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Preconcentration Mini Column Technique For The Determination Of Cu (II) In Water And Alloy Samples With Spectrophotometry



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ABSTRACT

4-amino methyl pyridine anchored silica gel (4-AMPS) was used as a sorbent in a simple sensitive spectrophotometry determination of Cu (II) in various samples using piperazine dithiocarbamate as a color developing agent (λ_{\max} 420 nm) at pH 5.0 ± 0.2 . Beer's law was obeyed over the range of 0.2 -13 $\mu\text{g ml}^{-1}$. The molar absorptivity and Sandell's sensitivity were $0.5731 \times 10^5 \text{ l mol}^{-1}\text{cm}^{-1}$ and $0.002280 \mu\text{g cm}^{-2}$ respectively. Under these conditions, the preconcentration factor obtained was 80, and the detection limit achieved was 5.0 ng ml⁻¹. The detailed study of various interfering ions made the method more sensitive and selective. The recovery of Cu(II) from various samples range from 94.20 to 99.10 %. The present method was successfully applied for the determination of Cu(II) in various water and alloy samples. The proposed method was compared with reported methods in terms of Student's 'T'-test and Variance ratio 'F'-test which indicates that there is no significant difference between proposed and literature method at 95 % confidence level.

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KEYWORDS

4-aminomethyl pyridine-silica gel (4-AMPS);
Preconcentration;
Piperazine dithiocarbamate;
Copper (II);
Spectrophotometer;
Water;
Alloy samples.

INTRODUCTION

Copper is available in nature in the free state in the form of sulphides, chlorides and carbonates. The

copper is utilised in electrical industries and industrially useful alloys. Biologically copper is essential in small amounts for the synthesis of haemoglobin. The deficiency of copper causes

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TABLE 1: Comparison of analytical parameters of the present method with others spectrophotometric method for the determination of copper

Reagent	λ_{\max} (nm)	Optimum pH range	Beer's law validity range ppm	Molar absorptivity mol ⁻¹ cm ⁻¹	M:L	Remarks	Ref.
8-Methoxy-2-chloroquinoline-3-carbaldehyde thiosemicarbazone	410	5.0	3.0	0.0026768	1:1	Interference no. of metal ions and poor sensitivity and selectivity	[19]
7-Methoxyl-2-chloroquinoline-3-carbaldehyde thiosemicarbazone	400	4.0	5.0	343.4	-	Mo(V) interfere, very poor sensitivity	[20]
2,5-Dihydroxy acetophenone benzoic hydrazone	-	5.00	0.3-3.00	0.011	-	High reagent consuming and poor selectivity	[21]
Pyruvaldehyde (N,N-dibutyl) bis-thiosemicarbazone	488	5.12	-	10900	1:1	Less sensitivity	[22]
2-Carboxy benzaldehyde thiosemi carbazone	346	-	0.5-5.0	12000	1:1	Less sensitivity	[23]
2,4-Dihydroxy-5-bromoacetophenone thiosemicarbazone	400	6.00	12.7	1450	1:1	Very poor sensitivity and selectivity	[24]
2,2-Dipyridyl-2 pyridye hydrozone	-	11.9-12.6	Upto 1.0	0.038	-	Interference of mutual ions and expensive reagent	[25]
Benzaldehyde-4-(2-hydroxy-5-sulfophenyl)-3-thiosemicarbazone	325	4.5	7.62	7.44	1:2	very poor sensitivity	[26]
4-Chlorosemimonso-acetophenone thiosemi carbazone	400	7.5-8.5	0.2-2.0	2518	1:2	Ag(I), Ni(II), Co(II), Pb(II), Cd(II) cyanide, tartarate and EDTA interfere, less sensitive	[27]
2,4-Dihydroxy benzophenone benzoic hydrazone	-	4.0	0.31-2.20	0.0155	-	Less sensitive and stable	[28]
2,4-Dihydroxy benzophenone isonicotinoyl hydrazone	-	2.0	0.063-2.550	0.0165	-	Less sensitive more reagent consumption	[29]
Benzildithiosemi carbazone	380	4.0	0.5-4.0	16347	1:1	Low detection limit and detection unit	[30]
2,5-Dimercapto-1,3,4-thiadiazole	390	0.02-0.014	-	0.000565	1:2	High reagent consumption and highly commercial	[31]
Piperazine dithiocarbamate	-	-	-	-	1:1	Low reagent consumption, economical color forming reagent, less interference, highly stable.	Present Method

