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Liquid-liquid Extraction and spectrophotometric determination of Cu (II) with acetophenone 2', 5'-dihydroxy thiosemicarbazone derivative as an Analytical reagent

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ABSTRACT

A simple and precise spectrophotometric method is coupled with solvent extraction technique and used for the determination of Cu (II) using Acetophenone 2',5'-dihydroxy thiosemicarbazone (ADHTS) as an analytical reagent. This reagent is synthesized in the laboratory and characterized by NMR, IR and elemental analysis for its purity [1] and [2]. The reagent form a yellow coloured stable complex with copper metal, which can be quantitatively extracted into n-Butanol at pH 7.4 This Cu (II)-ADHTS complex in n-butanol exhibit intense absorption peak at 410 nm. The study of change of color intensity of Cu (II)-ADHTS complex with varying concentration of reagent showed that 1 ml of 0.1% of reagent is sufficient for full color development of 5 ppm copper solution. Beer's law is obeyed in the range of 1 to 5 ppm of copper solution giving linear and reproducible graph. The stoichiometric ratio of complex studied by Job's continuous variation method, mole ratio method and slope ratio method. The stoichiometry of Cu (II)-ADHTS complex is 1:1 the molar absorptivity and Sandell's sensitivity are also calculated. The molar absorptivity is 0.59047 X 10^4 L $mol^{-1}cm^{-1}$ and Sandell's sensitivity is 0.01070 µg cm^{-2}. The newly developed method is then applied to various commercial samples successfully and observed to be compatible with earlier known methods.

Keywords: Copper, Spectrophotometric determination, n-butanol, Acetophenone, 2', 5'-dihydroxy, thio semicarbazone derivative.

INTRODUCTION

Copper is one of the most important metals after Iron [3]. It plays a vital role in many fields either as metal or its salts such as industry, laboratory, medicine, food, and beverage. Copper and its salts are highly toxic to lower organisms much more than man. However, it is an essential constituent of certain proteins. It is found in the human liver and in many Mollusca and Arthropoda such as snail and spider [4]. It is believed that in the plants the metal is present because of mechanical storage, but in Mollusca it is in the form the nucleus of respiratory protein and in Arthropoda it is the nucleus of hemocyanin, which play a same role as ferruginous hemoglobin in the red blooded animals. The major portion of the copper is used in electrical

industries and remainder is combined with other metal to form alloys such as brass (Cu-Zn), bronze (Cu-Sn) etc. Recent literature suggests that taste is impaired when copper deficiency is induced. Its toxic effect is main cause of Wilson's disease [4]. In plant physiology it is essential as a component of a number of different plant enzymes. It is one of the most harmful impurities in semiconductor materials. CuO is one of the oldest catalyst reported for oxidation purpose. Several compounds are known to react with the metal ions to give coloured complexes [5] and have been employed for the quantitative extraction and spectrophotometric determination of metals at trace level [6-9].

MATERIALS AND METHODS

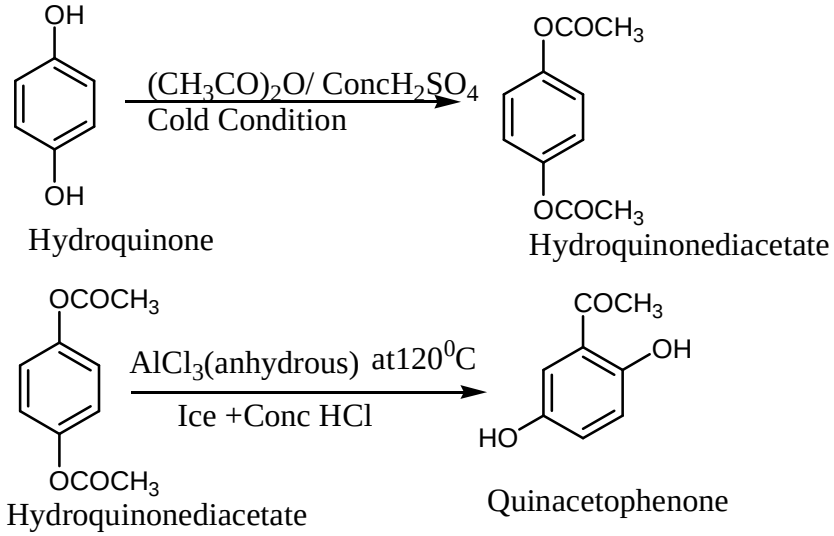
Synthesis of the reagent Acetophenone 2', 5' - dihydroxy thiosemicarbazone (ADHTS): Synthesis of ADHTS involves three steps. First two stages have been synthesized as reported in literature [1] and [2].

