UM MÉTODO ESPECTROFOTOMÉTRICO SIMPLES PARA A DETERMINAÇÃO TRAÇOS DE COBRE (II)

A SIMPLE SPECTROPHOTOMETRIC METHOD FOR THE TRACE DETERMINATION OF COPPER(II)

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Received 28 July 2012; received in revised form 1 August 2012; accepted 24 August 2012

RESUMO

O cobre é um nutriente traço essencial para plantas e animais. É extremamente importante em baixos níveis para funções metabólicas específicas, mas é prejudicial em níveis elevados. Quantidades significativas de cobre estão largamente espalhadas no ambiente em diversas fontes. Um método espectrofotométrico simples é apresentado para a determinação de quantidades traço de cobre usando Hidrazona Ácida Salicilsalicílica (SSAH) como reagente espectrofotométrico. O método proposto apresenta como vantagens a sensibilidade, rapidez e seletividade sem qualquer separação ou extração anterior. O método foi baseado na reação entre SSAH e Cu (II) em meio ácido produzindo um complexo de cor esverdeado-amarelado. O complexo tem absorção máxima em 420 nm. A Lei de Beer é obedecida na faixa de concentração 0,2497 a 2,2471 $\mu\text{g mL}^{-1}$. Diversos parâmetros como constante de estabilidade (1.13×10^7), coeficiente de absorção molar ($8.560 \times 10^4 \text{ L mol}^{-1} \text{cm}^{-1}$), Sensitividade de Sandell ($0.0007 \mu\text{g cm}^{-2}$), faixa de calibração linear, estequiometria do complexo (1:1), limite de detecção do método ($0.0299 \mu\text{g mL}^{-1}$), limite de quantificação ($0.0598 \mu\text{g mL}^{-1}$), desvio padrão (2.624%–3.567%) etc. foram calculados e apresentados. O efeito de íons externos na determinação foi apresentado. O método foi aplicado com sucesso para a determinação de cobre em amostras de água com lascas e amostras com ligas metálicas.

Palavras-chave: Espectrofotometria, determinação de traços de Cu (II), composição do complexo, estudo de interferência, aplicações.

ABSTRACT

Copper is an essential trace nutrient for plants, animals. It is very essential at lower levels for specific metabolic functions, but is harmful at elevated levels. Significant amount of copper is widespread in the environment from variety of sources. A simple spectrophotometric method is presented for the determination of trace amounts of copper using salicyl salicyclic acid hydrazone (SSAH) as a spectrophotometric reagent. The proposed method has the advantages of sensitivity, rapidity and selectivity without any prior separation or extraction. The method was based on the reaction between SSAH and Cu(II) in acidic medium to produce a greenish-yellow colored complex. The complex has an absorption maximum at 420 nm. Beer's law is obeyed in the concentration range 0.2497 to 2.2471 $\mu\text{g mL}^{-1}$. Several parameters like stability constant (1.13×10^7), molar absorption coefficient ($8.560 \times 10^4 \text{ L mol}^{-1} \text{cm}^{-1}$), Sandell's sensitivity ($0.0007 \mu\text{g cm}^{-2}$), linear calibration range, stoichiometry of the complex (1:1), method detection limit ($0.0299 \mu\text{g mL}^{-1}$), limit of quantification ($0.0598 \mu\text{g mL}^{-1}$), standard deviation (2.624%–3.567%) etc were calculated and presented. The effect of foreign ions on the determination was presented. The method was successfully applied for the determination of copper in spiked water samples and alloy samples.

INTRODUCTION

Copper is essential trace element for animals and human beings (Richter *et al.*, 1997). The Recommended Dietary Allowance for copper in normal healthy adults is 0.97mg/day (Food Nutrition Board, Washington, D.C., 1980). Copper containing proteins have diverse role in biological electron transport and oxygen transportation (Lippard and Berg, 1994; Decker and Terwilliger, 2000; Ganjali *et al.*, 2011; Banci *et al.*, 1992). Copper plays a critical role in the manufacture of hemoglobin in the blood. Because of its role in facilitating iron uptake, copper deficiency can produce anemia-like symptoms, neutropenia, bone abnormalities and abnormalities in glucose and cholesterol metabolism. On the other hand, accumulation of copper in body tissues causes Wilson's disease (Brewer and Gurkan, 1992). Therefore, sensitive and accurate determination of copper is very important. When compared to the various methods for Cu(II) determination (Blair and Diehl 1961; Shijo *et al.*, 1996; Shijo *et al.*, 1994), electrochemical methods (Fabio *et al.*, 2008; Liu *et al.*, 2011; Jianjun *et al.*, 2004; Hakan *et al.*, 2011), atomic absorption spectrometric methods, (Baysal *et al.*, 2011; Tulin *et al.*, 2011; Pavla *et al.*, 2010), spectrophotometric methods are preferred due to the fact that they involve less expensive instrumentation and impart rapid results. Many of the spectrophotometric procedures employed involve tedious extraction procedures such as solid phase extraction (Puls *et al.*, 2009), liquid-liquid extraction (Skrlikova *et al.*, 2011) or cloud point extraction (Xiang *et al.*, 2010). The aim of this article is to develop simple, rapid, selective, sensitive and inexpensive method for the trace determination of copper.

