DEVELOPMENT OF METHOD FOREXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF COPPER(II) WITH N-BENZOYL THIOUREATHIOSEMICARBONZONE(MAAPHE) AS AN ANALYTICAL REAGENT

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ABSTRACT

TheA simple, rapid and sensitive spectrophotometric method has been developed for the determination of Cu (II) by using N-Benzoyl Thioureathiosemicarbazonesynthesized and characterized by elemental and spectral analysis. MAAPHE extractsCu(II) quantitatively(99.5%) into chloroform from an aq. solution of pH range 5.5-6.5 . The chloroform extract shows an intense peak 450nm (λ_{max}). Beer's law is obeyed over the Cu(II) concentration range 0.1-4.2 µg/ml. The Sandell's sensitively and molar absorpitivity for Cu-MAAPHE system is $0.00252\mu g\ cm^{-2}$ and 25700 L/mol/cm respectively. The composition of extracted species are found is 1:2 (Cu:MAAPHE) by Job'scontinuous variation and mole ratio method. Interference by various ions has been studied. The proposed method has been successfully applied for determination of Cu(II) in alloy .

Key Words : Extractive Spectrophotometry, Copper(II), MAAPHE, Alloy.

INTRODUCTION

Copper is most important transition metal after iron and has a history of use that is 10,000 years old. In ancient India, Copper was used in holistic medical science. Ancient Egyptians used copper for sterilizing wounds and drinking water for headache, burns and itching. It distributes widely in anima tissues and is also one of the essential element in human body. Therefore lack of copper in the body results in health problems such as anemia, leucoderma etc. Abnormality of copper metabolism in the body causessome hereditary diseases. It is an essential element only at very low levels and is toxic at higher levels in plants. In plant physiology it is essential as a component of a number of different plant enzymes[1]. As far as most living organisms are concerned, copper at about 40ng/ml is needed for their normal metabolism. Hence it is necessary to

seek highly sensitive accurate and selective analytical methods for quantitative determination of copper at trace levels. Copper (II) forms chelate complex with many organic reagents which are bonded through Nitrogen, Oxygen and Sulphur atoms.

Solvent extraction technique has grown into one of the most promising method in the separation of metal ions at trace level because of its simplicity, rapidity and versality.

Among the Various reagentthiosemicarbazone complexes can be used in selective and sensitive determination of Copper ions.[2-6]The present paper describes very selective, sensitive, direct and derivative spectrophotometric methods for determination of micro amounts of copper in aqueous DMF medium by complexing with N-Benzoyl thioureathiosemicarbazone (MAAPHE).

EXPERIMENTAL

The absorbance measurements were made on Shimadzu UV Spectrophotometer.An ELICO-LI 127 pH meter was employed for pH-measurements.

A stock solution of Cu(II) was prepared by dissolving accurately weighed copper sulphate in water containing sulphuric acid and it wasstandardized by gravimetrically[7]. Working solutions of Cu (II) were made by suitable dilution . All the reagents used were of AR grade and all the solutions were prepared by doubly distilled water.

Synthesis of N-Benzoyl Thiourea Thiosemicarbazone (MAAPHE) :

The reagent MAAPHE(1,6-Dimercapto-1,6-Diamino-2,4,5-Triaza-3-Phenyl-3-Hexene) was prepared by refluxing equimolar concentrations of Thiosemicarbazide and N-Benzoyl Thiourea in ethanolic medium for 3 to 4 hours. The resulting products were cooled and filtered. Silky crystals were obtained. The crystals were washed successively with DMF, cold ethanol and dried in vaccuo and analysed (m.p.= 232 ± 2^0C) as $C_9H_{11}N_5S_2$.[8]
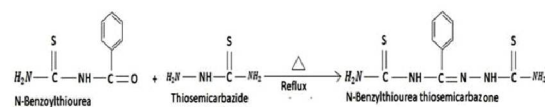
Procedure for the extraction and separation of Cu (II) :

An aliquot solution containing 1-100μg of Cu (II), 1 ml of 1% solution of MAAPHE prepared in DMF were mixed in 25 ml beaker. The pH of solution was adjusted to the desired value with dilute solution of HCl/NaOH, keeping the total volume to 10 ml with distilled water. The resulting solution was then transferred into 125 ml separatory funnel. The beaker was then washed with 5 ml portion of organic solvent an each washing was added to the solution in the separatory funnel. After the separation of two phases pH of the equilibrated aqueous phase was measured and copper content in each phase was estimated by Diethyldithiocarbamate method[5].

The extraction was carried out with different solvents to find out the best extracting solvent.On the basis of copper content inaquous and organic phase extraction coefficient and percentage extraction was calculated.