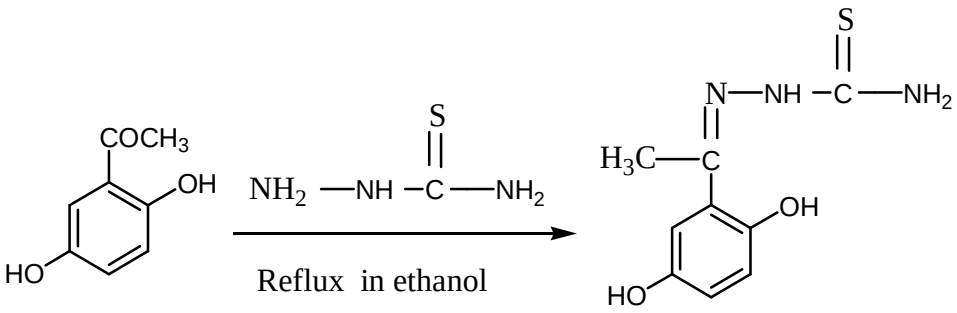
1. Conversion of hydroquinone to hydroquinone diacetate: To a cooled mixture of hydroquinone (11g, 0.1 moles) and acetic anhydride (20ml, 21.6g, 0.21mole) a drop of conc. sulphuric acid is added. The suspension is shaken; the hydroquinone dissolves with evolution of heat. The clear solution thus obtained is poured on crushed ice the separated product is filtered and washed with cold water and the product is recrystallized from dil alcohol. The yield was about 70%.

2. Conversion of hydroquinone diacetate to 2', 5'- dihydroxy acetophenone: A mixture of hydroquinone diacetate (10g, 0.052 moles) and anhydrous aluminum chloride (23 g, 0.172 moles) is heated at 110 -120 °C for one hour and then at 162-165 °C in oil bath three hour till the evolution of HCl gas ceased. It should be noted that the reaction is carried out at the anhydrous condition. The complex is hydrolyzed by adding crushed ice and HCl (20ml). The solid obtained is filtered and washed with water, the yellow tiny needles are obtained the yield is 89%.

3. Synthesis of thiosemicarbazone derivative of 2', 5'- dihydroxy acetophenone: Equimolar mixture of sodium acetate and semicarbazide hydrochloride is dissolved in minimum quantity of water and then it is to methanolic solution of 2',5'-dihydroxy acetophenone. After addition stirring is continuous for about one hour. The yellow coloured compound is precipitate out, which is washed and then recrystallized by using methanol as solvent.

Reactions





Quinacetophenone

Thiosemicarbazone derivative of 2',5'-dihydroxy acetophenone

Preparation of stock solution: The stock solution of Cu (II) was prepared by dissolving a weighed amount of copper sulphate in double distilled water containing dilute sulphuric acid and then diluted to the desired volume with double distilled water and standardized by EDTA method [10]. Absorbance and pH measurements were carried out on a Shimadzu UV-Visible 2100 spectrophotometer with 1 cm quartz cells and digital pH meter with combined glass electrode respectively.

Procedure for the extraction: 1.0 ml of aqueous solution containing 0.05µg of copper metal and 1 ml of reagent were mixed in a 50 ml beaker. The pH of the solution adjusted to 7.4. It must be noted that the total volume should not exceed 10 ml. The solution was transferred to 100 ml separatory funnel. The beaker was washed twice with n-butanol and transferred to the same funnel. The two phases were shaken for two minutes and allowed to separate. The organic phase was collected in 10 ml measuring flask and made up to the mark with organic solvent if required. Cu(II) in the organic phase is determined spectrophotometrically.

RESULTS AND DISCUSSION

The reagent ADHTS forms yellow coloured complex with Cu (II), which was extracted into organic phase. The extraction of Cu(II)-ADHS complex from an aqueous phase by n-Butanol is studied over a wide range of experimental condition. The results of various studies are discussed below.

Extraction as a function of pH : The extraction of Copper with Acetophenone 2',5'-dihydroxy, thiosemicarbazone has been studied over the pH range 1-10 and was observed that percentage extraction of copper is maximum from pH range 6.8 to 7.8,So further study is carried out at pH 7.4 (fig.1.)

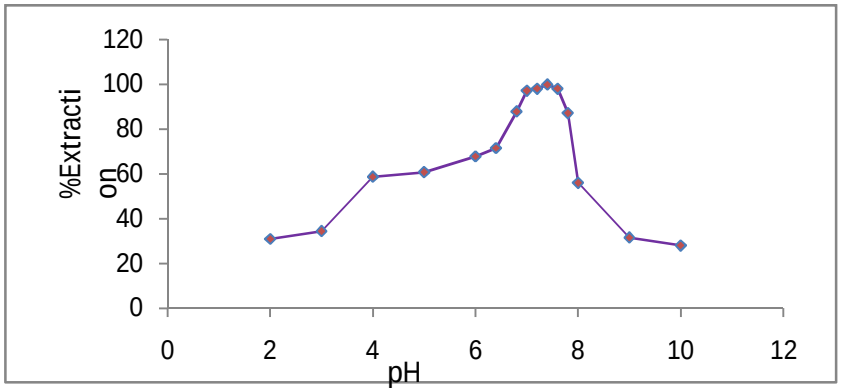


Fig. 1. The effect of pH on the extraction of Copper with ADHTS in n-Butanol.

