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A study on synthesis of novel chromogenic organic reagent 3,4-dihydroxy-5-methoxy benzaldehyde thiosemicarbazone and specrtrophotometric determination of Ruthenium (III) 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 Ruthenium (III) by spectrophotometry. The novel chromogenic reagent 3,4-dihdroxy-5-methoxybenzaldehyde thiosemicarbazone (DHMBTSC) form yellow coloured complexe with Ruthenium (III). The colour complexe shows maximum absorption at $_{max}$ 425 nm. The beer's law validity range 0.2021 to 2.3246 (μg/ml) and optimum concentration range is 0.4042 to 2.1224 (μg/ml). The molar absorptivity and sandells sensitivity of the complex was found to be 2.72×10^{4} L. mol^{-1}. cm^{-1} and 0.00371 μg/cm^{2} respectively. The Ruthenium (III) forms M:L (I:I) colour complexe with DHMBTSC and stability constant of the complex was found to be. 7.24×10^{6}.

KEYWORDS

Chromogenic organic reagent;
Derivative spectrophotometry;
Ruthenium (III) and samples.

INTRODUCTION

Number of complexe of chromogenic organic reagents were reported for the spectrophotometric estimation of the Ruthenium (III). In the present research work we report the new chromogenic analytical reagent for the estimation of Ruthenium (III) 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

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

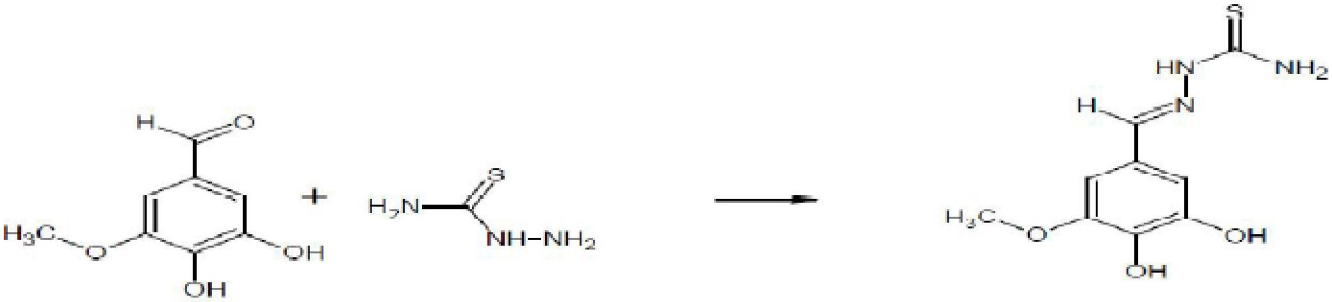

TABLE 1: Analytical properties of DHMBTSC complexes in solution

Metal ion	$\lambda_{\text{max (nm)}}$	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
Ruthenium (III)	425	2.0 to 4.0	Yellow	1:1

stated. All solutions were prepared with distilled water.

REAGENT

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

3,4-dihydroxy-5-methoxybenzaldehyde (0.42035g, 0.01 mole) dissolved in hotmethanol, 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 vacuum.

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.

RECOMMENDED PROCEDURE

Estimation of Ruthenium (III) (zero order)

An aliquot of the colour mixer solution containing μg/ml of Ruthenium (III), 3 ml of buffer solution pH 2.0 to 4.0 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 425 nm in a 1.0 cm cell again corresponding reagent blank prepared in the same way but without Ruthenium (III) metal solution. The absorption spectra of DHMBTSC and its Ru (III) complex under the optimum conditions are shown in fig no:1. The Ru (III)-DHMBTSC complex shows the maximum absorbance at 425 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 Ruthenium (III) using DHMBTSC

The metal ion Ruthenium (III) reacts with DHMBTSC in basic buffer medium to give yellow

