

Development of Extractive Spectrophotometric Determination of Cobalt (II) with [N - (O - Hydroxy Benzylidene) Pyridine - 2 - Amine]

Ritika M. Makhijani, V. D. Barhate

V.E. S. College of Arts, Science and Commerce, Sindhi Society, Chembur, Mumbai - 400071

Abstract- A simple, rapid and sensitive spectrophotometric method has been developed for the determination of Co (II) by using N - (o - hydroxy benzylidene) pyridine - 2 - amine (NOHBPA) as an analytical reagent. NOHBPA has been synthesized and characterized by elemental and spectral analysis. NOHBPA extracts Co (II) quantitatively (99.78%) into ethylacetate an aqueous solution of pH range 8.5 – 9.5. The ethylacetate extract shows an intense peak at 520 nm (λ max). Beer's law is obeyed over the Co (II) concentration range of 0.1 - 10 $\mu\text{g/ml}$. The sandell's sensitivity and molar absorptivity for Co - NOHBPA system is 0.007142 μgcm^{-2} and 8250.82 L mole $^{-1}\text{cm}^{-1}$ respectively. The composition of extracted species is found to be 1:2 (Co: NOHBPA) by Job's Continuous Variation and Mole Ratio Method. Interference by various ions has been studied. The proposed method has been successfully applied for determination of Co (II) in Pharmaceutical samples.

Index Terms- Extractive Spectrophotometry, Cobalt (II), N - (o - hydroxy benzylidene) pyridine -2- amine (NOHBPA).

I. INTRODUCTION

Cobalt is one of the most important seven trace elements essential for biological system. It is a constituent of vitamin B₁₂. It plays a very important role in animal nutrition. Animals suffering from cobalt deficiency usually show marked improvement in appetite and other conditions within 3-7 days after cobalt is supplied. It is obvious that the study of the role of cobalt in trace quantities in various matrices is very much dependent on rapid and selective method of its separation from other elements and its determination in trace quantities^[1-2]

A solvent extraction is becoming important separation technique in chemistry. For the determination of cobalt at trace level solvent extraction coupled with spectrophotometry provides a good selective method^[3-5].

Many reagents have been used widely for the extractive spectrophotometric determination of cobalt^[6-8].

In present communication [N - (o - hydroxy benzylidene) pyridine - 2- amine] (NOHBPA) has been found to be a sensitive reagent for the extractive spectrophotometric determination of cobalt in pharmaceutical sample and high speed steel alloy.

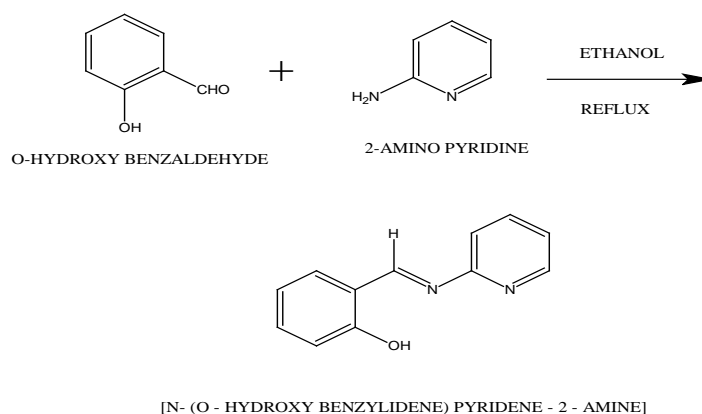
EXPERIMENTAL

ELICO - SL 159 spectrophotometer with optically matched quartz or glass cells of 1cm path length was used for

absorbance measurement. An ELICO LI 127 pH meter was employed for pH measurements.

General procedure for preparation of [N - (o - hydroxy benzylidene) pyridine - 2 - amine] (NOHBPA)

The reagent NOHBPA was synthesized by refluxing equimolar amount of ethanolic solution of o - hydroxy benzaldehyde with 2 - amino pyridine for 6 hours. On cooling the reaction mixture, a sharp yellow crystal product separated out (yield 80%, m.p.70⁰-71⁰C) which was collected by filtration. The resulting NOHBPA was recrystallised using aqueous ethanol as the procedure recommended by Vogel^[9].



Procedure for preparation of Cobalt stock solution

A stock solution of Co (II) was prepared by dissolving accurately weighed amount of cobalt sulphate in double distilled water containing sulphuric acid and it was standardized by Nitroso Salt method^[10]. Working solutions of Co (II) were made by diluting the stock solution to an appropriate volume. All other reagents used were of AR grade and all the solutions were prepared in doubly distilled water.

