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Research Article

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A study on synthesis of novel chromogenic organic reagent 3,4-dihydroxy-5-methoxy benzaldehyde thiosemicarbazone and specrtrophotometric determination of Cobalt (II) in presences of Triton X-100

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ABSTRACT

The present research work 3,4-dihdroxy 5-methoxybenzaldehyde thiosemicarbazone (DHMBTSC) is proposed as a novel chromogenic organic reagent for the estimation of Cobalt (II) with specterophotometry. The novel chromogenic reagent 3,4-dihdroxy 5-methoxybenzaldehyde thiosemicarbazone (DHMBTSC) form yellowish brown coloured complexe by Cobalt (II). The colour complexe shows maximum absorption at λ_{max} 389 nm. The beer's law validity range is 0.14733 to 1.4733 (µg/ml) and optimum concentration range is 0.2946 to 1.3259 (µg/ml).The molar absorptivity and sandells sensitivity of the complex was found to be $1.65x10^4$ $L.mol^{-1}.cm^{-1}$ and $0.00357 \mu g/cm^2$ respectively. The cobalt (II) forms M:L(I:I) colour complexe with DHMBTSC and stability constant of the complex was found to be. 2.41 x 10^6 . The first order derivative amplitude was measured at 432 nm. This proposed developed method is selective, rapid and applied for the estimation of Cobalt (II) in trace leveles in tea leaves samples.

Key words: chromogenic organic reagent, derivative spectrophotometry, Cobalt (II) and tea leaves samples.

INTRODUCTION

Cobalt is found generally in the form of ores. It is frequently associated with Nickel and Copper. So it is produced as a byproduct of Nickel and Copper mining activities. Cobalt is a micro nutrient for many living organisms, including human beings. 0.13 to 0.30 mg/kg of Cobalt in soils markedly improves the health of grazing animals. Cobalt plays an important role in the nitrogen fixation by bacteria and also an integral part of vitamin-B_{12}. Mammals required small amount of Cobalt salts. Plants and different food materials contain extremely low concentration of cobalt. Its deficiency leads to diseases like stunted growth; at high concentration it inhibits biosynthesis and enzyme activities.

Number of complexe of chromogenic organic reagents were reported for the spectrophotometric estimation of the Cobalt(II). In the present research work we report the new chromogenic analytical reagent for the estimation of Cobalt (II) at trace levels. Today several analytical techniques and novel methods were extensively used such as AAS, ICP-AES, X-Ray flourenscence spectroscopy, voltametry, polorography, specteophotometry and other techniques. specterphotometric methods are preferred because they are cost of instrument is low, high sensitivity, accuracy results are obtained in short time.

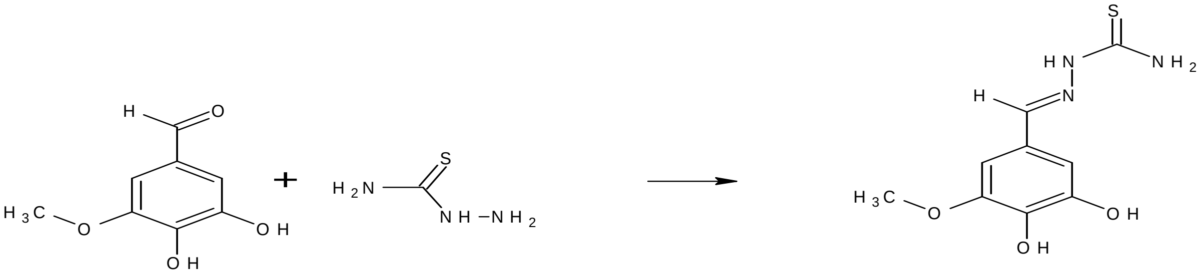
EXPERIMENTAL SECTION

Spectrophotometric measurements were made in a shimadzu 160 a micro computer based UV–Visible spectrophotometer equipped with 1.0 cm quartz cells, an ELICO LI- 120 digital pH meter. All reagents used were of analytical reagent (AR) grade unless otherwise stated. All solutions were prepared with distilled water

REAGENT

Synthesis of 3,4-dihydroxy 5-methoxy banzaldehyde thiosemicarbazone

3,4-dihydroxy-5-methoxybenzaldehyde (0.42035 g, 0.01 mole) dissolved in hot methanol, hot methanolic solution of thiosemicarbazide (0.2275 g, 0.01 mole) were taken in a 250ml ml round bottom flask. The contents in flask were refluxed for 30 minutes using a water condenser. On cooling the reaction mixture, light yellow coloured product was separated out. It was collected by filtration and washed several times with hot water and cold methanol. This compound was recrystallised and dried in vacuom



Characterization of 3,4-dihydroxy -5-methoxy banzaldehyde thiosemicarbazone was characterized with the help of Infrared, ^{1}H-NMR and Mass spectral data.

