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2-HYDROXY-1-NAPHTHALIDENE-SALICYLOYLHYDRAZONE AS AN ANALYTICAL REAGENT FOR EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF A BIOLOGICALLY AND INDUSTRIALLY IMPORTANT METAL COBALT (II)

SWAPNIL G. PRABHULKAR and R. M. PATIL*

Department of Chemistry, The Institute of Science, 15, Madam Cama Road,
MUMBAI – 400 032 (M. S.) INDIA.

ABSTRACT

2-Hydroxy-1-naphthalidene-salicyloylhydrazone (HNSH) was used as an analytical reagent for the extractive spectrophotometric determination of cobalt (II). The optimum extraction conditions were evaluated by studying parameters like pH, time, solvent, reagent concentration and stability of complex etc. 2-Hydroxy-1-naphthalidene-salicyloylhydrazone gave a golden yellow coloured complex with Co (II) and quantitatively extracted into iso-butyl methyl ketone in the pH range of 8.0 to 9.0. The absorption spectrum of Co-HNSH shows maxima at 430 nm and obeys Beer's law in the range of 0.0 to 10.0 ppm. The molar absorptivity and Sandell's Sensitivity were 1.616×10^3 L mol^{-1} cm^{-1} and 0.036 µg mL^{-1} cm^{-2}, respectively. The composition of Co (II)-HNSH was determined by Job's continuous variation method and confirmed by mole ratio method. The standard deviation and variation from mean at 95% confidence limit were 0.15 and ± 0.107, respectively. The effects of diverse ions have been studied. The proposed method is rapid, sensitive and precise. It has been applied for the determination of cobalt in synthetic and real samples.

Key words: Aroyl hydrazones, Cobalt metal, Extractive spectrophotometry, Solvent extraction, 2-Hydroxy-1-naphthalidene-salicyloylhydrazone.

INTRODUCTION

Cobalt has many applications at the biological and industrial level[1]. Its spectacular and remarkable properties enforce it to be used in various fields. The most common use of cobalt in metallic form is in the magnetic alloy, high duty steel alloy, super alloy and high speed steels. Cobalt is an essential metal for the nutrition in living organisms. The

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* Author for correspondence; E-mail: sapu9@rediffmail.com, rmpatil_2006@yahoo.co.in.

incorporation of cobalt into vitamin B_{12} molecule enables it to perform the essential functions of our body. The active isotope ^{60}Co is obtained by neutron irradiation of natural cobalt in a nuclear reactor, consisting entirely of ^{59}Co. In the medical field, ^{60}Co sources are used for radiation therapy of malignant tumors. ^{59}Co in metallic form is used as a radioactive tracer in many fields, e.g. in biology for plant and animal nutrition studies and in engineering for the study of metallic wear. ^{57}Co is used in Mossbaur's spectroscopy as γ-ray source. According to some authorities, certain cancerous diseases are related to the increased amount of some elements in the organism, Co is one of them. It has been reported that Co-deficiency causes loss of appetite and thriftness. The inhalation of anhydrous Co (II)-acetate causes nausea, vomiting, colic pain and corrosion of mucous membrane of mouth and pharynx. Although it is not considered as toxic as most of the heavy metals, it has been found to cause paralysis of extremities and death. Prolonged exposure to fine Co-dust may produce allergic sensitization and chronic bronchitis. Irritation of cornea may also be caused by cobalt. It has been shown to have toxic effects on the thyroid function. Various reagents have been reported for spectrophotometric determination of cobalt[2,3]. However, these methods have their own limitations such as required longer equilibration time, required excess reagent. In this paper, 2-Hydroxy-1-naphthalidene-salicyloylhydrazone (HNSH) is proposed as analytical reagent for extractive spectrophotometric determination of cobalt (II).

EXPERIMENTAL

A Testronix 511 digital pH-meter was employed for the pH measurements while absorbance measurements were carried out on Elico SL-150 digital UV-Visible Spectrophotometer.

A stock solution of cobalt (II) (5000 μg/cm^3) was prepared by dissolving calculated amount of $CoSO_4.7H_2O$ in deionized distilled water containing 2 cm^3 of conc. H_2SO_4. The solution was then diluted to 250 cm^3 with deionized distilled water and standardized by known method[4]. Dilute solutions were prepared from this stock solution as required. The reagent HNSH was synthesized by the procedure reported in the literature by the reflux heating reaction of 2-hydroxy bezoylhydrazide and 2-hydroxy-1-naphthaldehyde in presence of ethyl alcohol with constant stirring in rotamantle[5]. The 0.025 per cent of reagent solution in DMF was used for all extraction studies.