diseases like anaemia, while excess of it will cause 'Jaundice' and 'Wilson disease'. As a pollutant, copper at higher concentrations is toxic to aquatic

organisms. In view of this, the separation and determination of copper from associated elements is indispensable. Several analytical techniques have

been monitored for the determination of Cu (II), it includes atomic absorption spectrometry^[1-8] voltammetry^[9-11] spectrophotometry^[12-14] inductive coupled plasma-atomic emission spectrometry^[15-17] and inductive coupled plasma-mass spectrometry^[18] was reviewed. A few reagents^[19-31] are available for the spectrophotometric determination of copper (II) as shown in TABLE 1. The above reported reagents suffer from several disadvantages such as poor sensitivity, selectivity, time consuming and few are required special conditions for the formation of stable complexes with the reagents and few are commercial to synthesis at ordinary laboratories.

In this investigation the novel, facile and sensitive sorbent, 2-aminomethylpyridine grafted silica gel (AMPSG) was successfully anchored for the preconcentration of Cu (II) in various water and alloy samples. Optimum experimental conditions were investigated with respect to a standard solution of the same matrix, in order to examine the possibility to obtaining the maximum extraction efficiency with minor sample treatment and minimal experimental conditions. Under these conditions, the preconcentration factor obtained was 80, and the detection limit achieved was 5.0 ng ml⁻¹. The method was successfully applied for the determination of Cu (II) in various water and alloy samples.

EXPERIMENTAL

Instrumentation

A HITACHI U 2001 spectrophotometer with 1.0 cm path length was used for electronic spectral measurements. An Elico Li-129 model pH meter along with glass-calomel combined electrode was used for are pH measurement.

Reagents and solutions

Double distilled water was used through out the experiment. Solutions containing 2.0 M of nitric acid (Merck, Mumbai, India) were used as eluent. A 1.0 g l⁻¹ copper (II) stock solution was prepared, dissolving 0.5000g of metallic copper (Merck, Mumbai, India) in 10 ml of 5M HNO₃. This solution was quantitatively transferred to a 500ml calibrated flask and the volume was made up to the mark with double dis-

tilled water. The working solution of copper (II) was prepared by appropriate dilution of stock solution. Piperazine dithiocarbamate (0.03 M) solution was prepared a freshly by dissolving 1.208 g of piperazine dithiocarbamate in 5ml of methanol and this solution was mixed with 150 ml of hot water (70-80°C), filtered into a 250ml volumetric flask, and the volume was made up to the mark with double distilled water.

Synthesis of sodium piperazine dithiocarbamate reagent

Carbon disulphide (80 g) was slowly added to a solution of piperazine (42.5 g) in 25 ml of water at 5°C with constant stirring, followed by 40 g of sodium hydroxide dissolved in 20 ml of water to form sodium salt of piperazine dithiocarbamate. The product was warmed to room temperature and washed 2-3 times with purified acetone. The reaction product was purified by recrystallization in acetone. The purified compound has a melting point of 209-212°C at 740 mm pressure.

Synthesis of 4-amino methyl pyridine-silica gel sorbent organo functionalization

A sample of 20 g of activated silica gel was suspended in 100 ml of dry toluene and 20 mL (108 mol) of 3- chloropropyltrimethoxy silane was added to this suspension. The mixture was mechanically stirred under reflux of the solvent in an inert atmosphere for 72 h the suspension was filtered and the solid was washed with toluene and dried under vacuum at 40°C for several hours, to give the modified silica named silica^[33].