Procedure for the extractive spectrophotometric determination of Cu(II):

To an aliquot of aq. solution containing 1-100 μg of Cu(II), 2ml of buffer solution of pH 6.0 and 1ml of 1% solution of MAAPHE prepared in DMF were added. The volume of solution was made upto 10ml with distilled water. The solution was then equilibrated with 10 ml of chloroform and the phases were allowed to separate the chloroform extract was collected in 10ml standered measuring flask and made upto mark. The absorbance of chloroform was measured at 450nm against reagent blank prepared under identical condition. The measured absorbance was used to compute the amount of Cu(II) present in the sample solution from predetermined calibration curve. To study the effect of other ions, the respective foreign ions were added to aq. phase before the extraction and adjustment of pH.

Procedure for the determination of Copper(II) in Alloy sample:

For the determination of Cu(II) in Al-Alloy 0.1-0.2g sample of Al- Alloy was dissolved in boiling with 10ml of aqua regia. The resulting solution was evaporated to dryness and the residue was dissolved in 10ml of 1M dilute HCl filter, if

required. The resulting solution was diluted to 250ml of distilled water. 1ml ofaliquot of this solution was analyzed for Cu(II) by the above procedure.

RESULTS AND DISCUSSION

Copper could be extracted by MAAPHE into chloroform from an aqueous solution of pH 5.8 to 7.5 . The organic solvents used for extraction of Cu(II) can be arranged on the basis of their extraction coefficient and % extraction value as: chloroform>ethylacetate>toluene>benzylalcohol> carbontetrachloride>nitrobenzene>benzene>nitro methane etc.

Chloroform was found to be the best extractivity solvent hence, it was selected for the extraction throughout the work. The chloroform extract of Cu:MAAPHE complex showed an intense peak 418nm (fig.1). The absorbance due to the reagent is negligible at this wavelength, so the absorption measurement were taken at this wavelength. The results shows that the system confirmed to Beer's law at this wavelength over a Cu(II) concentration range of 0.1 to 4.2µg/ml (fig.2). The molar absorptivity and Sandell's sensitivity of the extracted complex on the basis of Cu(II) content was calculated to 25700 L/mol/cm and 0.00252µgcm^{-2}. It was found that 1ml of 1%DMF solution of MAAPHE was sufficient to extract 100µg of Cu(II).The colour of chloroform extract was found to be stable at least 36hours at room temperature.

Cu(II) (60µg) was determined in the presence of other ions. The following ions in the amount indicated, did not interfere in the Spectrophotometric determination of Cu(II) (60µg):10mg of each Mg(II), Ca(II), Li(II),Sr(II), Ag(II), Mo(VI), Ba(II) etc. 20mg each of chloride, bromide, fluoride, sulphite, sulphate, phosphate, nitrate, acetate, etc. interference due to citrate, tartarate and oxalate could be removed by adding sodium molybdate.

The composition was found to 1:2 (Cu:MAAPHE) by Job's continuous variation (fig.3) and the mole ratio method.

The precision and accuracy of the method were tested by analyzing the solution containing a known amout of Cu(II) following the recommended procedure. The average of 10 determination of 10µg of Cu(II) in 10ml of solution was 10.01µg which is varied between 9.8µg and 10.22µg at 95% confidence limit and the standard deviation was ±0.21. The proposed method has been applied for determination of Cu(II) in aluminium alloy.

The result of the analysis of the samples were compared with those obtained by the diethyldithiocarbonate method[15] for Cu(II).

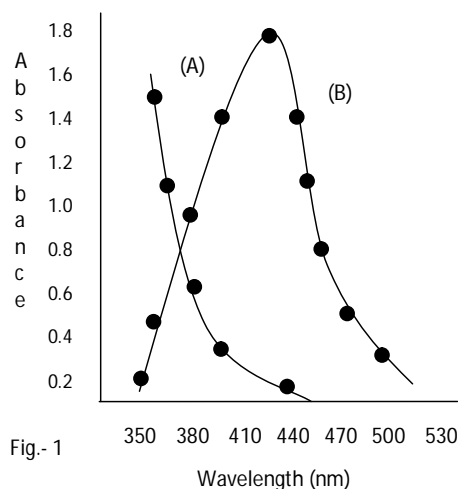| Sample	Cu(II) found by present method (%)	Cu(II) found by DMF method (%)
Al- Alloy	10.02	9.98

Fig.- 1
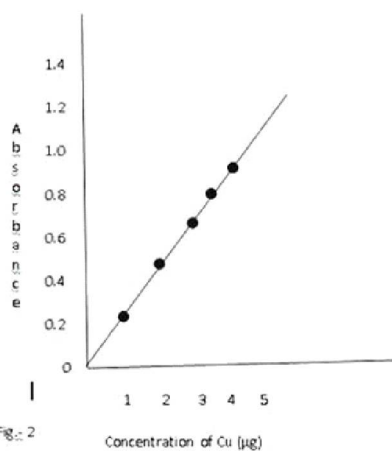

Fig.- 2

CONCLUSION

The proposed method can be used for precise determination of copper at µg level. It offers advantages like reliability, reproducibility and good sensitivity, in addition to being simple and minimum iterferences. The results obtained are in good agreement with the certified valueand are comparable to these obtained by known method.

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