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Direct and Derivative Spectrophotometric Determination of Cobalt(II) Using 3,5-Dimethoxy-4- hydroxyben-zaldehydebenzoylhydrazone (DMBBH)

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Abstract: A rapid, simple, sensitive and selective spectrophotometric method has been developed for the determination of Cobalt (II) using newly synthesized Chromogenic reagent 3,5-Dimethoxy-4-hydroxybenzaldehydebenzoylhydrazone(DMBBH) in cationic surfactant of C-Tab-(5%) (micellar medium). Cobalt (II) forms a Orange coluored water-soluble complex with 3,5-Dimethoxy-4-hydroxyben-zaldehydebenzoylhydrazone(DMBBH) in the pH range 5.0-9.0. The complex shows maximum absorbance at λmax 439 nm and in the pH range 5.0-6.0. At λmax 439 nm, the complex shows maximum absorbance while the reagent blank shows negligible absorbance. Hence, analytical studies are carried out at λmax 439 nm and at pH 6.0 (Phosphate buffer) against reagent blank. Beer's law is obeyed in the range 0.2946 to 3.5358µg/mL and the optimum concentration range obtained from ringbom plot is 0.5893 - 2.9465µg/mL of Coobalt (II). The molar absorptivity and Sandell's sensitivity for the coloured solution are found to be 2.685 x 10^4L $mol^{-1}cm^{-1}$ and 0.001862-µg.cm^{-2} respectively. The interference effect of various diverse ions has been studied. The complex shows 1:2 [Co (II): DMBBH] stoichiometry with stability constant 11.24x10^{10} obtained from job's method. The standard deviation of the method in the determination of Copper (II) is 0.0005and the Relative standard deviation is 0.05. First and second order derivative spectroscopic method is developed at λmax 500 nm and 512 nm respectively for the determination of Cobalt (II), which is more sensitive than the zero order method. The developed method has been used for the determination of Cobalt (II) in Soil samples and Vitamin B_{12} samples. The results are in good agreement with the certified values.

Keywords: Cobalt(II), DerivativeSpectrophotometry, DMBBH,Soil, Vitamin B_{12}.

1. Introduction

The potential analytical applications of hydrazone derivatives have been reviewed by Singh et al [1]. Hydrazones are important class of known analytical reagents [2-9]. In the light of analytical potentialities of hydrazones herein we report the synthesis, characterization and analytical properties of reagent hydrazones.1-Nitroso-2-naphthol proposed by Ilion sky et al[8] was one of the first organic reagents employed for the determination of cobalt. In the light of the above herein we report the first order and second order derivative spectrophotometric methods for the determination of Co(II) using DMBBH in soil and vitamin B-12 samples.

Derivative spectrophotometry is a very useful approach for determining the concentration of single component in mixtures without overlapping spectra as it may eliminate interferences. In this paper first order and second order derivative spectrophotometric methods are described for the determination of Cobalt (II) in soil and Vitamin B-12 samples.

2. Experimental

The reagent 3,5-Dimethoxy-4-hydroxybenzaldehydebenzoylhydrazone (DMBBH) was prepared by simple condensation of 1 mole of 3,5-Dimethoxy-4-hydroxybenzaldehyde with Benzhydrazide. The structure of the reagent is presented in Fig-1.

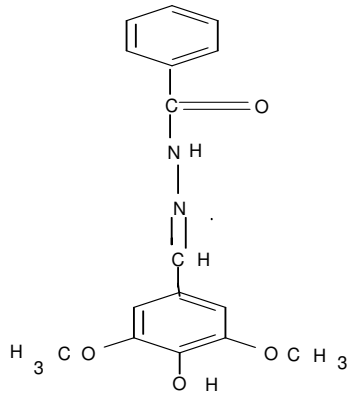

Fig.1. Structure of 3,5-Dimethoxy-4-hydroxybenzaldehyde benzoylhydrazone(DMBBH)

A reagent solution (0.01M) was prepared by dissolving suitable quantity (0.30033 g) of the compound in 100 ml of di methyl form amide. The reagent solution is stable for 1 h.1M hydrochloric acid- 1M sodium acetate (pH 0.5-3.5); 0.2 M acetic acid-0.2M sodium acetate (pH4.0-6.0) and 2M ammonium chloride-2M ammonium hydroxide (pH 8.0-11.0) buffer solutions were used in the determination of P^{ka} values of the reagents. The standard cobalt (II) solution ($1x10^{-2}$M) was prepared using analytical reagent grade cobalt nitrate (AR, BDH). Solutions of diverse ions of suitable concentrations were prepared using AR grade chemicals.

Shimadzu 160A UV-Vis spectrophotometer equipped with 1.0 cm quartz cells and an Elico model LI-120 digital pH meter were used in the present study.