Incorporation of 4-amino methyl pyridine

A sample of 5.0 g of silica reacted with 3.50 mL (0.034 mol) of the compound 4-AMP in 50 mL of toluene, containing 5.0mL of triethylamine in order to facilitate the reaction equilibrium^[34]. The suspension was kept under reflux and mechanically stirred for 72h at 40°C. The final product 4 -AMP-silica gel was filtered, washed with toluene followed ethanol, and dried under vacuum at 40°C for 24h.

General procedure

4-AMPS (1.0 g) was first packed in a glass col-

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umn (10cm length×10mm diameter) between frists, using the method recommended by the manufacturer^[35]. The column was treated with 2 M HNO₃ (25 ml) and washed with double distilled water until free from acid. A suitable aliquot of the sample solution containing Cu²⁺ in the concentration range of 200-800 µg ml⁻¹ was passed through the column after adjusting its pH to the optimum range (acetate buffer of pH 5.0±0.2) with a flow rate of 1.0-5.0 ml min⁻¹. The column was washed with double- distilled water to remove free metal ion. The bound metal ion (Cu²⁺) was stripped from the column with 2 M HNO₃ (8 to 10 ml) passed at a flow rate of 2.0-4.0ml min⁻¹. The eluent was then mixed with 0.03 M piperazine dithiocarbamate to form yellow colored product, which was measured spectrophotometrically at wavelength 420 nm against reagent blank as shown in figure 3.

Procedure for the determination of Cu (II) in natural water samples

Different water samples (tap water, river water, spring water) were collected from various places in and around Tirupati, A.P., India. The samples (500 ml) were stored at 0-5°C in metal free polyethylene bottles. Water samples were filtered through Whatman filter paper No.41 and clean solution was collected into 1l beaker. The contents are diluted up to the mark with double distilled water. 50 ml of this solution is further diluted to get working solution for determination of Cu (II) as described in above procedure and compared with the reported method^[29] with statistical validation. The results were summarized in TABLE 2.

Procedure for the determination of Cu(II) in alloys samples

1 g of alloy sample was dissolved in a 10 ml of aqua regia, and evaporated to minimum volume, extracted with 10 ml of 2 M HNO₃ and then diluted with double distilled water to a suitable volume (10

TABLE 2: Determination of copper (II) in various samples

Sample	Copper added µg ml ⁻¹	Proposed method				Reported method[32]	
		Found ^a µg ml ⁻¹	Recovery (%) ^a	t-test	F-test	Found ^a µg ml ⁻¹	Recovery (%) ^a
Synthetic mixture	0.6	0.59	98.3±0.15	4.52	0.21	0.57	95.0±0.09
	1.2	1.19	99.1±0.11	1.52	0.45	1.17	97.5±0.06
	1.8	1.75	97.2±0.08	1.21	0.25	1.73	96.1±0.47
WLake water ^b	-	0.38	-	-	-	0.36	-
	0.8	1.18	97.3±0.05	5.82	0.21	1.16	95.0±0.36
	1.2	1.58	98.5±0.04	4.21	0.74	1.56	97.5±0.05
River water ^b	-	0.39	-	-	-	0.37	-
	0.6	0.99	94.0±0.52	2.62	0.12	1.17	92.3±0.03
	1.0	1.39	93.3±0.12	1.21	1.12	1.57	91.9±0.09
Spring water ^b	-	0.19	-	-	-	0.18	-
	0.6	0.79	95.5±0.07	4.23	0.53	0.58	93.3±0.12
	0.8	0.99	95.3±0.11	5.21	0.15	0.78	94.0±0.04

