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Extraction and Spectrophotometric Determination of Cobalt

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Abstract: 2-Hydroxy-4n-butoxy-5-bromo propiophenone oxime (HBBPO) is proposed as a new reagent for the selective extraction and spectrophotometric determination of Co(II). The reagent forms a stable yellowish brown complex in then pH range 7 to 10. The complex can be extracted into chloroform layer. They exhibits λ_{max} at 410 nm and 650 nm. The effect of various experimental parameter such as effect of pH, composition of complex, stability constant of complex, effect of diverse ions have been studied and optimum conditions were evaluated to extract, separate and estimate cobalt at ppm level by spectrophotometry. The proposed method is selective and rapid for estimation of cobalt at trace level.
Keywords:Cobalt(II),2-Hydroxy-4n-butoxy-5-bromo propiophenone Oxime , Spectrophotometric determination.

Introduction

Through ages, number of complexing agents have been used to determine cobalt in presence of other diverse ions. Oximes[1-6], hydrazones[7-9], thiosemicarbazone[10-12] and other chelating agents have been extensively used for the the determination and separation of cobalt. In the present work, we report the applicability of 2-Hydroxy-4n-butoxy-5-bromo propiophenone oxime (HBBPO) for extraction and spectrophotometric determination of Co(II). In slightly basic medium cobalt forms a yellowish brown complex, extractable into chloroform. Measurements at 650 nm show that Beer's law is valid over a concentration range 14.73-117.86 ppm. Effect of pH, composition of complex, diverse ions effect etc. on the extraction behaviour have been studied. The nature of the extracted species has also been studied.

Experimental

All reagents and chemicals of A.R. grade were used. Spectrophotometric measurements were made with a Systronics UV/VIS spectrophotometer (model-118) using 10mm glass cells. All pH measurements were made with Systronic pH meter (model-324).

Respropiohenone was prepared from resorcinol, propionic acid,anhydrous zinc chloride. 2-hydroxy-4n-butoxy propiophenone (HBP) has prepared by reported method[13].   2-hydroxy-4n-butoxy-5-bromo propiophenone (HBBP) was prepared by Bromination[14] of HBP.The oxime of HBBP was prepared by sodium acetate method. It was crystallised from ethanol, colourless needle like crystals were obtained, with m.p. of $68 \pm 1^{\circ}$C.

A stock solution of 0.01M cobalt chloride was prepared in distilled water and standardised by known method[15]. The dilute solution of cobalt of desired concentration was prepared by appropriate dilution of stock solution.Standard solution of diverse ions were

prepared from their chloride or sulphate or from alkali salts. Dilute HCl and/or NaOH were used to maintain different pH.

Results and Discussion

IR spectra of ligand and complex were recorded on model No.8400 FTIR, Shimadzu-Japan using Nujol as a solvent. IR bands for the ligand and complex are presented in Table-1. This indicates that chelation takes place through the oxygen of –OH group and nitrogen of =N-OH group. The possible structure of the metal complex was found to be
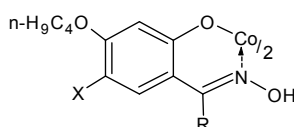
HBBPO where, R = -C_2H_5 ; X = -Br

Absorption Spectra : The absorbance spectrum of cobalt complex in chloroform shows maxima at 410nm and 650nm,but the measurements were carried out at 650 nm using solvent blank because at this wavelength reagent shows negligible absorption. The sensitivity of the method as defined by Sandell is 0.19 µg/cm^2 at 650 nm. Beer's law is obeyed between the range 14.73 – 117.86 ppm of Co(II).

Effect of pH : The yellow coloured complex of Co(II) takes place in the pH range 7 to 9 but the maximum colour intensity was observed at pH 8 with ligand. Thre is no colour intensity up to a week. Hence, all the measurements were done at pH 8.0.

