%. The lowest detection limit for this metal was found to be 3×10^{-6} mol.dm⁻³.

The interfering effects of foreign ions, in the determination of Cu (II) with DDTC in presence of

Brij-35 have been studied. For Cu ions, KSCN, KClO₃, 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 DDTC is highly selective with NH_4^+ / NH_3 buffer at pH 8, using the surfactant Brij-35.

Table-2: Foreign ion quantities below which interferences are not produced in the Cu(II) determination in a conc. of 2.5 $\mu\text{g ml}^{-1}$ in Brij -35

Ion / salt	Tolerance limits ($\mu\text{g ml}^{-1}$)
KSCN	1000
Na F	600
Na ₂ C ₂ O ₄	500
KClO ₃	1000
Na ₂ tartarate	1000
Na ₂ 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

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.

Application

The proposed spectroscopic method was applied to the determination of Cu (II) in goat liver and fly ash samples. Results are given in Table 3.

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

Sr. No.	Sample	Amount of Cu(II) determined (mg)		
		Present method	FAAS	C.V %
1.	Goat Liver (mg/kg)	6.80	7.21 \pm 0.13	2.571
2.	* Fly Ash	57.97	58.40 \pm 0.47	2.571

At 95% t-test, n=6

* Lakhra Thermal Power Station, Jamshoro.

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. Diethyldithiocarbamate solutions were freshly prepared in distilled water just before use to avoid acid decomposition [19]. Polyoxyethylene-dodecylether (Brij-35) $6 \times 10^{-3} \text{ mol.dm}^{-3}$ was prepared by dissolving 0.706 g/100 ml in freshly prepared double distilled water. Sodium acetate (0.2 mol.dm^{-3}) buffer solution was prepared and adjusted to pH 8 with acetic acid (0.2 mol.dm^{-3}). 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, diethyldithiocarbamate and Brij-35 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) 3×10^{-6} - $1.5 \times 10^{-4} \text{ mol.dm}^{-3}$, diethyldithiocarbamate $5 \times 10^{-4} \text{ mol.dm}^{-3}$ and Brij-35 $6 \times 10^{-3} \text{ mol.dm}^{-3}$. The surfactant concentration, pH values and analytical wavelength used are listed in Table 1.

Spectrophotometric Metal Ion Determination After Extraction with CCl_4 .

Appropriate volumes of stock metal and diethyldithiocarbamate aqueous solutions were placed into a separating funnel and 10 ml of 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 CCl_4 . For the 25 ml total volume of the organic layer, absorbance was measured at the appropriate wavelength for metal ion [20].

Determination of Cu(II) in Real Samples

(a) Goat Liver

Goat Liver (10g) samples were ashed at temperature $550-600^\circ\text{C}$. [21]. The residue was dissolved in concentrated nitric acid (40-50 ml) and then evaporated to dryness. The residue thus obtained was dissolved in distilled water, filtered and diluted up to 250ml. Appropriate amounts of Brij-35 and diethyldithiocarbamate was added to a 25 ml calibrated flask to obtain final concentration of $6 \times 10^{-3} \text{ mol.dm}^{-3}$ in Brij-35 and $5 \times 10^{-4} \text{ mol.dm}^{-3}$ in diethyldithiocarbamate. 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.

(b) Fly Ash

A 10g sample of the fly ash from Lakhra Thermal Power Station, Jamshoro, was digested with 100 ml of 1:1 nitric acid for 0.5 h, cooled, filtered and diluted to 250 ml with distilled water. Appropriate amounts of Brij-35 and metal ion solution was added to a 25 ml calibrated flask to obtain final concentration of $6 \times 10^{-3} \text{ mol.dm}^{-3}$ in Brij-35 and $5 \times 10^{-4} \text{ mol.dm}^{-3}$ in diethyldithiocarbamate. Then 5 ml of the sample was added and the absorbance was measured against water. The same sample, 25 ml was then analyzed for FAAS analysis

Conclusion

Determination of trace amount of Cu (II) is carried out directly using diethyldithiocarbamate in nonionic micellar media of Brij-35 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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