Spectrophotometric Determination of Co (II) To an aliquot of aqueous solution containing 1.0 -100.0 μg of Co (II), 2ml of buffer solution (0.1 M disodium hydrogen phosphate) of pH 9.2 and 1ml of 2% solution of NOHBPA prepared in DMF were added. The volume of solution was made up to 10 ml with distilled water followed by heating on boiling water bath for 10 minutes. The solution was first cooled at room temperature and then equilibrated for 1 minute with 10 ml of ethyl acetate and the phases were allowed to separate. The ethyl acetate extract was collected in a 10 ml measuring flask and made up to mark with ethyl acetate, if necessary. The absorbance of ethyl acetate

extract was measured at 520 nm against a reagent blank prepared under identical conditions. The measured absorbance was used to compute the amount of Co (II) present in the sample solution from predetermined calibration curve. To study the effect of other ions, the respective foreign ions were added to aqueous phase before the extraction and adjustment of pH.

Determination of Co (II) in pharmaceutical sample

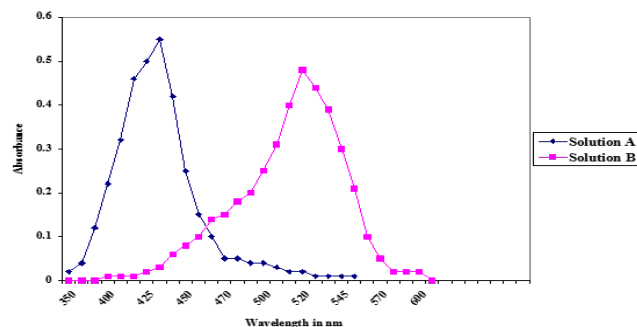
0.5g of pharmaceutical sample of was dissolved in boiling with 10 ml of aquaregia. The solution was evaporated to dryness and the residue was dissolved in 10 ml of 1MHCl filter, if required and solution was diluted to 100ml with doubly distilled water. To an aliquot of this solution 1ml was analyzed for Co (II) by the procedure as described earlier.

Determination of Co (II) in High-speed steel alloy

Sample of high speed alloy (0.1-1.0 g) was dissolved by boiling with aquaregia (10 ml). The solution was evaporated to dryness and the residue was dissolved in 1MHCl (5 ml) and resulting solution was diluted to 100 ml. An aliquot of this solution was treated with 2 ml of 0.5 M sodium tartarate solutions to mask Cr (III) and 2 ml of 0.5 M sodium citrate to mask Fe (III). The aliquot of this solution(1ml) was analyzed for Co (II) by the procedure as described earlier.

RESULTS AND DISCUSSION

Co (II) could be extracted quantitatively (99.78%) by NOHBPA into ethylacetate from an aqueous solution of pH 8.5 to 9.5 in the presence of 2ml of buffer solution (0.1 M disodium hydrogen phosphate) of pH 9.2 and 1 ml of 2 % solution of NOHBPA prepared in DMF. Solvents used for extraction of Co (II) can be arranged on the basis of their extraction coefficient values as ethyl acetate > n-amyl alcohol > toluene > chloroform > carbon tetrachloride > xylene > benzyl alcohol > n-butanol > nitrobenzene. Ethyl acetate was found to be the best extracting solvent (99.78%) hence; it was selected for the extraction throughout the work. The ethyl acetate extract of Co - NOHBPA complex showed an intense peak at 520 nm [Fig - 1]. The absorbance due to the reagent is negligible at this wavelength, so the absorption measurements were taken at this wavelength. The result shows that the system confirmed to Beer’s law at this wavelength over a Co (II) concentration range of 0.1 - 10.0 µg/ml [Fig -2]. The molar absorptivity of the extracted complex on the basis of Co (II) content was calculated to be 8250.82 L mole⁻¹ cm⁻¹. It was found that 1ml of 2% solution of NOHBPA prepared in DMF was sufficient to extract 100 µg of Co (II). The colour of the ethyl acetate extract was found to be stable at least 24 hrs. at room temperature.



Solution A: Absorbance spectra of NOHBPA
Solution B: Absorbance spectra of Co -NOHBPA complex
Fig – I ABSORTION CURVE

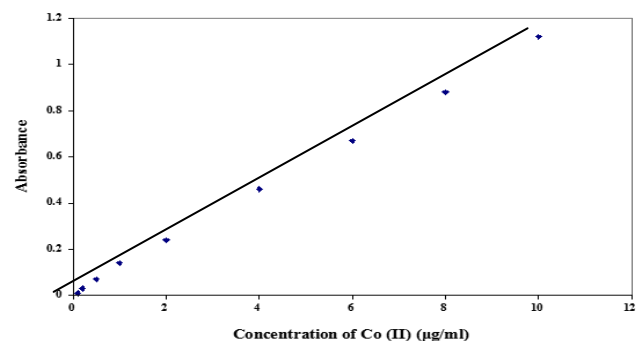


Fig - II Calibration Curve for Co (II)

Effect of Other Ions

Co (II) (40 µg) was determined in the presence of various ions. The following ions in the amount indicated, did not interfere in the spectrophotometric determination of Co (II) (40 µg): 10 mg each of Mg(II), Ca(II), V(V), Ni(II), Cu(II), Co(II), Zn(II), Mo(VI), Ce(IV), Be(II), Ba(II), Bi(III), Li(I), Zr(IV), Pd(II), Pt(IV), Ce(IV), Sn(III), Th(IV), W(VI) and 1mg of Cr(III); 20 mg each of chloride, bromide, iodide, fluoride, chlorate, bromate, iodate, carbonate, sulphate, thiocyanate, phosphates, acetate, citrate, persulphate and thiosulphate and 1mg of oxalate. Interference by the various ions were removed by using appropriate masking agent hich

TABLE 1 : Masking Agents.

