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A SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF TRACE COPPER(II) BY ADSORPTION OF ITS3-ALLYL-1-(5-BROMO-2-PYRIDYL) THIOUREA

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ABSTRACT

Anovel, economic yet accurate spectrophotometric determination of copper (II) by adsorption of its 3-ally1-1-(5-bromo-2-pyridyl)thioureacomplex on microcrystalline naphthalene is described. First a complex was formed between copper and the reagent,3-allyl-1(5-bromo-2-pyridyl)thiourea allowed to adsorb on microcrystalline naphthalene which was dissolved in dimethylformamide. The absorbance of the solution was measured at 435 nm against the reagent blank. Beer's law is obeyed in the concentration range 08-130µg of iron (III) in 10 ml of dimethylformamide. The molar absorptivity was found to be 1.48 x 104 1 ml^{-1} cm^{-1} and sensitivity being 0.8 $x10^{-2}$µg for the absorbance of 0.001. The effect of various parameters namely pH, buffer solution, reagent concentration and naphthalene concentration have been investigated.

KEYWORDS: Thiourea, Naphthalene, absorbance, Iron(III) complex, etc

INTRODUCTION

Pyridyl substituted thioureas have selective complex forming affinity towards many metals (Mathur Et Al., 1973) and its derivatives have got wide applications as corrosion inhibitors, antiviral agent, potential pesticides and insecticides.

Many substituted thioureas have exhibited analgesic, anti-inflammatory (JL Archibald *et al*., 1986), antihypertensive (A Singh *et al.*, 1985), hypoglycemic (M Satake, 1987) activities. Derivatives of isothioureas can be used as potential growth inhibitors (D V Gordon *et al*., 1982). Another important therapeutic uses of thiourea derivatives are their antithyroid (D E Beer *et al*., 1936), anesthetic (V S Mishra *et al.*, 1974) and anticonvulsant activities (L A Ignatova *et al.*, 1985).

Apart from their biological importance, thioureas are well known for their analytical applications (B P Cohen *et al*., 1968.)

3-ally1-1-(5-bromo-2-pyridyl)thiourea, a newly synthesized reagent has been found to possess interesting analytical applicants. It forms water insoluble colored complexes with various metal ions viz. Fe (III), Cu (III), Bi (III), Ag(I), U(VI), Ni(II) and Cd(II). The presence of thioketo (>C=S) group in this reagent is responsible for the characteristic color reactions with metal ions. The iron complex is easily adsorbed on microcrystalline naphthalene and trace iron is determined photometrically.

A New method "Analysis of metals by solid liquid separation after liquid-liquid extraction" (M Satake and Y Takagi, 1977) has been employed for the determination of copper(II). 3-allyl-1-(5-bromo-2-pyridyl)thiourea)

Thiourea-copper complex was adsorbed on naphthalene in aqueous solution on vigorous shaking naphthalene is aqueous solution on vigorous shaking. The absorbed mixture of the complex and naphthalene was filtered dried and dissolved in dimethylf1ormamide.

The absorbance of the solution was measured at 435 nm and trace amount of iron was determined.

EXPERIMENTAL

Standard Copper (II) Solution

A standard stock solution (1000 ppm) of copper(II) was prepared by dissolving requisite amount of copper sulphatepentaahydrate in distilled water. A 15 ppm solution of iron (III) was prepared by diluting 15 ml of stock solution of copper sulphatewere diluted to 1000 ml with distilled water. Amount of copper (µg) present in sample solution was determined gravimetrically.

3-ally1-1-(5-bromo-2-pyridyl)thiourea Solution

A 0.2% solution of 3-ally1-1-(5-bromo-2-pyridyl)thiourea was prepared by dissolving 0.2 g of reagent in 100 ml of methanol.

Naphthalene-Acetone Solution

A 20% naphthalene solution was prepared by dissolving 20g of naphthalene in 100 ml of acetone.

Buffer Solutions

A series of buffer solutions were prepared by mixing required volumes of 1M acetic acid and 1M ammonium acetate solution for pH range 3-6 and 1M aqueous ammonia and 1M ammonium acetate solution for pH range 8-11.

All the chemicals used were of analytical reagent grade.

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Apparatus

A Toshniwal spectrophotometer (Model CL-10) was used for all absorbance measurements.

The pH measurements were made with Toshniwal pH meter (Model CL-43) equipped with glass and calomel electrodes.

Procedure

An aliquot of standard sample solutions of copper (II) containing 60-120 µg of copper was taken in dry clean, tightly stoppered Erlenmeyer flask. To it, 2.5 ml of acetate buffer solution was added to adjust the pH of the solution to6 and5 and then 3.0 ml of 0.2% 3-ally1-1-(5-chloro-2-pyridyl) thiourea solution was mixed. The contents of the flask were kept standing in hot waterbath 60^0C for 25 minutes. Then 3.0 ml of 20% naphthalene solution were added to the solution of iron (III) followed by 3.0 ml of 0.2% potassium iodide solution and shaken vigorously for 2 minutes. The copper (II) complex of 3-ally1-1-(5-chloro-2-pyridyl) thiourea and potassium iodide were adsorbed on microcrystalline naphthalene. It was filtered off, washed with water dried in oven at 60^0C. This dry solid was dissolved in dimethylformamide and diluted to 10 ml. The absorbance measurements of copper (II) complex were taken at 435 nm wavelength against the reagent blank which was prepared similarly.