Analytical properties of DHMBTSC*:*

In the present work, the colour reactions of some important metal ions were examined in presence of various bufer solutions medium The analytical characteristics of the metal complexes are incorporated in table :1 The colour solution samples were prepared in 10 ml standard volumetric flasks by adding 3 ml of buffer (pH 1.0-11), 0.5 ml of metal ion (1x10^{-3}M) and 0.5 ml of(1x10 $^{-2}$ M) DHMBTSC solutions. The colour solution mixture was diluted up to the mark with distilled water. The absorbance was measured in 300-800 nm range against reagent blank.

Table :1 Analytical properties of DHMBTSC complexes in solution

Metal ion	$\lambda_{max\ (nm)}$	pH	Colour of the complex	Nature of the complex
Cobalt(II)	389	4.0	Yellowish brown	1:1
Nickel(II)	385	8.5	Light yellow	1:1

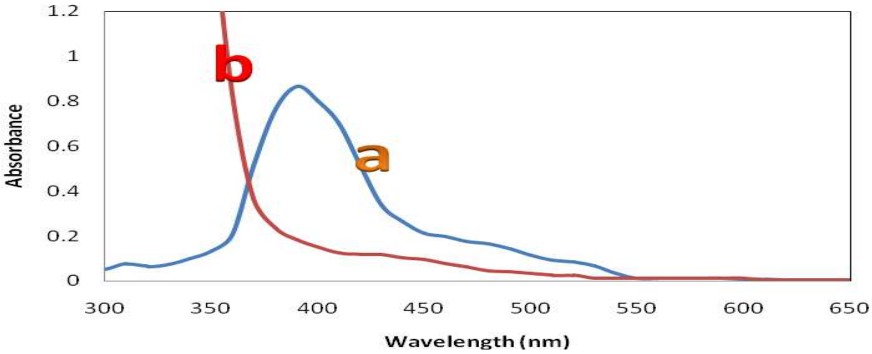


Fig no. 1*:* Absorption spectra
(a). [Co (II)-DHMBTSC] complex vs reagent blank (b). DHMBTSC vs buffer blank.

RECOMMENDED PROCEDURE

Estimation of Cobalt (II) (zero order)

An aliquot of the colour mixer solution containing 0.1473 to 1.4733 μg/ml of Cobalt (II), 3 ml of buffer solution pH 3.0 to 5.0 and 0.5 ml of ($1x10^{-2}M$) novel DHMBTSC reagent were taken in a ten ml standard volumetric flask and the colour solution was diluted up to the mark with distilled water. The intensive absorbance of the solution was recorded at 389 nm in a 1.0 cm cell again corresponding reagent blank prepared in the same way but without Cobalt(II) metal solution. The absorption spectra of DHMBTSC and its Co (II) complex under the optimum conditions are shown in fig no:1.The Co (II)-DHMBTSC complex shows the maximum absorbance at 389 nm, where as the reagent blank does not absorb appreciably.

RESULTS AND DISCUSSION

In the present work 3,4-dihdroxy 5-methoxybenzaldehyde thiosemicarbazone(DHMBTSC) analytical reagent is a blend of a carbonyl compound and a thiosemicarbazide. The reagent solution is stable for more then six hours. in presence of buffer medium. The ligand presumably associated with the metal ions to give a neutral water soluble complex.

Estimation of Cobalt (II) using DHMBTSC*:*

The metal ion Cobalt (II) reacts with DHMBTSC in acdic buffer medium to give yellowish brown coloured water-soluble complex. The colour reaction between Cobalt (II) and DHMBTSC are instantaneous even at room temperature in presences of the pH range 3.0 to 5.0 and Triton X-100 (5%) surfacteant solution The absorbance of the yellowish brown coloured species remains stable for more than three hours. The maximum colour intensity is examined at pH 4.0. A 10-fold molar excess of analytical reagent is used for bright colour development. The order of addition of buffer solution, metal ion and reagent has no adverse effect on the absorbance. The intensive colour complex formation reaction between Cobalt (II) and DHMBTSC has been examined in detail based on the composition of the complex as determined by using Job’s and molar ratio methods. Important analytical parametrs of Cobalt (II) and DHMBTSC are incorporated in table-2.

Table-2: Physico-Chemical and analytical characteristics of [Co(II) – DHMBTSC] complex

Characteristics	Results
Colour	yellowish brown
λ_{max} (nm)	389
pH range (optimum)	3.0-5.0
Mole of reagent required per mole of metal ion for full colour development	10 - folds
Molar absorptivity ($l.mol^{-1}.cm^{-1}$)	$1.65x 10^4$
Sandell’s sensitivity ($\mu g.cm^{-2}$)	0.00357
Beer’s law validity range (μg/ml)	0.1473 to 1.4733
Optimum concentration range (μg/ml)	0.2946 to 1.3259
Composition of complex (M:L) obtained in Job’s and mole ratio method	1: 1
Stability constant of the complex (jobs method)	$2.41 x 10^6$
Relative standard deviation (%)	0.01