Table-1. IR frequency data of the ligand and complex

IR frequencies(cm^{-1})	HBBPO	Co-HBBPO
OH (Phenolic) Str.	3473	-
OH (Oximino) Str.	2966	2956
C-H (Alkane) Str.	2943,2902,2875	2935,2871
C=N Str.	1629,1610	1589
C=C Aromatic Str.	1577,1541,1508	1527,1460
C-H-H bending	1473,1456	1400
C-H bending	1377,1338	1329
C-O-C (Ether)	1298,1280,1261	1276,1238
C-Br Str.	621	669

Table-2. Physico-chemical data of Co(II)-HBBPO

Characteristics	Results
Beer's law Limit (ppm)	14.73-117.86
Opt. Conc. Range(ppm)	29.47-103.13
Molar absorptivity, ε(L mole^{-1} cm^{-1})	392
Sandell's sensitivity(µg/cm^2)	0.15
Stability constant (K)	5.30 x 10^8
ΔG^0 (k.cal)	-12.10
M:L	1:2

Table-3. Stability constant of Co(II)–HBBPO complex at 30°c

Method Employed	Em	Es	α = (Em-Es)/Em	K (n=1)
Job's	0.393	0.363	0.07634	5.19×10^8
	0.784	0.746	0.04847	5.22×10^8
Mole ratio	0.490	0.458	0.06531	5.37×10^8
	0.588	0.554	0.05782	5.41×10^8
Average K				5.30×10^8

Composition of the complex

The composition of the yellowish brown Co(II) complex was determined by Job's as continuous variation[16] method, mole ratio method[17] and slope ratio[18] following the adopted procedures. The M:L ratio was found to be 1:2.The composition was verified by mole ratio method. A plot of absorbance against increasing ligand concentration gave at metal to ligand ratio of 1:2.

Stability Constant of the Complex

The stability constant of the complex was calculated using the following conventional relationships :

$$\alpha = (Em-Es)/Em \quad \text{and} \quad K= (1- \alpha)/4C^2\alpha^3$$

The average stability constant was found to be 5.30 x 10^8 and free energy of formation ($\Delta F = - RT \ln K$) was –12.10 kcal/mole at 30°C are given in Table-3.

Effect of Diverse ions : In the present case, the effect of foreign ions on the spectrophotometric determination of Cobalt was studied by adding these ions in quantities ranging from 5,000 to 5 µg to a solution containing 14.73 µg of Cobalt. After adjusting the pH of the solution at 8.0, Co(II) was exctracted as Co(II)-HBBPO complex in the usual manner and the absorbance of the organic layer was measured. A difference of $\pm$ 2% in the absorbance is taken as tolerance limit. The limit for various ions expressed in micrograms are as follows :

up to 100000 µg : Cl^-, NO_3^-, SO_4^-, CH_3COO^-, Na^+, K^+, NH_4^+

up to 10000 µg : Ca^{+2}, Ba^{+2}, Sr^{+2}, Mg^{+2}, Al^{+3}, Zn^{+2}, Cd^{+2}, $S_2O_3^-$, MoO_4^-, Citrate, tartrate, oxalate

up to 10000 µg : Ag^+, Cr^{+3}, UO_2^{+2}, Pd^{+2}

up to 100 µg : Vanadium, Cu^{+2}, Mn^{+2}, Fe^{+3}

up to 10 µg : EDTA

Determination of cobalt in alloy and synthetic mixtures : The complex formed between Co(II) and HBBPO is stable and can be used for analysis. The method has been applied for the analysis microgram quantities of cobalt in alloy and some synthetic mixtures. The result are shown in Table-4.

Table-4. Analysis of cobalt in various sample

Sr.No.	Sample	Cobalt taken (µg)	Cobalt found* (µg)
1	Vitallium	1022.4	1014.7
2	Synthetic Mixture-1	589.30	580.28
3	Synthetic Mixture-2	883.95	877.94
4	Synthetic Mixture-3	441.98	443.48

(* indicate average value of three result)

Conclusions : The reagent (HBBPO) is used for the determination of cobalt in microgram quantities. The Molar absorptivity and Sandell's sensitivity are 392 lmole^{-1} cm^{-1} and 0.15 µg/cm^2**,** respectively**.** The method has been applied for the analysis cobalt in synthesized mixtures and also in alloys.

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