Development of the method

To an aliquot of Co (II) solution, was added 1 cm^3 of 0.025 per cent solution of

HNSH in DMF, followed by 2 cm^3 of buffer to adjust the pH to 8.5. The volume was made to 10 cm^3 with deionized distilled water and equilibrated with 10 cm^3 of iso-butyl methyl ketone for 30 s. The golden-yellow coloured organic phase was separated and anhydrous sodium sulphate was added to remove traces of water. The absorbance of the organic phase was measured against a similarly prepared reagent blank at 430 nm. The amount of cobalt present was computed from the standard calibration curve.

Effect of diverse ions

Cobalt (II) could be extracted in the presence of large number of foreign ions. Under the optimum experimental conditions, the effect of diverse ions on the extraction of cobalt (II) (10 μg) was investigated. The solutions of diverse ions, required for interference studies, were prepared by dissolving their commonly available chemically pure salts in deionized distilled water or in dilute acids to give ≤ 10 mg/cm^3 conc. of the cations and ≤ 20 mg/cm^3 concentration of the anions.

Determination of cobalt in synthetic mixtures

The usefulness of the method developed was demonstrated by determination of cobalt in various synthetic mixtures of associated elements (Table 1 A). The results obtained were in good agreement with those obtained by known technique.

Table 1. Determination of cobalt in various synthetic and real samples

Sr. No.	Names of Samples	Amount found*	Certified value
A	**Synthetic mixtures[b]**		
1	Co (10) + Fe (50) + Hg (50)	9.8	-
2	Co (10) + Mg (100)	9.9	-
3	Co (10) + U (50)	9.9	-
B	**Standard samples**		
1	Eldervit (Injection)	105.2	105.7
2	Bexfort (Tablet)	36.0	36.0

[b] Values in parentheses are in μg.
* Average of the three determinations.

Determination of cobalt in pharmaceutical samples

The pharmaceutical sample was treated with 10 cm^3 of aqua-regia and heated near to dryness, followed by treatment with 1 cm^3 $HClO_4$ to decompose organic matter. Finally the residue obtained was extracted with dilute H_2SO_4 and diluted to known volume. Suitable aliquots of this solution were used for cobalt determination (Table 1 B). Replicate analyses were carried out. Interfering ions were masked by using suitable masking agent.

RESULTS AND DISCUSSION

The absorption spectrum of cobalt (II)-HNSH complex, extracted into isobutyl methyl ketone recorded against a similarly prepared reagent blank showed an absorption maximum at 430 nm (Fig. 1, Curve A), where absorption due to the reagent blank was negligible (Fig. 1, Curve B). Hence, all absorption measurements were carried out at 430 nm against a similarly prepared reagent blank.

The effect of pH on the extraction of cobalt (II) into isobutyl methyl ketone (MIBK) was studied over a wide pH range. It was found that the complex could be quantitatively extracted in pH range of 8.0 to 9.0 where extractions were found to be over 99.8 per cent. A pH of 8.5 was therefore employed by HCl/NH_3 buffer in all the subsequent studies. The reagent was always added prior to pH adjustment to avoid precipitation.

Cobalt (II) was extracted with HNSH into various solvents like, isobutyl methyl ketone, diethyl phthalate, n-butanol, dichloromethane, benzene, nitrobenzene, toluene, chloroform, xylene, carbon tetrachloride, cyclohexane and n-hexane. The extraction of cobalt (II) was quantitative in isobutyl methyl ketone (MIBK) (99.8 per cent), which was therefore selected as solvent for further studies.

The effect of HNSH concentration was studied by carrying out extraction at fixed pH (pH 8.5) but at varying concentration of reagent. 0.025 percent of the reagent in DMF was found to be sufficient for the quantitative extraction of cobalt (II) into MIBK. Excess of reagent does not have any significant effect on the recovery of cobalt. 1 cm^3 of 0.025 per cent reagent was therefore used for further studies.

The colour development was instant ; however, equilibration period was varied between 10 to 80 s. The optimum period of equilibration required for the complete transfer of the coloured complex into organic phase was found to be 30 s. The studies on the absorbance of the organic extract at different time intervals revealed that the extracted Co (II)-HNSH complex was stable for 6 hrs.

