



## EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF Co (II) USING 4-HYDROXY ACETOPHENONE THIOSEMICARBAZONE

R. S. LOKHANDE\*, MADHAVI JADHAV and SHEETAL DAPALE

Department of Chemistry, University of Mumbai, Vidyanagari, Kalina, Santacruz (E), MUMBAI – 400 098, (M. S.) INDIA

### ABSTRACT

Spectrophotometric method has been developed for the determination of cobalt (II) using 4-hydroxy acetophenone thiosemicarbazone (HATSC) as an analytical reagent. The reagent reacts with Co (II) giving a yellow coloured complex which can be quantitatively extracted into n-butanol at pH 9.6. Beer's law is obeyed giving a linear and reproduction graph under optimum conditions. The molar absorptivity is found to be  $0.52 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$  and Sandell sensitivity is  $0.88 \times 10^{-5} \mu\text{g cm}^{-2}$ . The stoichiometric ratio of the complex was found out to be 1 : 2. The effect of diverse ions has been studied. The method developed has been applied for the determination of cobalt in real and synthetic samples.

**Key words :** 4-Hydroxy acetophenone, thiosemicarbazone, cobalt (II), spectrophotometric.

### INTRODUCTION

Since the discovery of antitubercular activity of thiosemicarbazones by Domagk<sup>1</sup>, studies on their pharmacology have acquired a great deal of interest. A few of these derivatives have been systematically investigated and the possibilities of their chelation with metal ions in relation to their antitumor and microbiological activity has been suggested<sup>2, 3</sup>.

Thiosemicarbazones act as monodentate, bidentate or multidentate complexing agents that produce coloured complexes, which are used in the selective and sensitive determination of metal ions. Literature survey reveals that a number of thiosemicarbazone derivatives have been used for the extraction and spectrophotometric determination of cobalt (II)<sup>4-7</sup>. There appears to be a scope for the proposed method giving good sensitivity and accuracy.

### EXPERIMENTAL

The stock solution of cobalt sulphate was prepared and standardized<sup>8</sup> and working solution of lower concentration was obtained by suitable dilution. The absorbance measurements were carried out on a Shimadzu UV visible 2100 spectrophotometer with 1 cm quartz cells, and the pH measurements were carried out using appropriate buffer solution with ELICO Li 120 pH meter.

**Procedure:** The extraction experiments were performed by shaking the appropriate organic and aqueous solutions at O/A phase ratio of 1. The reagent HATSC formed a yellow coloured complex with cobalt (II) which was transferred in a separating funnel. It was extracted into n-butanol ( $2 \times 5$  mL) and was transferred to 10 mL volumetric flask with some amount of sodium sulphate in order to absorb trace amounts of water. The amount of cobalt present in the organic phase was determined quantitatively by spectrophotometric method by taking absorbance at 400 nm and that in the aqueous phase was determined by known method.

## RESULTS AND DISCUSSION

The extraction of Co (II) from an aqueous phase by HATSC in n-butanol is studied over a wide range of experimental conditions. The results of various studies are discussed below–

### Extraction as a function of pH

In order to obtain the optimum extraction condition for cobalt, the extraction was carried out at various pH (2.0–10.0) keeping the organic to aqueous volume ratio of 1 : 1. The extraction was found to be quantitative at pH 9.6 and hence, pH 9.6 was selected for further studies.

### Absorption spectrum

The absorption spectrum of Co (II) : HATSC in n – butanol shows an intense absorption peak at 400 nm. The absorption due to the reagent is negligible at this wavelength and hence, the absorption measurements were taken at this wavelength using a reagent blank.

### Effect of solvent

The suitability of various solvents was investigated using organic solvents such as chloroform, carbon tetrachloride, ethyl acetate, n – butanol, diethyl ether, methyl isobutyl ketone, ethyl methyl ketone, hexane etc. The extraction of cobalt with HATSC was found to be quantitative when both were dissolved in aqueous solution containing n – butanol as the solvent. Therefore, n – butanol was used as the solvent as it gave better and quick phase separation.

### Effect of salting out agents

The presence of 0.5 M salts of alkali and alkaline earth metals do not show any improvement in the percentage extraction of cobalt between n – butanol and aqueous phase. Hence, these salts have not been added in the aqueous phase before extraction for subsequent studies.