^an=5, ^b Collected around Tirupati area

TABLE 3: Determination of copper (II) in alloy samples

Samples	Standard Reference Sample	Amount of copper(II) found				
		Certified value	Present method	Reported method ²⁹	t-test	F-test
1.	Tin base white metal	3.50	3.49±0.08	3.47±0.12	0.03	0.58
2.	Devard's alloy	47.90	48.40±0.05	47.88±0.07	0.56	1.04
3.	BCs 180/2	67.12	68.18±0.15	67.10±0.09	0.15	0.68
4.	BA _s 106	4.08	5.14±0.08	4.01±0.18	0.07	0.17
5.	BCs 179/3	57.35	57.52±0.02	57.39±0.16	0.65	0.05
6.	Gun metal	0.78	0.29±0.08	0.23±0.05	0.02	0.41

^an = 5

ml) it serves as stock solution, the experimental solution is prepared by pipetting out 10 ml of the stock solution into the 100 ml standard flask and the solution is made up to the mark with distilled water. A known volume of this solution is placed in a 10 ml standard flask and made up to the mark and analysed was the general procedure. The results were shown in TABLE 3.

RESULT AND DISCUSSION

Effect of pH

The effect of pH on the peak height of Cu (II) at different concentrations was investigated with a fixed 0.03 M piperazine dithiocarbamate concentration. The pH of acetate buffer was changed in the range of 3.0-7.0 and the peak height wave measured for each concentration level of Cu (II). At all concentration levels of Cu (II) maximum peak height were found between 4.0 and 6.0. Therefore, a pH 5.0 ± 0.2 of acetate buffer system was chosen throughout in the study as represented graphically in figure 1.

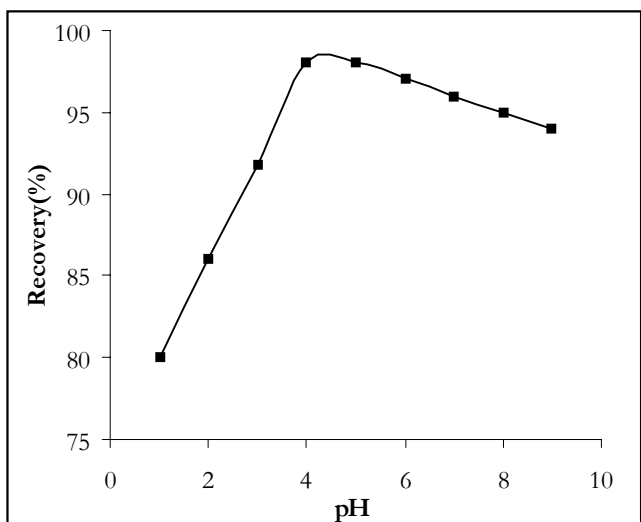


Figure 1: Effect of pH on the complexation of Cu (II) with [PTTC]

Effect of piperazine dithiocarbamate concentration

The effect of concentration of piperazine dithiocarbamate on the peak height was investigated at pH 5.0 ± 0.2 by using 2.0 and $3.5 \mu\text{l}^{-1}$ Cu (II) solutions. The concentration of piperazine dithiocarbamate was varied in the range. 0.001-0.10 M. Maximum peak

height was obtained at a concentration of 0.03 M piperazine dithiocarbamate as color developing reagent for lower concentration level of Cu (II) solution.

Efficiency of elution

The choice of selecting an eluent was a difficult problem. In addition to an eluent should not destroy the solid support in the column. Hence, for the determination of the preconcentrated Cu (II) by spectrophotometry, the elution was performed with 0.5-3.0 M HNO_3 and is dependent on the concentration of HNO_3 as solution in figure 2. Quantitatively copper (II) was achieved for 6 ml of 2 M HNO_3 . Hence, 6ml of 2 M HNO_3 was chosen the optimum eluent for the Cu(II) determination and recoveries were higher than 99%.

