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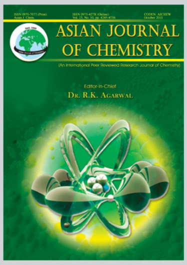

Spectrophotometric Determination of Copper(II) Using Nicotinohydroxamic Acid

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A simple, direct, highly sensitive and selective spectrophotometric method has been developed for the determination of copper(II). It is based on the reaction at pH 9.2 between nicotinohydroxamic acid and Cu(II) forming a stable green coloured complex. It exhibits a constant and maximum absorption at 800 nm. The system obeys Beer's law over a wide range of concentration. The proposed method can be applied for the determination of Cu(II) without interference from a variety of ions. The proposed procedure has been successfully applied to the analysis of Cu(II) in natural samples, industrial effluents and alloys.

Key Words: Spectrophotometry, Nicotinohydroxamic acid, Copper(II), Industrial effluents, Natural and alloy samples.

INTRODUCTION

Copper is a widely distributed metal in nature[1] and is extensively used by man. It is an essential metal required by almost all living organisms in some of their biological activities. Deficiency of copper may lead to certain physiological disorders in both plants and animals, but at higher concentrations it works essentially as a pollutant. Anthropogenic origin of copper is mainly from mining activities, use of copper fungicides, industrial applications such as metallurgical units and alloy manufacturers, copper electroplating and chemical industries. Mining effluents and industrial wastes can sometimes pose serious river pollution problems. Most of the copper toxicity is due to copper ions rather than the copper complexed with organic matter bound with the inorganic pesticides like bordeaux mixture and copper oxychloride. In water and soil, the bound copper can be solublized by certain microorganisms. Copper is however toxic to most aquatic life such as algae and different species of fish. In higher organisms, copper interfere with –SH groups of certain enzymes and can result in brain damage. Copper is essential to humans[2], as the adult daily requirement has been estimated to be 2 mg. Increase of copper contamination in water due to industrial effluents can cause hazardous effects in humans. Copper salts are also used in water supply systems to control biological growths in reservoirs and distribution pipes. It is also used as catalyst in the oxidation of manganese. Trace amounts of copper in various substances may be vital, objectionable or perhaps indicative of contamination or malfunction. Copper traces promote rancidity and off-flavors in foods and beverages. Its determination in biological samples such as blood, liver tissue, hair *etc*., can be of considerable significance in medical diagnosis and biochemical research. Chronic copper poisoning causes gastrointenstinal catarrh and haemochromatosis. Hence rapid and sensitive methods for its determination are in great demand. Several analytical techniques are available for the determination of copper(II), they include atomic absorption spectrometry[3-10], voltammetry[11-13], spectrophotometry[14-16], inductive coupled plasma-atomic emission spectrometry[17-19] and inductive coupled plasma-mass spectrometry[20]. But spectrophotometry and atomic emission or absorption methods are most commonly used. The spectrophotometry still represents an attractive technique for the determination of metal ions in aqueous media because of its simplicity, being inexpensive and is readily available. Although a vast number of reagents are available for the spectrophotometric determination of copper, most of them lead to extractive spectrophotometric methods. Most of the extractive spectrophotometric methods developed for copper are based on reactions with suitable colour producing reagents such as dithizone[21], sodium diethyldithiocarbamate[22], neo-cuproin[23], thio-2-thenoyltrifluoroacetone[24], 5-bromosalicylaldoxime[25], *m*-tolyl-*p*-methoxy benzohydroxamic acid[26], biacetyl*bis*(2-quinolhydrazone)[27], 1-phenyl-4,4,6-trimethyl (1*H*,4*H*)pyrimidine-2-thiol[28] and picolinamidoxime[29]. These reported reagents suffer from several disadvantages and limitations, such as poor sensitivity, selectivity and a few require special conditions for the formation of the complexes with the reagents, few need longer periods of time for phase separations, weak stability of coloured complexes. Since copper is both vital and toxic for many biological systems depending on its concentration[30,31], therefore, the determination of trace amounts of copper is becoming increasingly important due to the increased interest in environmental pollution[32]. In the proposed work, the coloured complex is highly stable with the procedure being rapid and non-extractive in nature for the selective separation and determination of copper(II) in natural water sample, industrial effluents and alloys. In continuation of the development of suitable methods for the determination of metals, especially in natural samples[33-35], we proposed a sensitive, selective, simple, direct and rapid spectrophotometric method for the determination of trace amounts of copper(II) using nicotinohydroxamic acid in natural water, industrial effluents and alloy samples. The developed method has been compared with the standard neo-cuproin method.

EXPERIMENTAL

A systronics spectrophotometer with 1 cm glass cells has been used for absorbance studies and a systronics pH meter with combined electrode has been used for the pH studies.