Interfering ion	Amount added in mg	Masking Agent 2ml of 0.5 molar solution
Hg(II)	10	Potassium Iodide
Ag(I), Ru(III) and Rh(III)	10	Thiourea
Pb(II)	10	Sodium thiosulphate
Mn(II)	10	Thiocyanate
EDTA	10	Copper sulphate

Cd(II),	10	Potassium Iodide
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Composition of the Extracted Complex

The composition of the extracted complex was found to be 1:2 (Co : NOHBPA) by Job's continuous variation [Fig - III] and Mole ratio methods. [Fig - IV]

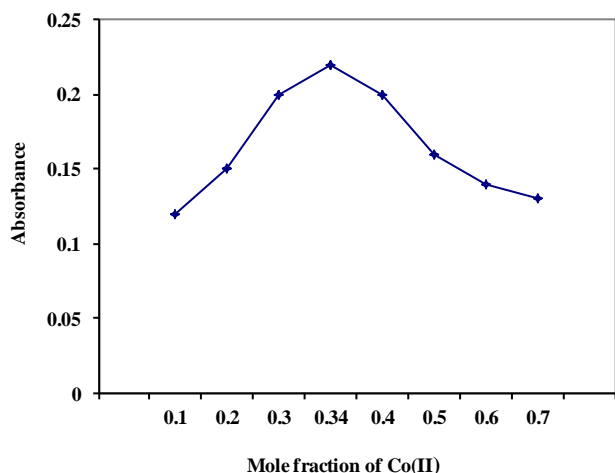
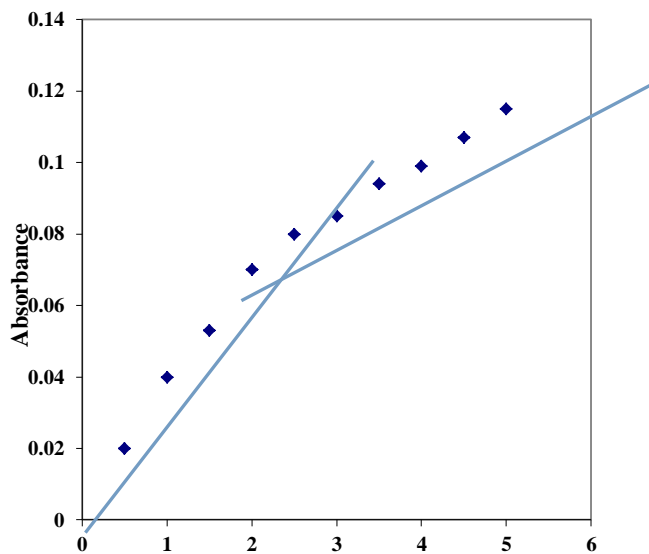


Fig III Job's Continuous Variation Method



Mole ratio [NOHBPA] / Co (II)

Fig IV Mole ratio Method

Precision, Accuracy, Sensitivity and Applications of Method

The precision and accuracy of the method were tested by analyzing the solution containing a known amount of Co (II) following the recommended procedure. The average of 10 determination of 10 µg of Co (II) in 10 cm³ solutions was 10.05

µg, which is varied between 10.318 and 9.7682 at 95% confidence limit. Standard deviation and Sandell's sensitivity of the extracted species is found to be ±0.1361 and 0.007142µgcm⁻² respectively.

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The proposed method has been applied for the determination of Co (II) in pharmaceutical samples.

The results of the analysis of the samples were comparable with those obtained by the standard method¹⁰ for Co (II)

Commercial Samples	Cobalt(II) found *	
	Present method % / (µg)	Reported value % / (µg)
Pharmaceutical (Becosules capsule)	14.55	14.61
High-speed alloy	46.134 %	46.182 %

Table - II. Determination of Co (II) in High speed alloy and Pharmaceutical Samples

*Average of three determinations

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AUTHORS



First Author – Ritika M. Makhijani, She has passed B.Sc. & M.Sc. in the year April 1987 & May 1989 respectively from Mumbai University. She has been awarded his Ph.D. in 2014 from Mumbai University. She is associate professor in VES College of Arts, Science & Commerce.. She has published 6 research papers in reputed research journals. She has also completed one research projects funded by Mumbai University .



Second Author – V. D. Barhate : He has passed B.Sc. & M.Sc. in the year April 1982 & May 1984 respectively from Nagpur University. He has been awarded his Ph.D. in 1988 from Institute of Science, Mumbai University. He is associate professor in VES College of Arts, Science & Commerce. He is recognized Ph.D. guide. He has guided 8 Ph.D. students & 9 M.Sc. students. He has published 60 research papers in reputed research journals. He has also completed two research projects funded by Mumbai University & UGC respectively.