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ANALYTICAL METHOD DEVELOPMENT FOR EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF Co (II) USING HYDRAZINE CARBOXAMIDE-2-[(2-HYDROXY-1-NAPHTHALENYL) METHYLENE] AS AN ANALYTICAL REAGENT

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ABSTRACT

A spectrophotometric method has been developed for the determination of Co (II) using hydrazine carboxamide-2-[(2-hydroxy-1-naphthalenyl) methylene] as an extractive reagent. The reagent forms a coloured complex, which has been quantitatively extracted into n-butanol at pH 8.2. The method obeys Beer's law over a range from 1 to 10 ppm. The Molar absorptivity and Sandell's sensitivity were 0.1532×10^4 L mol^{-1} cm^{-1} and 0.1829 μg/cm^{-2}, respectively. The proposed method is very sensitive and selective. The method has been successfully applied to synthetic and commercial samples.

Key words: Cobalt, Spectrophotometric determination, n-Butanol, Hydrazine carboxamide-2-[(2-hydroxy-1-naphthalenyl) methylene].

INTRODUCTION

The significance of cobalt as a transition metal lies in its wide spectrum of applications covering many frontier areas of study, particularly in industrial and consumer products. Hence, owing to the significance of cobalt, it's determination from associated elements by extractive spectrophotometry has been of considerable importance. A wide variety of reagent has been reported for the spectrophotometric determination of cobalt. A number of reagents such as hydrazone[1-5], thiosemicarbazone[6-9], oxime[10-15], etc. have been used for the determination of Co (II). The literature survey of the past few years reveals the

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fact that a significant development in the field of biological activity of metal chelates plays a vital role in the cause and treatment of cancer[16,17]. The synthesis of semicarbazone derivative and their applications towards metal ions have been reported. A method, far superior in sensitivity and selectivity to those reported in the literature, is developed for the extractive spectrophotometric determination of cobalt with hydrazine carboxamide-2-[(2-hydroxy-1-naphthalenyl) methylene]. A close literature survey indicates that HCHNM has so far not been employed for either coordination or analytical studies. The proposed method is free from limitations.

EXPERIMENTAL

The reagent hydrazine carboxamide-2-[(2-hydroxy-1-naphthalenyl) methylene] was synthesized by the given procedure[18]. The stock solution of Co (II) was prepared by dissolving a weighed amount of sulphate in double distilled water containing dilute sulphuric acid, which was diluted to the desired volume with double distilled water and standardized by nitroso-R- salt method[18]. Absorbance and pH measurements were carried out on a Shimadzu UV-Visible 2100 spectrophotometer with 1 cm quartz cells and digital pH meter with combined glass electode respectively.

Procedure for the extraction

The extraction experiments were performed by shaking the appropriate organic and aqueous solution at O/A phase ratio of 1 : 1. The reagent HCHNM formed a yellow coloured complex with cobalt (II), which was transferred in a separating funnel. It was extracted into 10 cm^3 n-butanol and then transferred to 10 mL volumetric flask by passing through some amount of sodium sulphate in order to absorb trace amount of water. The amount of cobalt present in the organic phase was determined quantitatively by spectrophotometric method by taking absorbance at 430 nm and that in the aqueous phase, it was determined by known method.

RESULTS AND DISCUSSION

The reagent forms yellow coloured complex with Co (II), which was extracted in organic phase and the results obtained are as follows.

Extraction as a function of pH

The extraction of cobalt with hydrazine carboxamide-2-[(2-hydroxy-1-naphthalenyl) methylene] has been studied over the pH range 1-10 and was observed that percentage extraction of Co (II) is maximum at pH 8.2.

Absorption spectrum

The absorption spectrum of Co (II): Hydrazine carboxamide-2-[(2-hydroxy-1-naphthalenyl) methylene] in n-butanol shows the maximum absorption at 430 nm. The absorption due to reagent at this wavelength is nearly negligible. Hence the absorption measurements were carried out at 430 nm.

Influence of diluents

The suitability of diluents was investigated using organic solvents such as chloroform, ethyl acetate, isoamyl alcohol, xylene, hexane, diethyl ether, toluene, n-butanol, carbon tetrachloride, MIBK, nitrobenzene, etc. The extraction of cobalt (II) was quantitative with HCHNM in n-butanol. Hence, n-butanol was used for further extraction studies as it gave better and quicker phase separation.

Effect of salting out agents

The presence of 0.1 M salts of various alkali and alkaline metals does not show any effect over the absorbance value of Co (II): Hydrazine carboxamide-2-[(2-hydroxy-1-naphthalenyl) methylene] complex extract. Therefore, no salting out agent was required during the extraction.

Effect of reagent concentration

Various volumes of 0.1% reagent solution were added to the sample solution containing 80 μg of cobalt at respective pH values. The absorbance remained nearly constant when the volume of the reagent solution used was more than 1 mL. Therefore, 1 mL of 0.1% reagent was chosen for the quantitative determination of the metal.

Effect of equilibration time and stability of the complex

The study of change in absorbance with variation in equilibrium time for extraction of extraction of the complex into organic solvent shows that equilibration time of 50 sec. is sufficient for the quantitative extraction of cobalt. The study of stability of colour of the Co (II): HCHNM complex with respect to time shows that the absorbance due to extracted species is stable up to 48.0 hours, after which slight decrease in absorbance is observed. Throughout the experimental work, for practical convenience, the measurements have been carried out within one hour of extraction of cobalt.