Nicotinohydroxamic acid (NHA): The free ligand[36] was synthesised by adding 2.3 g of sodium in 50 mL methanol to 6.9 g of hydroxylamine hydrochloride dissolved in 100 mL methanol. The mixture was cooled to room temperature and 15.12 g of ethyl nicotinate was added with slow stirring and stirred for 40 min. To this solution 2.3 g of sodium in methanol was slowly added and stirred for another 10 min. The mixture was filtered to remove the precipitate of sodium chloride and acidified with concentrated HCl. The filtrate was left overnight and the crystals were removed by filteration and recrystallized from EtOH. Stock solution of 2×10^{-2} M nicotinohydroxamic acid was prepared by dissolving the accurately weighed amount (0.56 g) of the reagent in EtOH (200 mL).

Copper(II) solution: A stock solution of copper(II) was prepared by dissolving known mass (*ca.* 0.29 g) of cupric sulphate in water and then making up the solution to mark in a standard flask (200 mL) with distilled water. The solution was standardised by conventional method[37]. Working solutions were prepared daily by appropriate dilution of the stock solution.

Buffer solution (pH 9.2): Disodium tetraborate (borax) (0.05 M) buffer, for the determination of copper(II).

Diverse ion solutions were prepared in suitable concentration using analytical reagent grade chemicals. All the reagents used were of analar grade.

General procedure: To measured aliquots of copper(II) (14.83-118.60 $\mu g\ mL^{-1}$) solution placed in a standard flask, buffer solution (1 mL) and the reagent (nicotinohydroxamic acid) (1 mL) was added and the resulting green coloured solution was quantitatively diluted (25 mL) with distilled water. The absorbance of the coloured solution was measured at 800 nm against a reagent blank prepared in the same manner.

RESULTS AND DISCUSSION

Absorption spectra: The absorption spectrum of copper-NHA complex was recorded in the range of 300-850 nm and the results showed a maximum absorbance at 800 nm, where the absorption of the reagent blank is almost negligible and hence all the absorbance measurements were carried out at 800 nm.

Stability of the complex: The formation of copper-NHA complex is instantaneous and the absorbance of the green coloured complex is stable for more than 12 h.

Effect of pH: Keeping the concentration of copper(II) constant, the complexation reaction between copper-NHA was studied over the pH range 1.0-14.0. A constant and maximum value of absorbance was obtained in the pH range of 9.2. Hence, the pH was fixed at 9.2 for further analysis, by use of disodium tetraborate (borax) buffer solution.

Analytical characteristics: The absorbance is a linear function of concentration of copper(II) in the range of 0.59-5.34 $\mu g\ mL^{-1}$ at 800 nm. The determinations for copper(II) were carried out in the range 1.19-4.15 $\mu g\ mL^{-1}$ of solution. The results of the determinations are given in Tables 1 and 2. The apparent molar absorptivity value obtained 1.349×10^4 L $mol^{-1}\ cm^{-1}$. The standard deviation and co-efficient of variation calculated for six replicate measurements are in good agreement with the standard method. It was found that the order of addition of reactants has no effect on the formation of the complex.

TABLE-2
STATISTICAL COMPARISON

Method	Average error* (%)	SD*	CV* (%)
Nicotinohydroxamic acid	0.45	0.24	0.53
Neo-cuproin	0.87	0.39	0.45

*6 replicates.

Effect of diverse ions: The effect of diverse ions on the determinations of copper(II) was studied and the results are shown in Table-3. The selectivity of the proposed method has been determined by the analysis of samples containing known amount (2.97 $\mu g\ mL^{-1}$) of copper(II) in the presence of various amounts of diverse ions. The results showed that the studied anions and most of the cations do not interfere with the determination of copper(II). The main interferences were shown

TABLE 1
DETERMINATION OF COPPER(II)

Cu(II) taken ($\mu g\ mL^{-1}$)	Nicotinohydroxamic acid method			Neo-cuproin method[38]		
	Cu(II) found ($\mu g\ mL^{-1}$)	Recovery (%)	Error (%)	Cu(II) found ($\mu g\ mL^{-1}$)	Recovery (%)	Error (%)
1.19	1.18	99.1	0.9	1.17	98.3	1.7
1.78	1.79	100.6	0.6	1.77	99.4	0.6
2.37	2.38	100.4	0.4	2.35	99.1	0.9
2.97	2.96	99.7	0.3	2.95	99.3	0.7
3.56	3.55	99.7	0.3	3.59	100.8	0.8
4.15	4.16	100.2	0.2	4.17	100.5	0.5