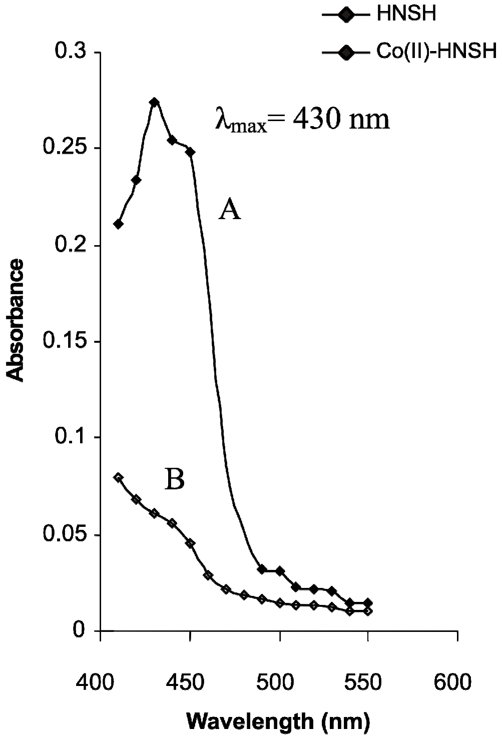

Fig. 1: Absorption spectra of HNSH and Co-HNSH complex extracted into isobutyl methyl ketone

The absorbance of the extracted species was a linear function of cobalt concentration in the range of 0.0-10.0 μg/cm^3 for cobalt (II) at 430 nm. The optimum working range was found to be 0.0 to 10.0 μg/cm^3. The Sandell's sensitivity of the method was found to be 0.036 μg/mL/cm^2, while the molar absorptivity was 1.616 × 10^3 L/mol/cm.

The tolerance limits for the diverse ions investigated were as follows: F^-, Cl^-, Br^-, I^-,ClO_3^-, BrO_3^-, IO_3^-, SO_4^{2-}, SO_3^{2-}, urea, acetate (20 mg each); Li (I), Ba(II), Mo(VI), W(VI), CO_3^{2-}, HPO_4^{2-}, $H_2PO_4^-$, NO_3^-, NO_2^-, HSO_4^-, SCN^-, $S_2O_3^{2-}$, thiourea (10 mg each); Ca(II), Se(IV), Sr(II), Cd(II), $S_2O_5^{2-}$, $S_2O_7^{2-}$, $S_2O_8^{2-}$, oxalate (5 mg each); Al(III), Bi(III), Ag(I), citrate, tartarate (2.5 mg each); Zn(II), Mn(II), Th(VI), U(VI), Mg(II) (1.0 mg each); Pb(II), Hg(II), Sb(III), Cr(III), V(V), TI(IV) (0.5 mg each); Fe(III), Fe(II), Ru(III) (0.25 mg each); Pd(II) (masked by thiourea), Zn(II) (masked by thiocyanate); Cu(II) interfered seriously. The tolerance limit was set as the amount of foreign ion that causes an error of not more than ± 2 per cent in the percentage recovery of the metal ion.

The precision and accuracy of the method were determined by analysing 10 sample solutions of same concentration. The average of ten determinations of 1 cm^3 of stalk solution of cobalt (10 $\mu g/cm^3$) was found to be 10.5 μg with a standard deviation of 0.15 and the variation from mean at 95 per cent confidence limit was ± 0.107.

The nature of the extracted cobalt (II)-HNSH complex was ascertained by the Job's continuous variation method and was found to be 1 : 2 (M : L) i.e. $Co[HNSH]_2$. This was confirmed by the mole ratio method, which shows a break corresponding to mole ratio 1 : 2. The reaction of cobalt (II) with the reagent may therefore be represented as follows:

$$\text{Co (II)} + 2\ \text{HNSH} \rightarrow \text{Co[HNSH]}_2 + 2\ \text{H}^+$$

CONCLUSION

The proposed method can be used for precise determination of cobalt at microgram level. It offers advantages like reliability, reproducibility, and good sensitivity, in addition to being simple and instant colour development and minimum interference. The method has been successfully applied for the determination of cobalt at micro level in synthetic as well as real pharmaceutical samples. The results obtained are in good agreement with the certified values and are comparable to those obtained by known method. The method has thus good potential for use in the scientific and industrial fields.

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