Calibration plot

A calibration plot of absorbance against varying cobalt concentration and fixed

HCHNM concentration gives linear and reproducible graph in the concentration range 1 to 10 ppm of cobalt (Fig. 1). This shows that the Beer's law is obeyed in this range. The molar absorptivity and Sandell sensitivity were calculated to be is 0.1532×10^4 L mol^{-1} cm^{-1} and 0.1829 µg/cm^{-2} respectively.

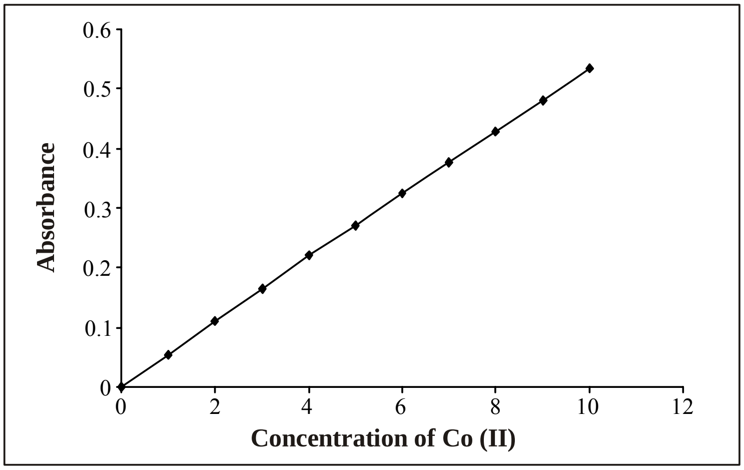

Fig. 1: Calibration plot of Co (II): HCHNM complex

Nature of extracted species

The composition of extracted species has been determined by Job's continuous variation method (Fig. 2), Slope ratio method and Mole ratio method. It shows that the composition of Co (II): HCHNM complex is 1 : 2.

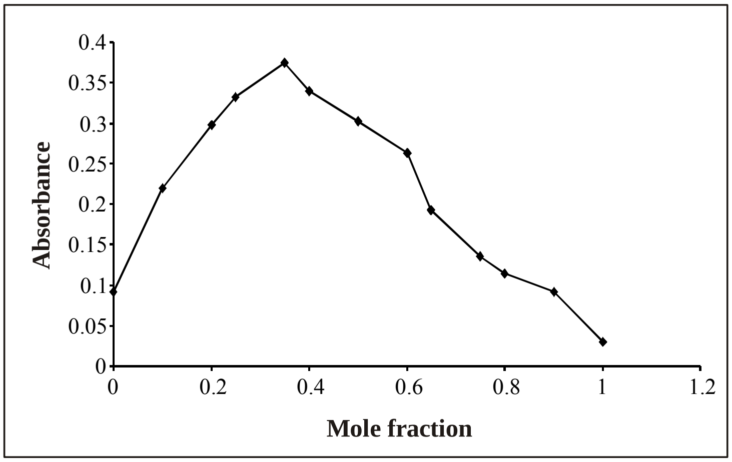

Fig. 2: Job's continuous variation method

Effect of divalent ions and foreign ions

The effect of other ions present in various amount indicated no interference in the spectrophotometric determination of 50 µg of cobalt. The ions which show interference in the spectrophotometric determination of cobalt were overcome by using appropriate masking agents (Table 1).

Table 1

Sr. No.	Metal	Amount added in mg	Absorbance at 430 nm
1	--	--	0.270
2	Na (I)	15	0.270
3	K (I)	17	0.270
4	Ag (I)	2	0.270
5	Sr (II)	10	0.270
6	Mo (II)	5	0.270
7	Mn (II)	9	0.270
8	Mg (II)	10	0.270
9	Hg (II)	12	0.270
10	Rh (IV)	11	0.270
11	Tl (I)	14	0.270
12	Th (II)	5	0.270
13	V (VI)	5	0.270
14	Ce (III)	6	0.270
15	Cd (II)	7	0.270
16	Zn (II)	4	0.270
17	Al (III)	6	0.270
18	Ni (II)	5 µg	0.270
19	U (VI)	10 µg	0.270
20	Cu (II)	10 µg	0.270
21	Fe (II)	10 µg	0.270

Precision and accuracy

The precision and accuracy of the developed spectrophotometric method have been studied by analyzing five solutions each containing 100 μg of Cobalt.

Applications

The proposed method was successfully applied for the determination of cobalt from various alloys, synthetic mixtures and pharmaceutical samples. The results found to be in good agreement with those obtained by the standard known method (Table 2).

Tabale 2: Determination of Co (II) using HCHNM from different samples

Sr. No.	Sample	Amount of Co (II)	
		Standard method	Present method
I	**Cobalt alloys**		
1	Cobalamine	68.9%	68.8%
2	Steel	9.67%	9.66%
II	**Synthetic mixture**		
1	Co (10) + Zn (10)	9.98 ppm	9.98 ppm
2	Co (10) + Mo (10)	9.98 ppm	9.96 ppm
3	Co (10) + Mg (10)	9.98 ppm	9.97 ppm
III	**Pharmaceutical samples**		
1	Surbex –T (Abott)	0.337 mg	0.336 mg
2	Vitamin B12	50 mg	49 mg

CONCLUSION

The proposed method is highly sensitive and selective than the other reported methods for the extractive spectrophotometric determination of microgram amounts of cobalt. It offers advantages like reliability and reproducibility in addition to its simplicity, instant colour development and suffers from less interference. It has been successfully applied to the determination of cobalt at trace level in synthetic mixtures, alloys and synthetic mixtures.

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