3. Recommended procedure

a) **Determination of Cobalt(II) (Zero order):** An aliquot of the solution containing 0.2946 to 3.5358µg/ml of cobalt(II), 3.0 ml of buffer solution (pH6.0) and 0.5 ml of 0.01 M reagent were taken in a 10 ml volumetric flask and the solution was diluted to the mark with doubly distilled water. The absorbance of the solution was recorded at 439 nm against the corresponding reagent blank. The absorption spectra of Co(II)-DMBBH was shown in Fig-2.

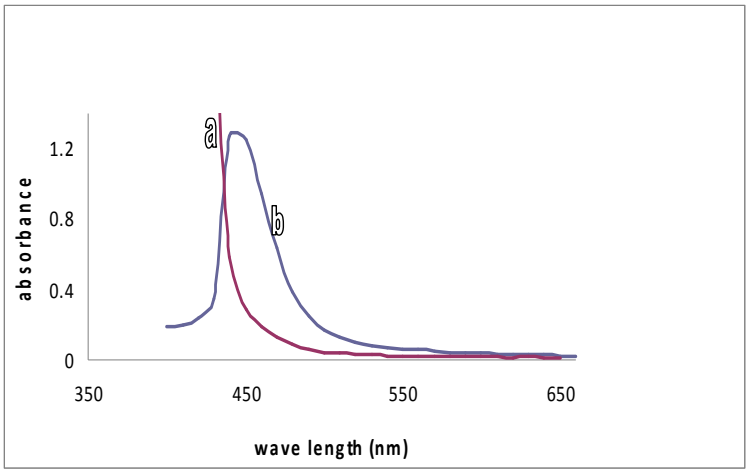

Fig. 2:Absorbance spectra of Co (II)-DMBBH Vs DMBBH Vs reagent blank.

a) DMBBH Vs Buffer blank (b) Co(II)-DMBBH Vs DMBBH

b) **First-order and second-order derivative spectrophotometric determination of Co (II):** For the above solutions, first-order and second order derivative spectrums were recorded in the wavelength range 400-650 nm. The derivative peak heights were measured by peak-zero method at 500 nm and 512 nm. . It is presented in Fig-3 and Fig-4.

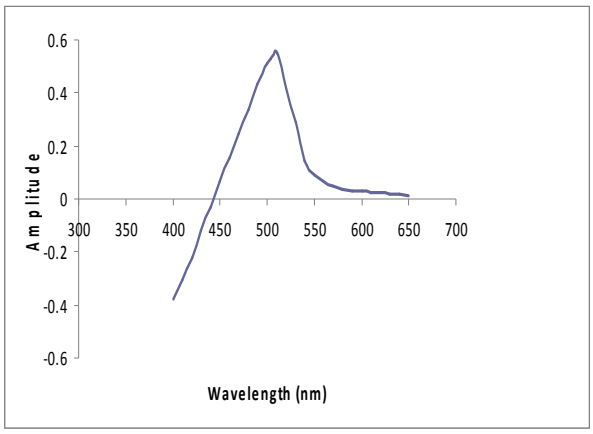

Fig.3 First order derivative spectrum

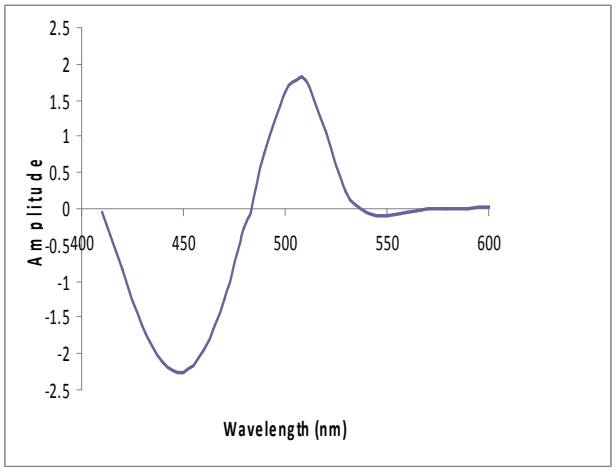

Fig.4 Second order derivative spectrum

4. Results and discussion

3, 5-Dimethoxy-4-hydroxybenzaldehyde benzoylhydrazone (DMBBH) is a blend of two functional groups, viz., aldehyde and hydrazine. Therefore DMBBH may be considered as a two-in-one ligand. This type of reagent is not exploited much for the spectrophotometric determination of metal ions.

The P^{ka} values are determined by recording the UV-Visible spectrum of micro molar ($1x10^{-4}M$) solution of reagent at various pH values. The complex formation reactions between cobalt (II) with 3, 5-Dimethoxy-4-hydroxybenzaldehyde benzoylhydrazone(DMBBH) have been studied in detail. The various physico-chemical and analytical properties of Co(II)-DMBBH complex are presented in Table-1.