### Effect of reagent

The effect of variation in concentration of HATSC shows that 1.0 mL of 1% ethanolic solution of HATSC is sufficient for colour development and extraction of 1.0 mL of 0.2 mg/mL of cobalt solution. (Fig. 1).

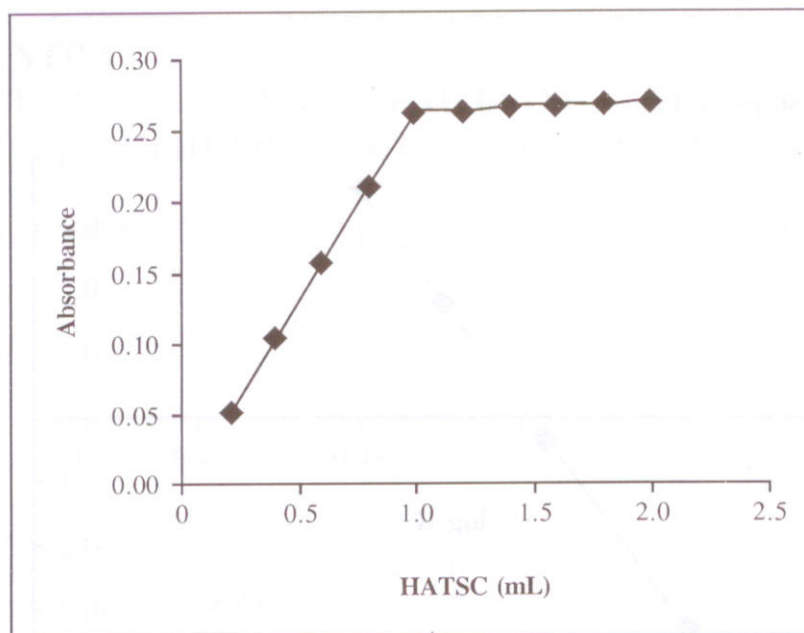


Figure 1. Effect of reagent concentration of Co (II)

#### Effect of equilibrium time

The study of change in absorbance with variation in equilibration time for the extraction of cobalt shows that equilibration time of 1 minute is sufficient for the quantitative extraction of Co (II).

#### Stability of the complex with time

The stability of the colour of the extracted species with time shows that the absorbance of the extracted species is stable upto 48.0 hrs. Throughout the experiment, for the reason of practical convenience, the absorbance measurements have been carried out within one hour of the extraction of cobalt.

#### Beer's law and sensitivity

Calibration graph for cobalt was constructed under optimum conditions. The graph obeys Beer's law in the range of 2–60  $\mu\text{g}$  for cobalt. The molar absorptivity and Sandell sensitivity are found out to be  $0.52 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $0.88 \times 10^{-5} \mu\text{g cm}^{-2}$ .

#### Nature of extracted species

The composition of the extracted species has been determined from Job's continuous variation method, slope ratio method and mole ratio method. These methods show that the composition of the Cobalt (II) : HATSC complex is 1 : 2 (Fig. 2).