Absorption spectrum: The absorption spectrum of Cu(II): Acetophenone 2',5'-dihydroxy thiosemicarbazone in n-Butanol shows the maximum absorption at 410 nm. The absorption due to reagent at this wavelength is nearly negligible. Hence the absorption measurements were carried out at 410nm.

Influence of diluents: The suitability of solvent was investigated using organic solvents such as chloroform, ethyl acetate, isoamyl alcohol, xylene, hexane, diethyl ether, toluene, n-butanol, carbon tetrachloride, nitrobenzene cyclohexanone, etc. The extraction of Cu(II):ADHTS was maximum in n-butanol. Hence, n-butanol was used for further extraction studies as it gave better and quicker phase separation.

TABLE 1. Observation table for effect of various solvents on Cu (II)- ADHTS complex

Sr. No.	Solvent	%Extraction
1	Nitro benzene	20.91
2	Cyclohexanone	27.12
3	Iso-amyl alcohol	48.94
4	Hexane	58.91
5	Ethyl acetate	88.89
6	n-butanol	99.99
7	chloroform	70.00
8	Diethyl ether	46.18
9	toluene	65.08
10	CCl4	28.18
11	xylene	22.73

Effect of salting out agents: The presence of 0.1M salts of various alkali and alkaline metals does not show any effect over the absorbance value of Cu(II): ADHTS complex extract. Therefore, no salting out agent was required during the extraction.

Effect of reagent concentration: The minimum amount of the reagent required for the color development of the metal Cu(II) in 10 ml of aqueous solution at pH 7.4 was found by varying the reagent concentration from 0.1ml to2.0mL of 0.1%ADHS in methanol keeping the other factors constant. The absorbance remained nearly constant when the volume of the reagent solution used was more than 1 ml Therefore, 1 ml of 0.1% reagent was chosen for the quantitative determination of the metal.

Effect of equilibration time and stability of the complex: The study of change in absorbance with variation in equilibrium time for extraction of the complex into organic solvent shows that equilibration time of 1 min is sufficient for the quantitative extraction of copper. The study of stability of color of the Cu(II)-ADHTS complex with respect to time shows that the absorbance due to extracted species is stable up to 32 hours, after which slight decrease in absorbance is observed. Throughout the experimental work, for practical convenience, the measurements have been carried out within one hour of extraction of copper.

Calibration plot: A calibration plot of absorbance against varying copper concentration and fixed ADHTS concentration gives linear and reproducible graph in the concentration range 1 to 5 ppm of Cu(II) (fig. 2). This shows that the Beer's law is obeyed in this range. The molar absorptivity and Sandell's sensitivity were calculated to be 7317.07 L $mol^{-1}cm^{-1}$ and 0.01075µg cm^{-2} respectively.

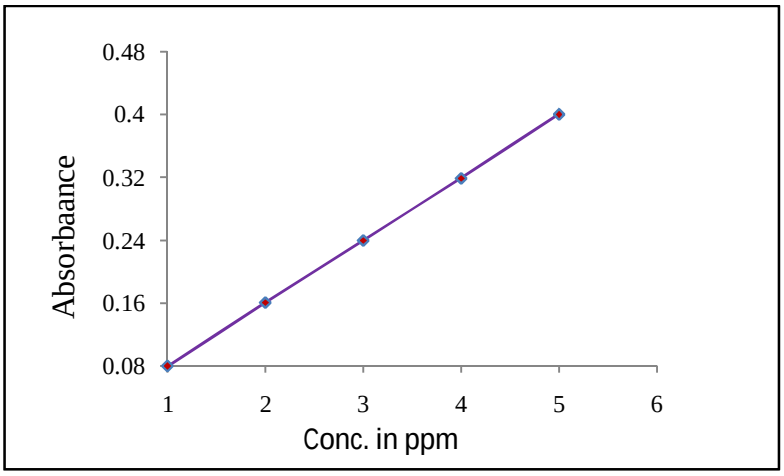


Fig1. Calibration plot of Cu (II) – ADHTS complex

Effect of foreign ions: The effect of other ions present in various amount indicated no interference in the spectrophotometric determination of 5ppm of copper. The ions which show interference in the spectrophotometric determination of copper were overcome by using appropriate masking agents.