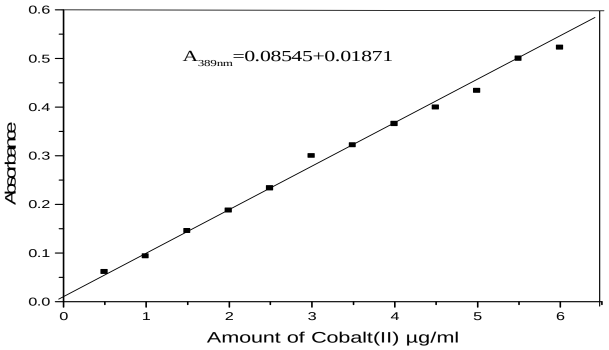


Fig no-2 zero order beer's law graph of [Co(II)-DHMBTSC] Vs reagent

The zero order beer's law verification graph suggest that this colour solution complex was sensitive and selective for estimation of Cobalt (II) ion as shown in fig no : 2. The first order derivative spectra was shown in fig no-3. This shows that the derivative amplitudes measured at 432 nm and first order were found to be proportional to the amount of Cobalt (II) respectively.

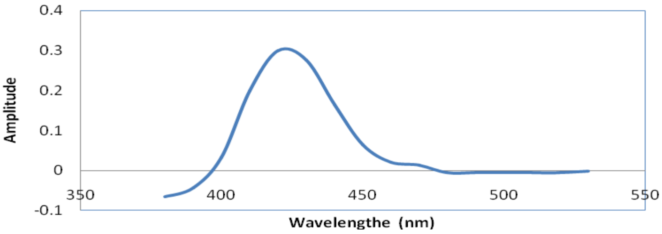


Fig no-3: First derivative spectra of [Co(II)-DHMBTSC] Vs reagent

EFFECT OF FOREIGN IONS

Derivative spectrophotometry is a very advanced technique in the sense that it is reduced the interference, i.e, increases the tolerance limit value of foreign ions of metal ions having overlapping spectra. The proposed method have been employed for the spectrophotometric determination of Cobalt (II).The effect of different diverse ions in the determination of Cobalt (II) was examined to find out the tolerance limit of foreign ions in the present method. The tolerance limit of a foreign ion was taken as the amount of foreign ion necessary to cause an inaccuracy of ± 2 % in the absorbance or amplitude. The outcome results are incorporated in table-3.

Table-3: Tolerance limit of foreign ions in the determination of 0.5893 µg/ml of Cobalt (II)

Ion Added	Tolerance Limit (µg/ml)	Ion Added	Tolerance Limit (µg/ml)
Iodide	1456	Al(III)	16
Sulphate	913	Ba(II)	296
Ascorbic acid	393	Mo(VI)	4.6
Urea	765	Hg(II)	31
Thiocyanide	598	Pb(II)	121
Bromide	965	W(VI)	198
Thiourea	1013	Sr(II)	106
Nitrate	423	Se(IV)	86
Tetra borate	1324	Bi(II)	34
Acetate	446	Ti(IV)	2.0
Phosphate	398	Ni(II)	3.0
Chlorides	932	Ce(IV)	45
Tartarate	1103	Fe(III) *	2.0
Citrate	1632	Cu(II)**	3.0
Fluoride	513	Ru(III)	7.54
Oxalate	1650	Pd(II)	2.19
U(VI)	54	Cd(II)	4.3
Sn(II)	65	Mn(II)	3.0

**Masked by Flouride 395 µg/ml.*
***Masked by Thiourea 421 µg/ml.*

APPLICATIONS

Estimation of Cobalt (II) in tea leaves sample

The tealeaf samples were supplied by Andra Pradesh Agricultural Research Institute (APARI), Hyderabad, India. 0.1 g of tealeaf sample was taken in a beaker and dissolved in Conc. nitric acid (≈ 5 ml) with heating. The solution was cooled, diluted, and filtered. The filtrate was made up to 100 ml with distilled water in a calibrated flask. The results are presented in table-4

Table-4: Determination of Co(II) in Tea leaves samples

Sample	Certified value	*Amount of Cobalt (II) (µg/ml) found	Error (%)
Tea leaves	0.12	0.116	-3.33

** Average of best three among five determinations*

CONCLUSION

This research work suggest that the 3,4-dihydroxy-5-methoxy benzaldehydethiosemicarbzone (DHMBTSC) has been proven as a sensitive and selective chromogenic organic reagent for the determination of Cobalt(II) . Molar absorptivity of the colour complexe was 1.65x 10^4 L.mole^{-1}. cm^{-1}. The present derivative method was sensitive campared with zero order method. The proposed method is especially selective with respect to metals, wich commonly seriously interfere with the estimation of Cobalt (II) as earlier method reported . The proposed method can be successfully applied to the estimation of Cobalt (II) in tea leaves samples.The present method was favorably compared which eariler reported spectrophotometric[1-20] methods .

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