TABLE 3
EFFECT OF DIVERSE IONS ON THE DETERMINATION OF COPPER(II) AMOUNT OF COPPER(II) TAKEN-2.97 μg mL^{-1}

Diverse ions	Tolerance limit (μg mL^{-1})
Barium(II)	500
Chloride, acetate, phosphate and magnesium(II)	150
Hydroxide, thiosulphate and sodium(I)	120
Bicarbonate, nitrate, carbonate, bromide, zinc(II) and calcium(II)	60
Oxychloride, molybdate, EDTA and zirconium(II)	35
Sulphate, iodide, citrate, nitrite, potassium(I) and bismuth(II)	30
Thiocyanate, tartarate, tin(II), strontium(II), lead(II) and cadmium(II)	25
Acetate, borate and fluoride	20
Nickel(III)[a], cobalt(II)[b] and iron(III)[c]	15
Ammonium(I), aluminium(III) and manganese(II)[d]	10

[a]Masked with sodium tartarate (1 % w/v, 5 mL), [b]Masked with NH_4OH (5 mL, 1 % w/v), [c]Masked with NaF (1 % w/v, 5 mL), [d]Masked with KI (5 mL, 1 % w/v).

by iron(III), cobalt(II), manganese(II) and nickel(II) solutions and they were effectively masked by using suitable masking reagents. Iron(III) was masked by the use of sodium fluoride (1 % w/v, 5 mL) solution, cobalt(II) with ammoniun hydroxide (1 % w/v, 5 mL), manganese(II) was masked using potassium iodide (1 % w/v, 5 mL) solution and nickel(II) with the use of sodium tartarate (1 % w/v, 5 mL) solution.

Application

Water and effluent samples: Water samples were collected from a bore well, effluent samples from a tannery and dyeing unit[38]. All samples were filtered before analysis and known amounts of copper(II) were added, as none of the samples contained any amount of copper(II). The samples were analyzed for copper(II) by the proposed method and the recoveries are shown in Tables 4 and 5. A close examination of the table reveals that the presently developed method can be applied for determination of copper(II) in these samples with a high degree of accuracy and precision.

TABLE-4
DETERMINATION OF COPPER(II) IN NATURAL WATER SAMPLE

Cu(II) aded (μg mL^{-1})	Cu(II) found (μg mL^{-1})	Recovery (%)
1.19	1.20	100.8
1.78	1.77	99.4
2.37	2.35	99.1
2.97	2.95	99.3
3.56	3.55	99.7
4.15	4.17	100.5

TABLE 5
DETERMINATION OF COPPER(II) IN EFFLUENT SAMPLES (TANNERY AND DYEING UNIT)

Cu(II) added (μg mL^{-1})	Tannery		Dyeing unit	
	Cu(II) found (μg mL^{-1})	Recovery (%)	Cu(II) found (μg mL^{-1})	Recovery (%)
1.19	1.18	99.1	1.16	97.5
1.78	1.77	99.4	1.74	97.7
2.37	2.35	99.1	2.33	98.3
2.97	2.96	99.7	2.95	99.3
3.56	3.57	100.3	3.54	99.4
4.15	4.13	99.5	4.11	99.0

Alloy samples: The method was applied for the determination of copper(II) in red brass and cupronickel by the presently developed method and the results are shown in Table-6. The results show that the recoveries are in good agreement with the certified values, indicating that the proposed method can be used in routine analysis of the metal in these alloys.

TABLE 6
ALLOY ANALYSIS DETERMINATION OF COPPER(II) IN RED BRASS AND CUPRONICKEL

Sample composition (%)	Cu(II) alloy taken (μg mL^{-1})	Cu(II) found (μg mL^{-1})	Cu(II) found (%)	Average Cu(II) found (%)
Red Brass (Cu -85, Zn - 15)	4.00	3.61	90.25	91.94
	8.00	7.19	89.87	
	12.00	11.23	93.58	
	16.00	14.79	92.44	
	20.00	18.78	93.90	
	24.00	21.99	91.62	
Cupro-nickel (Cu-90, Ni-10)	1.60	1.45	90.62	94.45
	3.20	2.99	93.44	
	4.80	4.42	92.08	
	6.40	6.19	96.72	
	8.00	7.71	96.37	
	9.60	9.36	97.50	

Conclusion

The method described in this paper allows for the rapid, precise and reliable determination of copper in trace amounts. The main benefits of the procedure are the enhanced sensitivity of the spectrophotometric method, low cost, fairly easy operation, speed of analysis, reproducibility in addition to be-ing simple with instant colour development and minimum interferences coupled with it being direct, accurate, selective, specific and non-extractive. The method has been successfully applied for the determination of copper at trace level in natural sample, industrial effluents and alloys. The results obtained are in good agreement with certified values and are comparable to those obtained by known method. The method has thus good potential for use by the industry.

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