EXPERIMENTAL

A SHIMADZU UV-visible spectrophotometer with 1.0 cm quartz cell was used for spectrophotometric studies. An ELICO digital pH meter was used for pH measurements.

All reagents used were of analytical reagent grade procured from Merck, India. The working solutions were prepared by using double

distilled water. 0.1 M Cu(II) solution was prepared by dissolving requisite amount of copper(II) sulphate in 100 mL of distilled water and was standardized by using the standard procedure mentioned in the literature (Vogel, 1989).

The buffer solutions were prepared by mixing 1M hydrochloric acid and 1M sodium acetate (pH 1.0-3.0) and 0.2M acetic acid and 0.2M sodium acetate (pH 3.5-7.0).

Synthesis of SSAH

Equimolar concentrations of salicyclic hydrazide and salicylaldehyde were taken into round bottom flask. The contents were refluxed for one hour after the addition of appropriate amount of methanol. Yellow product obtained after cooling was recrystallized in 1:1 dimethylformamide. (melting point: 284-286°C)

Figure 1. Structure of salicyl salicycyclic acid hydrazone

General experimental procedure

5 mL of buffer solution of pH 2, 1 mL of Cu(II) solution 1 mL of SSAH solution and 1 mL of dimethylformamide were taken in a 10 mL volumetric flask. The solution was diluted to 10 mL with double distilled water. The contents were shaken well and absorbance of the solution was measured at 420 nm against the reagent blank solution.

General procedure for the preparation of alloy solution

Appropriate amount of the alloy sample was dissolved in a 10 mL of aquaregia, evaporated to minimum volume and extracted with 10 mL of 2M HNO₃. The stock solution was prepared by diluting the resulting solution to a suitable volume. The solution was further diluted as required. General procedure mentioned above

was followed to find out the amount of copper (II) present in the alloy sample solution.

RESULTS AND DISCUSSION

pH studies

The pH dependence of the absorption of metal complex is shown in the Figure 2. The spectra of Cu(II)-SSAH complex was studied in the pH range 1-7. It was found that the absorbance was maximum in the solutions of pH 2. In view of maximum absorbance and reproducibility of the spectrum, a medium pH 2 was selected for the further analytical studies.

Absorption spectra

The absorption spectra of the Cu(II) solution against the buffer blank, the reagent solution against the buffer blank and that of solution containing Cu(II)-SSAH complex against the reagent blank were recorded in the wavelength region 400-520 nm in the media of pH 2. Typical spectra are presented Figure 3. The spectra revealed the absorption maximum at 420 nm. However, at this wavelength, both the reagent and the metal showed negligible absorbance. Hence it was confirmed that the absorption spectrum (C) was due to Cu(II)-SSAH complex and the further analytical investigation was carried out at 420 nm. The absorbance of the Cu(II)-SSAH complex solution was measured at different time intervals to ascertain the stability of the complex. The chromogenic reaction between Cu(II) and SSAH was found to be instantaneous and the absorbance of the solution was stable for more than 36 hours. It was found that an optimum reagent concentration of 5 fold was sufficient for the complexation. It was also found that the presence of excess of the reagent does not alter the chromogenic reaction and hence the absorbance.

Composition of Cu(II)-SSAH complex

Composition of the Cu(II)-SSAH complex formed was determined by Job's method of continuous variation (Job, 1928). Figure 4, a plot of absorbance versus mole fraction of Cu(II) reveals that Cu(II) forms 1:1 (Metal:Ligand) complex with the reagent (SSAH). The value of stability constant calculated from the Job's method was found to be 1.13×10^7 . The

stoichiometry of the Cu(II)-SSAH complex was confirmed by mole ratio method (Yoe and Jones, 1944).