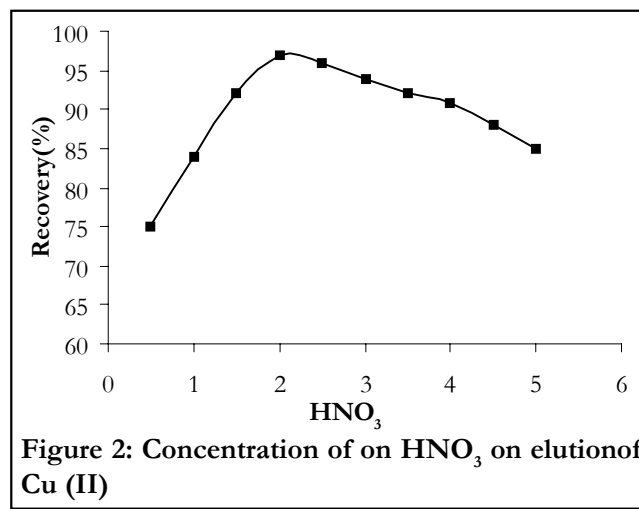


Figure 2: Concentration of on HNO_3 on elution of Cu (II)

Effect of volume of a sample on elution

The effect of the sample volume on the extraction of Cu(II) was studied by taking different volumes of water samples in the range of 100, 200, 300, 400, 500 and 600 ml. As the volume of sample increases, the recovery of metal ion increases gradually. In this case the recovery obtained was higher than 99% at 500 ml volume. However, the efficiency of recovery slightly decreases when the sample volume more than 600ml. Hence, the 500 ml of water sample was chosen for the present study.

Effect of volume of an eluent on percentage of elution of Cu(II)

The effect of volume of an eluent on elution of

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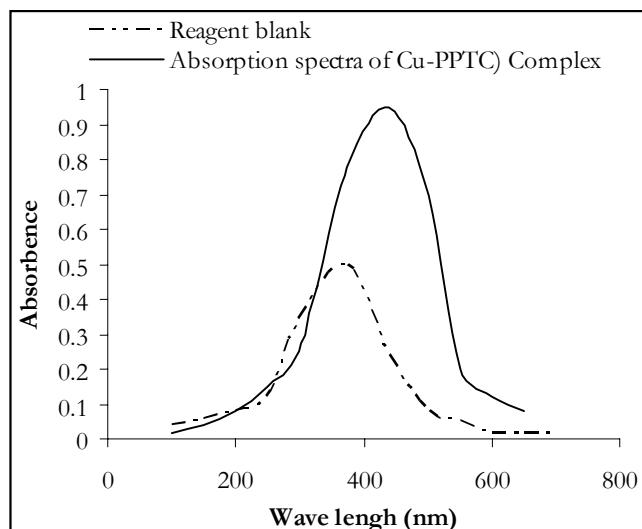


Figure 3: Absorption spectra of (Cu-PPTC) complex

Cu(II) for various water and alloy samples on 4-aminomethylpyridin-silicagel measured at 30-35°C. It can be observed that the percentage of recovery increases with the increase in the volume of eluent to some extent. After increasing the volume of an eluent, the elution percentage slightly decreases. Thus 6.0 ml of 2 M HNO₃ was chosen for 100 % recovery of Cu(II) ion.

Ringbom plot for red colored derivative

Ringbom's plot is the established standard adopted to know the optimum range of concentration for a system that obeys Beer's law. The plot is drawn between log C of Cu(II) and (1-T) (where T is the transmittance). The plot has a sigmoid shape with a linear segment at intermediate absorbance values (4.0-12.0) and concentration values (0.2-1.4 μg ml⁻¹). The slope of Ringbom plot from figure 4 is 0.5620. Hence, the ratio between the relative error in concentration and photometric error is 0.70, for a concentration of 0.9, for 0.5% photometric error.