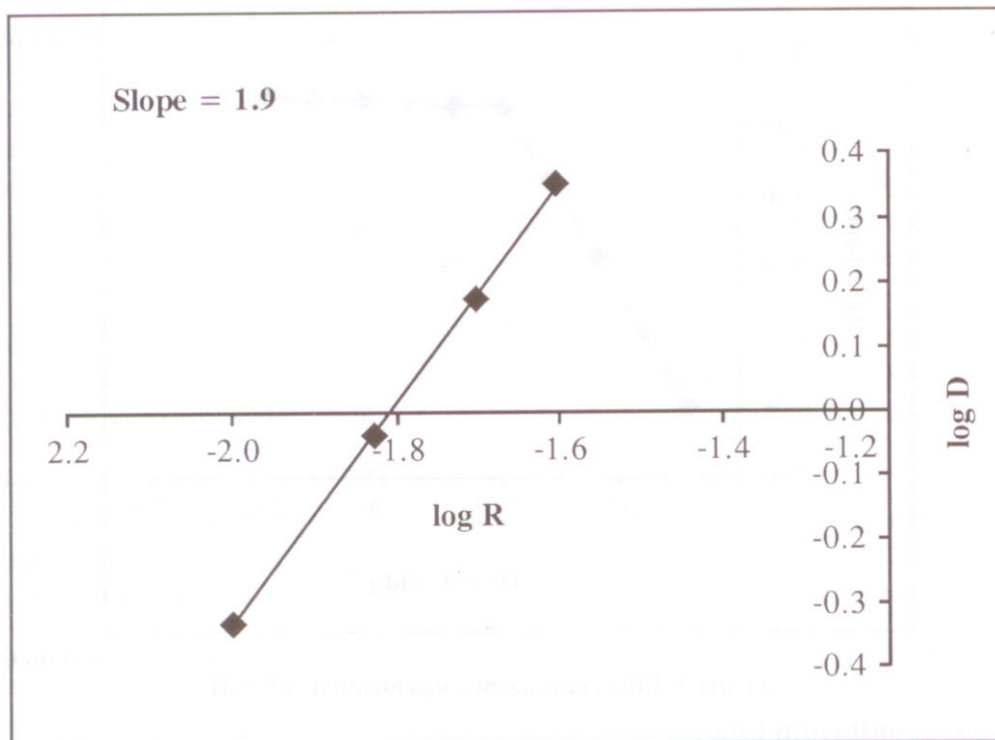


Figure 2. Stoichiometric ratio of metal to reagent complex of Co (II) with HATSC in *n*-butanol from aqueous media

### Influence of diverse ions

The effect of foreign ions like  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Ba}^{+2}$ ,  $\text{Sr}^{+2}$ ,  $\text{Al}^{+3}$ ,  $\text{Be}^{+2}$ ,  $\text{Pb}^{+2}$ ,  $\text{Hg}^{+2}$ ,  $\text{As}^{+2}$ ,  $\text{V}^{+5}$ ,  $\text{W}^{+6}$  present in various amounts do not interfere in the spectrophotometric determination of 30  $\mu\text{g}$  of cobalt. The ions which show interference in the spectrophotometric determination of cobalt were overcome by using appropriate masking agents.

### Precision and accuracy

The precision and accuracy of the spectrophotometric method has been studied by analyzing five solutions each containing 30  $\mu\text{g}$  of cobalt.

### Applications

Various commercial samples and synthetic mixtures containing Co (II) were analysed according to the recommended procedure and the results were compared with those obtained by standard method. The results obtained are shown in Table 1 and Table 2.

**Table 1 . Separation of Co (II) with HATSC from various binary mixtures**

Binary mixture metal taken (ppm)	Cobalt found	
	Std. method	Present method
(a) Co (5), V (5)	5.01	0
(b) Co (5), Cr (5)	4.99	8
(c) Co (6), Zr (5)	6.02	1
(d) Co (5), Mo (5)	5.01	0

\*Average of three determinations

**Table 2. Determination of Co (II) from real samples**

Sample	Certified value	Present method	Std. method
Surbex – T tablet (Abbot)	0.326	0.320	0.319
High Speed Steel 3082	9.64	9.63	9.64
Vitamin B <sub>12</sub> Injection	50	48	49

\*Average of three determinations

## CONCLUSION

The results obtained indicate that the reagent HATSC in n – butanol can be effectively used for the quantitative extraction of Co (II) from aqueous media. The equilibrium time required is very less i.e. only minute and the complex is stable for 48.0 hrs. The proposed method is simple, rapid, precise and reproducible. The results obtained by the proposed method are found to be in good agreement with those obtained by standard method.

## REFERENCES

1. G. Domagk, R. Behnish, F. Mietzsch and H. Schmidt, *Naturwissenschaften*, **33**, 315 (1946).
2. L. A. Saryan, K. Mailer, C. Krishnamurti, W. Antholine and D. H. Petering, *Biochem. Pharmacol.*, **30**, 595 (1981).
3. S. Jayasree and K. K. Aravindakshan, *Polyhedron*, **12**, 1187 (1993).
4. A. J. L. Gomez, J. M. Camoparon, and F. Pinoperez., *Talanta*, **23**, 460 (1976).
5. G. V. R. Murthy and J. S. Reddy, *Chim. Acta. Truc.*, **17**, 189 (1989).
6. R. S. Lokhande, N. Srinivasan and A. B. Chaudhary, *J. Ind. Coun. Chem.*, **19**, 12 (2002).

7. S. L. Sharma, R. J. Kumar, C. Jaya and V. A. Reddy, *Anal. Lett.*, **36**, 605 (2003).
8. A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis", 3<sup>rd</sup> Edition, Longman Green and Co. Ltd., London (1975).

Accepted : 1.11.2004