

Determination of Ruthenium (III) Spectrophotometrically with complexation of a novel and freshly synthesized chromogenic organic reagent 3,4-dihydroxy-5-methoxybenzaldehyde thiosemicarbazone

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Abstract: The proposed a novel chromogenic organic reagent for the determination of Ruthenium (III) is '3,4-dihydroxy-5-methoxybenzaldehydethiosemicarbazone' (DHMBTSC) using Spectrophotometer.

This novel chromogenic reagent forms yellow coloured complex with Ruthenium (III), shown by maximum absorption at λ_{\max} 425nm. The Beer's law validity range 0.2020 to 2.3245($\mu\text{g/ml}$) and optimum concentration range is 0.4042 to 2.1224($\mu\text{g/ml}$). The molar absorptivity and Sandells sensitivity of the complex was found to be $2.73 \times 10^4 \text{ L. mol}^{-1} \cdot \text{cm}^{-1}$ and $0.00372 \mu\text{g/cm}^2$ respectively. The Ruthenium (III) forms M:L (I:I) colour complex with DHMBTSC and stability constant of the complex was found to be 7.239×10^6

Key Words: Chromogenic organic reagent Derivative spectrophotometry; Ruthenium (III) and samples

Introduction:

Studies show that many chromogenic organic reagents were used in determining Ruthenium (III) spectrophotometrically. 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 fluorescence spectroscopy, voltametry, polarography, spectrophotometry and other techniques. Spectrophotometric methods are preferred because the cost of instrument is low, high sensitivity, accuracy results are obtained in the 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

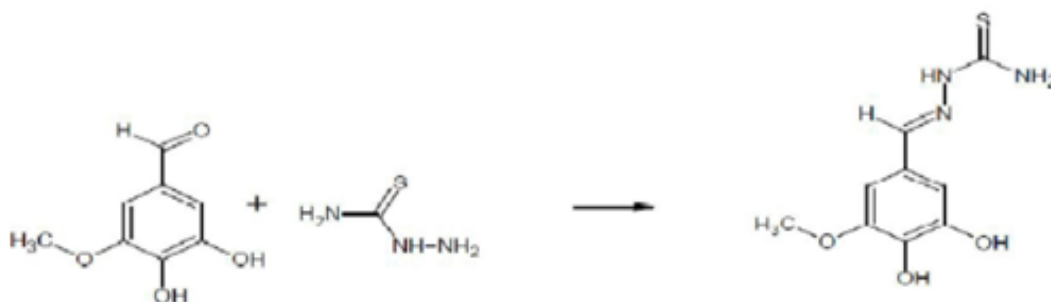


TABLE 1: Analytical properties of DHMBTSC complexes in solution

Metal ion	λ_{\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 benzaldehyde thiosemicarbazone:

3,4 - dihydrox y-5 - methoxybenzaldehyde(0.42035g, 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 recrystallized and dried in a vacuum. Characterization of 3,4-dihydroxy -5-methoxy benzaldehyde thiosemicarbazone was characterized with the help of Infrared, $^1\text{H-NMR}$ 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 vari-ous bufer solutions medium The analytical characteris-tics 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 ($1 \times 10^{-3}\text{M}$) and 0.5 ml of ($1 \times 10^{-2}\text{M}$) 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

Determiration of Ruthenium (III) (zero order)

An aliquot of the colour mixer solution containing $\mu\text{g/ml}$ of Ruthenium (III), 3 ml of buffer solution pH 2.0 to 4.0 and 0.5 ml of ($1 \times 10^{-2}\text{M}$) novel DHMBTSC re-agent were taken in a 10 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 corre-sponding 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 absor-bance at 425 nm, where as the reagent blank does not absorb appreciably.

RESULTS AND DISCUSSION

In the present work 3,4-dihydroxy-5-methoxybenzaldehydethiosemicarbazone(DHMBTSC) analytical reagent is a blend of a carbo-nyl 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

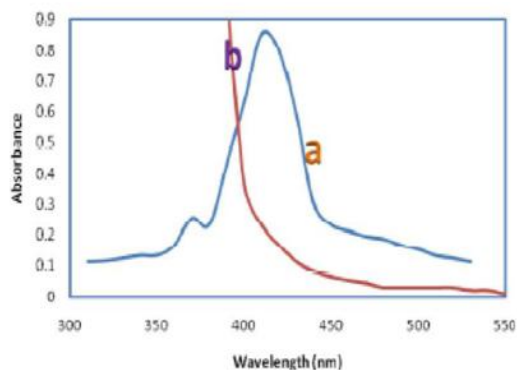


Figure 1 : Absorption spectra, (a). [Ru (III)-DHMBTSC] complex vs reagent blank; (b). DHMBTSC vs buffer blank.