Nature of extracted species: The composition of extracted Cu(II):ADHS complex has been determined by Job's continuous variation method, Slope ratio method (fig. 2) and Mole ratio method. It shows that the composition of Cu (II): ADHTS complex is 1:1.

Precision and accuracy: The precision and accuracy of the developed spectrophotometric method have been studied by analyzing ten solutions each containing 4µg of copper in the aqueous phase. The average of ten determinations was 3.991 and variation from mean at 95% confidence limit was ±0.00858.

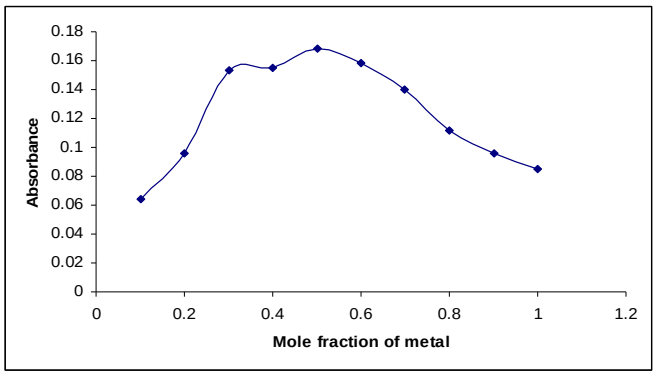


Fig.2. Job's continuous variation curve

Effect of foreign ions: The tolerance limit of different metal ions was studied by carrying out determinations of 4 µg of Cu (II) in presence of large number of foreign ions. It shows no interference with

most of the foreign ions on the extraction of copper. The interference of some metal ions are masked by using appropriate masking agents (table 2)

Table 2. Masking agents used

Sr. No.	Interfering Ion	Masking agent
1	Co (II)	Sodium fluoride
2	Fe(III)	Sodium fluoride
3	Ni (II)	DMG
4	V (V)	Thiourea
5	EDTA	Boiled with concentrated HNO3
6	CN-	Boiled with concentrated HNO3 and formaldehyde

APPLICATIONS

The proposed method was successfully applied for the determination of copper from various alloys, ores and pharmaceutical samples. The results found to be in good agreement with those obtained by the standard known method. (table 3).

TABLE 3. Observation table for determination of Cu (II) using ADHTS from different samples

Sr .No.	Sample	Standard method	Present method
Copper alloys			
1.`	Devardas alloy	71.2 µg	71.18 µg
2.	Cupro-Nickel alloy	22.25 µg	22.20 µg
Milk Sample			
1	Raw Milk	4.3 ppm	4.2 ppm
Pharmaceutical Sample			
1	Multi vitamin capsule	5.0 mg	4.89mg
Synthetic mixture			
1	Cu(55)+Cd(45)	55 ppm	54.51 ppm
2	Cu(100)+Fe(100)+W(100)	100 ppm	99.10 ppm

CONCLUSIONS

The proposed method is more highly sensitive and selective than the reported methods for the extractive Spectrophotometric determination of microgram amounts of copper. It offers advantages like reliability and reproducibility in addition to its simplicity, instant color development and suffers from less interference. It has been successfully applied to the determination of copper at trace level in synthetic mixtures and alloys.

REFERENCES

[1] V.K.Ahluwalia, P.Bhagat, R.Aggarwal, R.Chandra, *Intermediates for organic synthesis*, I.K. International Pvt. Ltd., **2005**.
[2] A.I.Vogel, *Textbook of Organic synthesis*, 3rd ed.; ELBS, London, **1957**.
[3] N.N.Greenwood, A.Earnshaw, *Chemistry of the elements*, 1st ed.; Pergamon press, **1989**.
[4] National Research Council. Copper. In: Recommended Dietary Allowances. Washington, D.C.: Food Nutrition Board, NRC/NAS, 151-154, **1980**.
[5] W.B.Jin, Z.J.Xu, X.P.Gao, *Guangpu Shiyanshi*, **2003**, 20, 796.
[6] A.E.Al, A.Orabi, *Anal. Chem.* **2003**, 1, 13.
[7] K.Reddy, N.Hussain, B.L.Prasad, *Indian J. of Chem.* **2004**, 42A, 111
[8] Zhang; Zhen-Wei; Cui, Yu; Gou-Xin; *Wuji Huaxue Xueban*, **2007**, 22, 1867.
[9] S.P.Janwadkar, R.S. Lokhande, S.M. Pitale, S.W.Kulkarni, S.K.Patil, *Int. J.Chemtech, Research*, **2011**, 3(4), 1765-1768.
[10] A.I.Vogal,'*Text Book of qualitative Inorganic Analysis*', Longman Green and Co. ltd., London, **1961**.