Table.1: Physico-chemical and analytical characteristics of Co (II)-DMBBH complex

Characteristics	**Results**
λ_{max}	439 nm
pH range	5.0-6.0
Mole of reagent required per mole of metal ion for full colour development	10 (folds)
Molar absorptivity ($L.mol^{-1}cm^{-1}$)	2.685×10^4
Sandell's sensitivity($\mu g/cm^2$)	0.001862
Beer's law validity range(μg/ml)	0.2946 - 3.5358
Optimum concentration range(μg/ml)	0.5893 - 2.9465
Composition of complex(M:L) obtained in Job's and molar ratio method	1:2
Stability constant of the complex	$11.24x10^{10}$
Standard deviation in the determination of μg/ml of Co(II) for ten determinations.	0.0005
RSD	0.05

Interference

Derivative spectrophotometry is a very useful technique in the sense that it decreases the interference, i.e., increases the tolerance limit value of foreign ions of metal ions having overlapping spectra. The recommended procedures have been employed for the spectrophotometric determination of cobalt (II). The effect of various diverse ions in the determination of Cobalt (II) was studied to find out the tolerance limit of foreign ions in the present method. The tolerance limit of foreign ions was taken as the amount of foreign ion required to cause an error of ±2% in the absorbance

Table.2: Tolerance limit of foreign ions in the determination of 1.4733 µg/ml of Co (II)

Ion added	**Tolarence limitµg/ml Zero order**
Sulphate	48
Nitrate	620
Sodium tetraborate	5031
Phosphate	10
Acetate	296
Chloride	178
Urea	901
Ascorbic acid	2642
Tartarate	2202
Citrate	2251
Bromide	400
Fluoride	95
oxalate	1320
Iodide	1270
EDTA	5584
Ca(II)	28.5
Sn(II)	12
W(VI)	18.5
Hg(II)	201
Zn(II)	33
Ce(IV)	1
Se(IV)	40
Fe(III)	0.5*
Pb(II)	0.5
Cr(VI)	0.5
Os(VIII)	190
Th(IV)	34.8
Ru(III)	0.50
Mo(VI)	10
$NH^{=}_{4}$	1
Sb(III)	122
Ni(II)	58
Mn(II)	83
Co(II)	30
Cu(II)	32#
Pd(II)	1

*Masked with 148 µg/ml Fluoride,
#Masked with 245 µg/ml thiourea

5. Applications

Determination of Cobalt (II) in Soil Sample: An exact mass of soil (0.100 g) was dried at 110 ^{0c} and treated with 3 ml of conc. Nitric acid and 6 ml of conc. Hydrochloric acid at low temperature until the evolution of brown oxides of nitrogen had ceased. The mixture was evaporated to dryness. The residue was decomposed by heating with 20 ml of 0.1 M sulphuric acid, the insoluble material was then filtered off and washed. The filtrate and washing water were collected in a beaker, and then heated to a small volume. The solution was neutralized with 0.1M sodium hydroxide, and then transferred into a 10 ml calibrated flask following the steps as in procedure for the determination of cobalt (II) in samples. The results are presented in Table: 3 the results were obtained in agreement with the stated values.

Table 3: Determination of cobalt in soil samples

Sl. No.	Sample	AAS method	Amount of Co(II) µg/ml present method	Error (%)
1	ESS-1	14.8	15.2	-2.70
2	ESS-2	25.6	25.9	-1.17

Average of five determinations

Determination of Cobalt (II) in Vitamin B_{12} injection: place the hydroxo cobalimin (Vitamin B_{12}) injection in a 250 ml flask, add 2 to 3 ml of nitric acid for dissolution, transfer into a 100 ml calibrated flask, dilute to the mark with distilled water and mix well, then follow the steps in general procedure. The results were presented in Table 4.

Table 4: Determination of Cobalt in Vitamin B_{12} injection.

Sl. No.	Sample	AAS method	Amount of Co(II) µg/ml present method	Error (%)
1	Vitamin B_{12}(910701)	0.85	0.86	-1.17
2	Vitamin B_{12}(920709)	0.82	0.80	+2.4

Average of five determinations

6. Conclusion

From the above discussion, it can be concluded that DMBBH is a potential reagent for the derivative spectrophotometric determination of Co (II). It is very easy to synthesize DMBBH, a novel class of reagent. The present derivative method is simple and rapid without the need for heating or extraction.the present method was compared with the other reagents used for the spectrophotometric determination of Co(II) and the results were presented in Table-5.

Sl. No	Reagent	λ_{max} nm	Molar absorptivity	Reference
1	p-methylisonitosoacetophenonehydrazone	520	$1.83x10^3$	10
2	Benzil di-2-pyridylhydrazone	531	$4.60x10^3$	11
3	Diacetylmonoxime isonicotinoylhydrazone(DMIH)	334	$1.25x10^4$	12
4	2(-3'-sulphobenzoyl)pyridine benzoylhydrazone	-	$2.17x10^4$	13
5	2,2'-pyridyl di-2-pyridylhydrazone	480	$2.54x10^4$	14
6	3,5-dimethoxy-4-hydroxybenzaldehydebenzoylhydrazone(DMBBH)	439	$2.685x10^4$	Present Work

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