Calibration graph

The extraction of a typical calibration is $p = 5031c + 4.93$, $r^2 = 0.9994$ (p , peak height; c , concentration). The calibration graph was obtained at the optimum working conditions; piperazine tetrathiocarbamate concentration 0.03 M, sample volume 500 ml; eluent concentration 2 M HNO₃ and volume of eluent 6.0 ml.

Effect of column performance

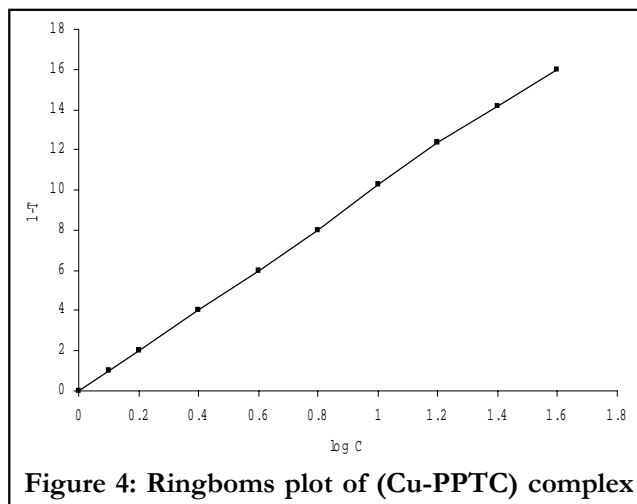


Figure 4: Ringbom plot of (Cu-PPTC) complex

In order to examine the long term stability of the support, it was subjected to successive adsorption and desorption cycles (6 runs in a day and the next 6 runs another day, and so on, total 30 runs) by 500 ml of metal solutions through the column. The stability and potential recyclables of the column containing support were assessed by monitoring the change in the recoveries of the analyte. After 15 runs, the recoveries of the analyte slightly decreased to <95 %.

Effect of foreign species

Several anions and cations were studied in detail. TABLE 4 summarizes the tolerance limits of interfering ions in the determination of 50 μg l⁻¹ Cu (II). The tolerance limits was taken as the amount causing an error of ± 2 % at the peak height.

Applications and statistical comparison of the present method with literature method

TABLE 4: Tolerance limits of foreign ions on the determination of 50 μg l⁻¹ Cu (II) ion

Tolerance limit (μg l ⁻¹)	Foreign ions
>50.000	K(I),Na(II),Ca(II),Mg(II),Cl ⁻ ,Br ⁻ , PO ₃ ³⁻ , CO ₃ ³⁻ ,SO ₄ ²⁻ , Al (III),Cr(III).
>10.000	NO ₃ ⁻ , Zn (II), Hg (II).
>5000	Pb(II), Cd(II).
>800	Fe (II), Fe (III), Mn(II) Co(II),Ni(II).

^aCan be masked up to 10.000 μg l⁻¹ by the addition of 2ml of EDTA, thiosulfate, cyanide.

^bCan be masked up to 5000 μg l⁻¹ by the addition of 2ml of 2%citrate solution.

^cCan be masked up to 800 μg l⁻¹ by the addition of 1% thiocyanate

The proposed preconcentration method for the determination of Cu(II) has been employed for water and alloy samples were presented in TABLES 2 and 3. The obtained results were compared with reported methods^[29,33] in terms of Student's 't' test and Variance ratio 'f'- test. The analytical data summarised in TABLES 2 and 3 suggest that the percentage recovery of Cu (II) from water and alloy samples range from 94.0 to 99.1 % which is more reliable and sensitive than the reported methods^[29, 33].

CONCLUSION

The proposed preconcentration spectrophotometric method is simple, highly sensitive and selective for the determination of Cu(II) in water and alloy samples. Synthesis of color forming reagent (sodium salt of piperazine dithiocarbamate) was economically feasible at ordinary laboratories and highly selective towards metal ion. The limit of detection of the proposed method is superior when compared to reported method^[29,33]. The column employed in this method is highly stable and can be regenerated several times. The efficiency of column was 99 % for 15 cycles.

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