Construction of calibration graph and statistical analysis

A series of experimental solutions containing different amounts of Cu(II) were prepared to find out the absorbance of each solution. A graph (Figure 5.) was drawn between absorbance and the metal ion concentration indicates that Cu(II) can be determined in the concentration range 0.2497 to 2.2471 $\mu\text{g mL}^{-1}$. The straight line plot so obtained can be fitted into the equation $A_{420\text{nm}} = 0.3183C + 0.0258$ (A is absorbance and C is concentration in $\mu\text{g mL}^{-1}$). The correlation coefficient was 0.998. The molar absorptivity and Sandell's sensitivity (Sandell, 1965) were found to be $8.560 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$ and $0.0007 \mu\text{g cm}^{-2}$ respectively. The relative standard deviation ($n = 5$) was in the range 2.624%–3.567% indicating that this method is highly precise and reproducible. The method detection limit and limit of quantification were found to be 0.0299 and 0.0598 $\mu\text{g mL}^{-1}$ respectively. The recovery data (100.7-101.0%) indicated in the Table 2 A reveals that the method is highly accurate.

Effect of diverse ions

The effect of contemporaneous ionic species on the proposed method was investigated by measuring the absorbance of the reaction mixture containing various ions. A change in absorbance of $\pm 2\%$ was taken as the tolerance limit for interference. The results are presented in Table 1. It can be concluded from the table that the method is free from interference of most of the ions generally associated with copper.

Applications

The proposed method was successfully applied to the determination of copper (II) in spiked water solutions and metal alloys. The results were shown in the Table 2 (A) and (B).

CONCLUSION

The article presents, a novel, simple and inexpensive method with the for the trace

determination of copper in water and alloy samples. The results obtained were in good agreement with the certified values and were comparable to those obtained by standard procedures. The method offers the advantages of sensitivity, rapidity and selectivity without any prior separation or extraction.

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Figure 2. pH dependence of the absorption spectra of SSAH-Cu(II) Complex. $[SSAH] = 5 \times 10^{-5} M$; $[Cu(II)] = 5 \times 10^{-6} M$; $pH = 2$.

Figure 3. Absorption spectrum of Cu(II) solution against the buffer blank, $[Cu(II)] = 5 \times 10^{-5} M$; $pH = 2$. SSAH solution against the buffer blank, $[SSAH] = 5 \times 10^{-5} M$; $pH = 2$. Cu(II)-SSAH complex against the reagent blank, $[SSAH] = 5 \times 10^{-5} M$; $[Cu(II)] = 5 \times 10^{-6} M$; $pH = 2$.

Figure 4. Job's method of continuous variation, $[SSAH] = 0.3 \times 10^{-4} M$; $[Cu(II)] = 0.3 \times 10^{-4} M$; $pH = 2$.

Figure 5. Calibration plot for the trace determination of copper (II), $[SSAH] = 5 \times 10^{-5} M$; $pH = 2$.

Table 1. Tolerance limit of diverse ions in the presence of 0.318 ppm copper (II)

Anion added	Tolerance limit (ppm)	Cation added	Tolerance limit (ppm)
Citrate	2333.00	Bi(III)	Does not interfere
Tartrate	1384.10	W(VI)	63.57
Iodide	945.30	Mo(VI)	39.30
Thiosulphate	1875.44	Fe(III)	45.85
Oxalate	1166.00	Mn(II)	102.78
Bromide	389.35	Ag(I)	167.00
Thiourea	608.96	Al(III)	294.00
Nitrate	726.45	Pb(II)	Does not interfere
Urea	480.00	Hg(II)	60.65
Acetate	354.00	Zn(II)	48.68
Thiocyanate	897.65	Fe(II)	45.85
Chloride	262.64	Ni(II)	165.44
Phosphate	479.48		
Fluoride	114.00		

Table 2 A). Determination of Cu(II) in synthetic mixtures

Amount of Cu(II) added	Found %		Recovery %	RSD %	SE %
	AAS Method	Proposed method*			
0.499	0.501	0.504 ±0.009	101.002	2.624	0.004
0.998	1.010	1.005±0.022	100.701	3.016	0.01
1.997	2.019	2.012 ±0.051	100.751	3.567	0.023

*t value at 95% confidence level is 2.26.

Table 2 B). Determination of Cu(II) in alloy samples

Sample name/number	Alloy composition	Copper (II) %		Error %
		Certified	Calculated	
BCS-CRM 387	Ni = 41.90%; Fe = 36.00%; Cr = 12.50%; Mo = 5.80%; Ti = 2.95%; Al = 0.24%; Co = 0.20%; Cu = 0.30%.	0.3	0.306	2.00
BAS 106	Cu = 4.10%; Ni = 1.93%; Fe = 0.03%; Mn = 0.19%; Si = 0.29%; Mg = 1.81%; rest Al.	4.1	4.21	2.683
Tin base white metal	Sn = 82.20%; Cu = 4.58%; Ni = 0.17%; Bi = 0.11%; Fe = 0.024%; Sb = 9.45%; PB = 3.18%; Cd = 0.14%; Zn = 0.040%.	4.5	4.624	2.756