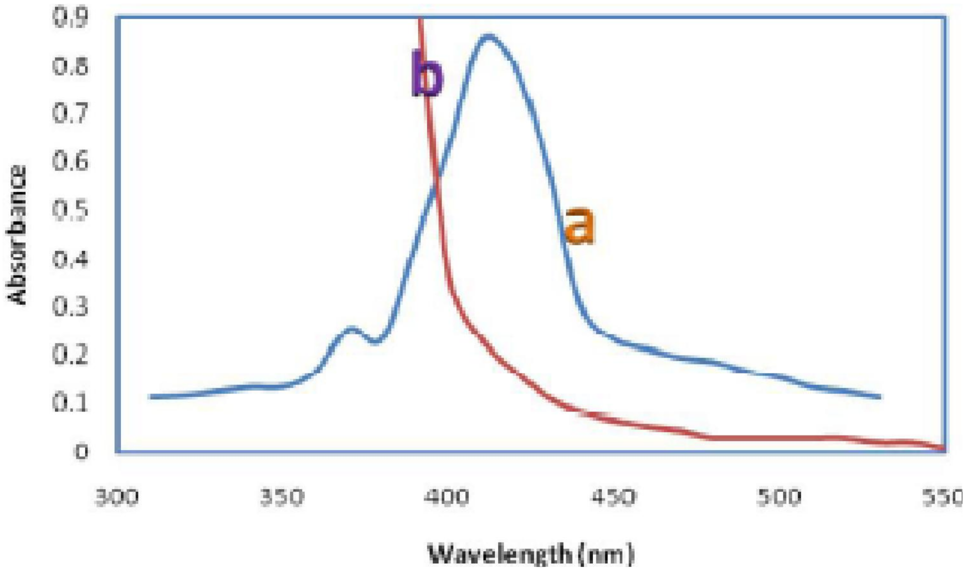

Figure 1 : **Absorption spectra, (a). [Ru (III)-DHMBTSC] complex vs reagent blank; (b). DHMBTSC vs buffer blank.**

TABLE 2 : Physico-Chemical and analytical characteristics of [Ru (III) – DHMBTSC] complex

Characteristics	Results
Colour	Yellow
λ_{max} (nm)	425
pH range (optimum)	2.0-4.0
Mole of reagent required per mole of metal ion for full colour development	10- folds
Molar absorptivity (L.mol^{-1}.cm^{-1})	2.72x 10^{4}
Sandell's sensitivity (µg.cm^{-2})	0.003711
Beer's law validity range (µg/ml)	0.2021 to 2.3246
Optimum concentration range (µg/ml)	0.4042 to 2.1224
Composition of complex (M:L) obtained in Job's and mole ratio method	1: 1
Stability constant of the complex	7.242x 10^{6}
Relative standard deviation (%)(RSD)	0.002
Regression coefficient	0.996

coloured water-soluble complex. The colour reaction between Ru (III) and DHMBTSC are instantaneous even at room temperature in presences of the pH range 2.0 to 4.0 and Triton X-100 (5%) surfacteant solution The absorbance of the yellow coloured species remains stable for more than two hours. The maximum colour intensity is examined at pH 3.0. 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 Ruthenium (III) 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 Ruthenium (III) and DHMBTSC are incorporated in TABLE 2.

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 Ruthenium (III). The effect of different diverse ions in the determination of Ruthenium (III) 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 in accuracy of ± 2 %

TABLE 3 : Tolerance limit of foreign ions in the determination of 0.7580 μg/ml of Ruthenium (III)

Ion added	Tolereance limit (μg/ml)	Ion added	Tolereance limit (μg/ml)
Bromide	1265	Cd (II)	1.34
Iodide	673	Zr (IV)	3.21
Sulphate	1065	Hg (II)	11
Bromide	1134	Pb (II)	9.67
Urea	569	W (VI)	8.3
Ascorbic acid	231	Ca (II)	54
Thiocynate	41	Mo (VI)	27
Citrate	3.0	Zn (II)	33
Thiourea	1.32	Co (II)	52
Na^+	86	Cu (II)	1.1
Ba (II)	62	Ni (II)	18
U (VI)	103	Bi (III)	7.6
Sn (II)	53	Ce (IV)	11.0

TABLE 4

Sample	Amount of Ru (III) (μg/ml)		Error (%)
	Amount added	Amount of found*	
Pb (II) (0.8) + Co (II) (20) + Os (VIII) (8.0)+ Ru (III) (IOO)	0.850	0.839	-0.012
	2.0	1.91	-0.045

Average of the three determinations among five determinations

in the absorbance or amplitude. The outcome results are incorporated in TABLE 3.

APPLICATIONS

Estimation of Ruthenium (III) in sample: Analysis of synthetic alloy sample

A 0.5g sample of the synthetic alloy was digested in 15ml of 2:1 ratio mixture off Conc. HCl and Conc. HNO_3. It was heated until it is dissolved and final volume reduced to 5 ml. 5ml of 5M HCl was added to the above and filtered. Then the filtrate was collected in a 25-ml volumetric flask and made up to the mark. Ruthenium (III) in this solution was determined by the recommended procedure from a pre determined calibration plot, the results obtained are presented in TABLE 4.

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 Ruthenium (III). Molar absorptivity of the colour complexe was 2.72x 10^4 L.mole^{-1}. cm^{-1}. The present derivative method was sensitive when campared with zero order method. The proposed method is especially selective with respect to metals, wich commonly seriously interfere with the estimation of Ruthenium (III) as earlier methods reported. The proposed method can be successfully applied to the estimation of Ruthenium (III) in samples. The present method was favorably compared which eariler reported spectrophotometric[1-23] methods.

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