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

Characteristics	Results
Colour	yellow
λ_{max} (nm)	425
pH range (optimum)	2-4
Mole of reagent required per mole of metal ion for full colour development	10 folds
Molar absorptivity (L.mol ⁻¹ .cm ⁻¹)	2.73×10^4
Sandell.s sensitivity ($\mu\text{g.cm}^{-2}$)	0.00372
Beer.s law validity range ($\mu\text{g/ml}$)	0.2020 to 2.3245
Optimum concentration range ($\mu\text{g/ml}$)	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	7.239×10^6
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%) surfactant 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 develop-ment. 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 parameters 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 has 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 $\pm 2\%$ in the absorbance or amplitude. The outcome results are incorporated in TABLE 3.

TABLE 3 : Tolerance limit of foreign ions in the determination of 0.7580 $\mu\text{g/ml}$ of Ruthenium (III)

Ion added	Tolerance limit ($\mu\text{g/ml}$)	Ion added	Tolerance limit ($\mu\text{g/ml}$)
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
Thiocyanate	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

Sample	Amount of Ru (III) ($\mu\text{g/ml}$)		Error (%)
	Amount added	Amount of found*	
Pb (II) (0.8) + Co (II) (20) + Os (VIII) (8.0)+ Ru	0.850	0.835	-0.012

Table-4: Average of the three determinations among five determinations

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 of Conc. HCl and Conc. HNO₃. 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:

It has been proved based on the research work that 3,4 - dihydroxy-5-methoxy Benzaldehyde Thio Semicarbazone (DHMBTSC) is sensitive and selective chromogenic organic reagent in determining the Ruthenium (III). Molar absorptivity of the color complex was $2.72 \times 10^4 \text{ L.mole}^{-1} \cdot \text{cm}^{-1}$. The present derivative method is sensitive when compared with zero order method. The proposed method is especially selective with respect to metals, which 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 with earlier reported spectrophotometric¹⁻²³ methods.

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REFERENCES

- [1] Effect of Triton X-100 on the spectrophotometric determination of Aluminium in the presence of Iron III – Application to various water samples Rafidain Journal of science, 2019, volume 28, Issue 1, pages 29-40
- [2] Biju Mathew, V. mini, Ancy Vinnifred; pelagia re-search library, Der chemica sinica, **1(3)**, 7-14 (2010).
- [3] Development of indirect spectroscopic method for quantification of Cephalaxin in pure form and commercial formulation using complexation reaction Khan.M.N.: Kalsoom.S: Saadiq.M., 2016-01-01.: WorldwodeScience.ORG
- [4] G.ChandraSekhar Reddy, N.Devanna, K.B.Chandrasekhar; International Journal of AppliedBiology and PharmaceuticalTechnology, **2(2)**, 133 (2011).
- [5]. Spectrophotometric determination of samarium(III) with Spectrophotometric determination of samarium(III) with chloride Mustafa Soylak *, Orhan u`rkog`lu Talanta 53 (2000) 125–129 ELSEVIER

- [6] Kiran kumar, M.Rameswar rao, K.B.chandrasekhar, N.Devanna; Asian journal of chemistry, **20(3)**, 2197-2204 (**2008**).
- [7] G.H.Ayres, J.A.Arno; Talanta, **18(4)**, 411-27 (**1971**).
- [8] M.Rameswar rao, K.B.chandrasekhar,N.Devanna; Chem.Met; Alloys, **5**, 42-49 (**2012**).
- [9] Maria Plemicamu, Olimpa Rusa; Indian journal of chemistry, **40A**, 1019-1020 (**2001**).
- [10] D.Gopal kirshna, N.Devanna,K.B.Chandrasekhar; International Journal of Inorganic andBioinorganic chemistry, **1(1)**, 8-12 (**2011**).
- [11] S.G.Kawatkar, P.S.Manoli;Acta Cien.Indica, **24C**,109 (**1998**).
- [12] M.Ramesh, K.B.Chandrasekhar, K.H.Reddy, Indian J.Chem., **39A**, 1337 (**2000**).
- [13] K.H.Reddy, K.B.Chandrasekhar, Indian J.Chem., **40A**, 727 (**2001**).
- [14] B.Chandrasekhar, K.H.Reddy, Indian.J.Chem.,**41A**, 1643 (**2002**).
- [15] N.Devanna, K.P.Satheesh, K.B.Chandrasekhar,Asian.J.Chem, **17**, 1767 (**2005**).
- [16] G.H.Rizvi, B.P.Gupta, R.P.Singh,Anal.Chim.Acta,**54**, 295 (**1971**).
- [17] C.G.R.Veer, Microchim.Acta, **62**, 611 (**1974**).
- [18] N.Kohli, R.P.Singh, Talanta, **21**, 638 (**1974**).
- [20] L.C.Kamra, G.H.Ayres; Anal.Chim. Acta, **81**, 117 (**1976**).