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NOTE

Extractive Spectrophotometric Determination of Cu(II) with 4-Chloro Isonitroso Acetophenone Thiosemicarbazone

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A method is proposed for the extraction and spectrophotometric determination of Cu(II) at microgram levels by using 4-chloro isonitroso acetophenone thiosemicarbazone (CINAPT) as an analytical reagent. Cu(II) forms reddish complex with CINAPT which can be extracted in chloroform in the pH range 7.5 to 8.5 under optimum conditions. The chloroform extract shows maximum absorbance at 400 nm wavelength.

Beer's law is obeyed over the range of 0.2 to 20 microgram per mL of Cu(II). The molar absorptivity is 2.518×10^3 L mol^{-1} cm^{-1}. The composition of the species is found to have 1 : 2 (metal : ligand) stoichiometry.

Interference due to diverse cations and anions has been investigated. The method has been applied for the determination of copper in alloys and pharmaceutical samples.

Copper is one of the coinage metals and it constitutes 70 ppm of earth's crust. Copper is one of the most important metals after iron. It plays a vital role in many fields in the form of metal or salt such as catalyst in organic reactions, in laboratory and industries, colour technology, medicine, food and beverage, etc. It has variety of engineering applications, especially in electrical industries.

Several isonitroso compounds are known to react with the metal ions to give coloured complexes and have been employed for the quantitative extraction and spectrophotometric determination of metals at trace levels. The proposed method is found to be simple, sensitive, rapid and precise.

The absorbance measurements were made on a Shimadzu 1601 UV visible spectrophotometer. An Elico pH meter-L1-120 model was used for pH measurements. The chemicals used were of A.R. grade. Stock solution of copper was prepared by dissolving $CuSO_4 \cdot 5H_2O$ and was standardised. The working solutions were prepared by appropriate dilution as required. The reagent 4-chloro isonitroso acetophenone thiosemicarbazone (CINAPT) was prepared as reported.

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Procedure

To a suitable aliquot of copper(II) solution was added an ethanolic solution of CINAPT (1 mL of 1% solution) and 2 mL 0.5 molar solution of sodium acetate was mixed in a beaker. The pH of the solution was adjusted to desired value using dilute solution of NH_4OH/NaOH.

The resulting mixture was shaken with 10 mL of chloroform for 1 min. The organic layer was separated and its absorbance was measured at 400 nm against the reagent blank prepared under identical conditions. Amount of copper in unknown solutions was determined from the standard calibration curve. To study the interference, the respective foreign ions were added to the aqueous phase before the extraction and pH adjustment.

Copper(II) can be quantitatively extracted by 4-chloro isonitroso acetophenone thiosemicarbazone into chloroform from an aqueous solution at pH = 8.0. Organic solvents can be arranged in the following order on the basis of the extraction coefficient values:

Chloroform > Diethyl ether > Benzene > Toluene > Carbon tetrachloride > Ethyl acetate > Nitrobenzene

The absorption spectrum of Cu: 4-Chloro isonitroso acetophenone thiosemicarbazone complex shows an absorption maximum around 400 nm wavelength. At this wavelength, Beer's law is found to be obeyed over a range of 0.2 to 20 microgram of copper per mL and the molar absorptivity is 2.518×10^3 L mol^{-1} cm^{-1} calculated on the basis of total amount of copper taken. The calibration plot of absorbance against concentration of copper(II) gives a linear graph in the range of 0.2 to 20 microgram per mL of copper. The extraction behaviour of Cu(II)-CINAPT complex was studied in the pH range 1 to 12. Quantitative extraction takes place in the pH range 7.5 to 8.5. The % extraction was found to be 99.6%. For quantitative extraction of Cu(II) 1 mL of 1% CINAPT was sufficient beyond which further increase in reagent concentration did not affect the absorbance. The extraction was found to be quantitative for minimum equilibration time of 60 seconds. The colour intensity of the Cu(II)-CINAPT complex remained stable for 16 h.

The average of 7 determinations of 10 microgram of Cu(II) was 9.90 microgram. The standard deviation and variance were found to be 0.12 microgram and 0.016 respectively. Deviation from mean at 95% confidence limit was found to be 0.1136.

The following ions when present in amounts indicated do not interfere in the spectrophotometric determination of Cu(II): 10 mg each of Na(I), K(I) Sr(II), Mn(II); 5 mg each of Li(I), Ba(II), Ca(II), Mg(II), Hg(II), Al(III), Bi(III), As(III), V(V), W(VI); 10 mg each of oxalate, phosphate, sulphate, thiosulphate, fluoride; 20 mg each of persulphate, sulphate, chloride, bromide, iodide, chlorate, bromate, iodate, nitrate, nitrite, cyanate, acetate, pyrophosphate, perchlorate and thiourea.

The interference by ions Ag(I), Ni(II), Co(II), Pb(II), Zn(II), Cd(II) cyanide, tartarate and EDTA can be removed by using appropriate masking agents. The composition of the extracted species has been studied by Job's continuous variation

and mole ratio method. The results suggest 1 : 2 (metal : ligand) stoichiometry for Cu(II). The method has been successfully applied for the determination of Cu(II) in alloys, synthetic mixtures and pharmaceutical samples.

The developed method was applied for the determination of copper in synthetic mixtures, pharmaceutical samples and alloys. The results obtained (Table-1) were found to be in good agreement with those reported or obtained by alternative method.

TABLE-1

S.No.	Sample	Copper found*	
		Certified value	Present method
1.	*Synthetic mixtures*		
	(a) Cu(100) Mn(100) Fe(100)	100 μg	99.8 μg
	(b) Cu(100) Zr(100) Zn(100)	100 μg	99.7 μg
	(c) Cu(100) As(100) Cd(100)	100 μg	99.8 μg
2.	*Pharmaceutical samples*		
	(a) Suparadyn (Nicholas Piramal)	6.7 mg	6.5 mg
	(b) Multivitamin capsules (Meyer Organics Ltd)	5.0 mg	4.9 mg
3.	*Alloys*		
	(a) Nimonic 901 BCSCRM 387	0.28%	0.30%
	(b) Magnesium alloy BCSRM 307	0.048%	0.050%

*Mean of 5 determinations

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