RESULTS AND DISCUSSION

Absorption Spectra

A sample solution 100 µg of copper (II)2.5 ml of 0.2% 3-ally1-1-(5-chloro-2-pyridyl) thiourea solution, 3 ml of 0.2% potassium iodide solution and2.5ml of acetate buffer solution (pH6) was prepared according to the recommended procedure. The copper (II) complex, so formed was adsorbed on microcrystalline naphthalene on vigorous shaking for 3 minutes. The solid mixture of naphthalene and copper (II) complex was dissolved in dimethylformamide and absorbance of the solution was measured at wavelengths between 350–600 nm. The data of absorbance was plotted against the wavelengths and absorption spectra of copper (II) complex solution was obtained against the reagent blank. The copprer (II) complex had the maximum absorption at 435 nm wavelength whereas the reagent blank had negligible absorbance at this wavelength. Hence, all absorbance measurements were carried out at 435 nm(λ max) wavelength.

Effect of pH

The relationship between the absorbance and pH of the sample solution containing 100 µg of copper was investigated in the pH range 2.0-12.0. The results are shown in table 1. The absorbance was increased with increase of pH upto 4.0 then gave a maximum and almost constant value over the pH range 4.0-8.75 and further decreased sharply beyond pH 8.75. In the present study, the absorbance was therefore measured at pH 6

Effect of Buffer Solution

The effects of varying amounts of buffer solution on the absorbance of copper (II) complex was discussed. The results are shown in table 2. It was found that the absorbance increases slightly with the addition of 1.0-2.5 ml of buffer solution. The absorbance was almost constant only in the range 2.5-5.0 ml of buffer solution. Hence 4.0 ml of buffer solution was chosen for all absorbance measurements.

Effect of 3-allyl-1-(5-bromo-2-pyridyl) thiourea

In order to investigate the effect of reagent concentration on the absorbance of copper (II) complex solution, different amounts of reagent solutions were added to the sample solution containing 100 µg of copper (II) at pH 6.

The results are illustrated in Table 3. Absorbance increased slowly upto the addition of 2.0 ml of the reagent solution and practically remained constant in the range 2.0-4.0 ml. Above 4.0 ml of reagent solution, absorbance started decreasing gradually. Therefore 3.0 ml of 0.2% reagent solution were added for the absorbance measurements.

Effect of Naphthalene Concentration

To study the effect of naphthalene concentration on copper (II) complex of3-ally1-1-(5-bromo-2-pyridyl) thiourea, thedifferent amounts of naphthalene solution were added and then the absorption studies were carried out at 435nm. The results are shown in Table 4. It was observed that a constant maximum absorbance in the range 2.0-4.0 ml and then a decrease of absorbance beyond 4ml of naphthalene. Therefore,4.0 ml of 20% naphthalene solution was added for the complete extraction of copper (II) complex from aqueous solution.

Choice of Solvent

The solubility of copper (II) complex of 3-ally1-1-(5-bromo-2-pyridyl) thiourea and potassium iodide was examined in various solvents. The chelate was easily soluble in dimethylformamide at room temperature. Therefore, dimethylformamide was chosen as the solvent.

Precision

The precision of the method was determined with the ten sample solutions containing 100 µg of copper. The standard deviation calculated to be 0.20%.

Table 1: Effect of pH on Absorbance

pH	Absorbance 435 nm
2.0	0.223
2.5	0.316
3.0	0.421
3.5	0.486
4.0	0.542
4.5	0.548
5.0	0.549
5.5	0.542
6.0	0.541
6.5	0.545
7.0	0.547
7.5	0.546
8.0	0.545
8.5	0.549
9.0	0.542
9.5	0.548
10.0	0.522
10.5	0.473
11.0	0.467
11.5	0.382
12.0	0.336
copper (II) : 100 µg; Naphthalene : 0.6 gm;	

Table 2: Effect of Buffer Solution

Buffer Solution (ml)	Absorbance 435 nm
1.0	0.436
1.5	0.464
2.0	0.498
2.3	0.516
2.5	0.545
2.7	0.542
3.0	0.549
3.3	0.543
3.5	0.544
3.7	0.547
4.0	0.539
4.5	0.542
5.0	0.526
5.5	0.468
6.0	0.375
6.5	0.367
7.0	0.316
Copper(II) : 100 µg; pH : 4.5; Naphthalene : 0.6 gm	

Table 3: Effect of Reagent Concentration

0.2% reagent (ml)	Absorbance 475 nm
0.0	0.324
0.5	0.427
1.0	0.492
1.5	0.543
2.0	0.549
2.5	0.545
3.0	0.541
3.5	0.486
4.0	0.457
4.3	0.452
4.5	0.379
5.0	0.336
5.3	0.315
5.5	0.288
6.0	0.234
copper (II) : 100 µg; pH : 4.5; Naphthalene : 0.6 gm	

Table 4: Effect of Naphthalene concentration

20% Naphthalene (ml)	Absorbance 435 nm
0.5	0.465
1.0	0.514
1.5	0.532
2.0	0.543
2.5	0.549
2.7	0.547
3.0	0.545
3.2	0.543
3.5	0.547
3.7	0.548
4.0	0.549
4.3	0.544
4.5	0.541
4.8	0.538
5.0	0.528
5.3	0.514
5.5	0.493
6.0	0.475
copper (II) : 100 µg; pH : 4.5; Naphthalene : 0.6 gm	

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