SPECTROPHOTOMETRIC DETERMINATION OF COBALT (II) BY ADSORPTION OF ITS N-p-BROMOPHENYL THIOBENZOHYDROXAMIC ACID COMPLEX ON MICRO CRYSTALLINE NAPHTHALENE

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ABSTRACT

The spectrophotometric determination of trace cobalt (II) after precipitation of its complex with N-p-Bromophenyl Thiobenzohydroxamic Acid (BPTBHA) is described. It is based on the formation of the complex of cobalt (II) with BPTBHA and adsorption of the complex with microcrystalline naphthalene, dissolution of the naphthalene mixture in DMF and the determination of cobalt (II) by absorbance measurement at 440nm. Its absorption obeyed Beer's law over the concentration range 5-70 µg of cobalt (II) in 10 ml. of DMF.

The molar absorptivity was found to be 6.8x104L. mole^{-1} cm^{-1} and the sensitivity being 0.01 µg cm^{-2} of cobalt (II) for the absorbance of 0.001.

Key Words – N-p-Bromophenyl Thiobenzohydroxamic Acid (BPTBHA), Cobalt (II), Absorptivity, Absorbance, Beer's law, DMF

INTRODUCTION

Hydroxamic acids and their thioanalogues have extensive applications as a spectrophotometric and gravimetric reagent for a large number of metal ions[1-6]. In present investigation, a new more sensitive and selective organic reagent viz. N-p-bromophenyl thiobenzohydroxamic acid has been selected as a complexing agent for the determination of Co (II) by photometric method. The reagent with Cobalt (II) form a water insoluble complex. The complexation between thiohydroxamic acid and metal ions is attributed to the availability of the -N-OH and > C=S groups.

The usual liquid-liquid extraction method can not be used directly for the extraction of metal ions that form complexes with the complexing reagent at a high temperature. This difficulty can be avoided with the method of solid-liquid separation after liquid-liquid extraction developed by Fujinaga and co-workers using naphthalene as an extractant[7]. This method has many advantages over the usual liquid-liquid extraction[8-9]. In order to over come drawbacks of liquid-liquid extraction method a different method i.e. solid-liquid separation after adsorption of metal chelate on microcrystalline naphthalene was developed[10-15]. This method is very convenient and less time consuming.

EXPERIMENTAL

Standard cobalt (II) solution

A standard stock solution of cobalt (II) was prepared by dissolving requisite amount of cobalt nitrate hexa hydrate in distilled water and volume was made to one litre. Stock solution was further diluted as required.

A 0.2% solution of BPTBHA was prepared by dissolving 0.2 gm. of reagent in 100 ml. of ethanol.

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

Buffer solutions having different pH values were prepared. To prepare buffer solution of pH range 3-6, 1 M acetic acid and 1 M ammonium acetate solution were mixed. Buffer solutions of pH range 8-11 were prepared by mixing 1 M aqueous ammonia and ammonium acetate solution.

All chemicals used were of spectrograde quality.

Apparatus

A spectrophotometer Ec model (Gs-5701) was used for all absorbance measurements and the pH measurements were taken with Toshniwal pH meter model (CL-43) equipped with glass and calomel electrodes.

Procedure

An aliquot of standard solution of Cobalt (II) containing 50 µg of cobalt were taken into a tightly stoppered and clean, dry Erlenmeyer flask and diluted to 40 ml. with distilled water. The pH of the solution was adjusted to 3.0 by adding 2.0 ml. of acetate buffer solution and to it 2.5 ml. of 0.2% solution of BPTBHA was added.

Contents were heated on water bath at 55°C for 35 minutes. Then 2.5 ml. of 20% naphthalene solution were mixed with vigorous shaking for 200 seconds. The cobalt (II) complex on BPTBHA was adsorbed on microcrystalline naphthalene. The solid complex was filtered off through whatman-42 filter paper washed with water and dried in oven at 60°C. It was then dissolved in 10 ml. DMF. The absorbance measurements of solution of cobalt (II) complex were determined at 440 mm wave length against the reagent blank which was obtained in the similar manner.

RESULTS AND DISCUSSIONS:

Absorption spectra

A sample solution containing 45 µg of cobalt (II), 2.5 ml. of 0.2% solution of BPTBHA and 2.0 ml. of acetate buffer solution (pH=3.0) were treated according to the recommended procedure. The cobalt (II) complex so formed was adsorbed on micro crystalline naphthalene on vigorous shaking for 200 seconds. The solid mixture of naphthalene and complex was dissolved in DMF and the absorbance of the solution was measured at the wave length between 380-650 mm. The absorption spectra of cobalt (II) complex with BPTBHA and of reagent blank at varied wave length. It was observed that cobalt (II) complex had the maximum absorption at 440 mm wave length, where as reagent blank and negligible absorption through out the range of wave length. Therefore, all the absorbance measurements were carried out at 440 mm wave length (λ_{max}).

Effect of BPTBHA concentration

The effect of varied concentration of BPTBHA, on the absorbance of cobalt (II) complex was investigated by adding different quantities of reagent solution to the solution containing 45 µg of cobalt at pH 3.0. The absorption of cobalt (II) complex increased up to 2.0 ml. of BPTEHA solution and almost constant in the range 2.0-4.0 ml. of reagent solution. Hence 2.5 ml. of 0.2% BPTBHA solution were added for all the absorbance measurements.

Effect of digestion time

The effect of digestion time on the absorbance was studied. For this purpose 2.5 ml. of 0.2% BPTBHA (pH 3.0) were added to the sample solution containing 45 mg of cobalt. This mixture was heated on water bath at 55 - 60 °C for different period of time in the range of 5-60 minutes. Then, the absorbance of the cobalt (II) complex solution in DMF was determined according to the procedure. The absorbance increased up to 20 minutes digestion time further no significant change in absorbance was noticed in the range 20-40 minutes digestion time. Hence, 35 minutes digestion time was chosen for the absorbance measurements.

Effect of naphthalene concentration

Different volumes of naphthalene solution were added to the aqueous solution containing cobalt (II) complex of BPTBHA and the absorbance measurements were taken at 440 nm wave length to study the effect of naphthalene concentration on the absorbance. Absorbance increased with the increasing amount of naphthalene solution up to 2.0 ml. and became maximum and almost constant in the range 2.0-5.0 ml. of naphthalene solution. Above 5.0 ml, the absorbance decreased sharply. Therefore, 2.5 ml. of 20% naphthalene solution were added to the aqueous solution containing cobalt (II) complex and the absorbance was measured according to the recommended procedure.

Effect of Diverse ions

Alkali metal salts and metal ions were added individually to the solution containing 45 µg of cobalt and their effect on the absorption of cobalt (II) complex with BPTBHA was examined. Both the categories alkali metal salts and metal ions did not interfere seriously.

Calibration curve of Cobalt (II)

With the optimum condition describe above the calibration curve for cobalt (II) determination was established at the wave length 440 nm. Bear's law was obeyed over the

concentration range 5 - 70 µg of cobalt in 10 ml. of DMF. The molar absorptivity was found to be $6.8x10^4 Lmol^{-1}cm^{-1}$ at 440 nm and sensitivity was calculated as 0.01 µg cm^{-2} of cobalt for the absorbance of 0.001.

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