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Microquantitative determination of ruthenium(III) spectrophotometrically using a schiff's base derived from a triazine

***Biju Mathew, Mini .V and Ancy Vinnifred**

Post Graduate Department of Chemistry, Fatima Mata National College, Kollam, Kerala, India

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ABSTRACT

A simple spectrophotometric method is described for the determination of ruthenium(III) using 4 - benzylideneamino -3- mercapto -6- methyl - 1, 2, 4 - triazine (4H) -5- one as the colour developing reagent . Accurate and reproducible results were obtained for 6-18 ppm of Ru(III) . The composition of the complex was studied by Job's method of continous variation and mole ratio method . Results from both the methods reveal the reagent forms ML_3 *type complex with the metal ruthenium. The average value of molar absorptivity and Sandell's sensititivity were computed and are obtained as 1.6545 x* 10^3*Lmol*$^{-1}$ *cm*$^{-1}$ *and 6.143 x* 10^{71} *gcm*$^{-2}$ *respectively. Interference due to various foreign ions were also studied.*

Keywords: Spectrophotometry, Ruthenium determination, triazine, Sandell's sensitivity, Molar absoptivity

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INTRODUCTION

Spectrophotometric method provides a simple means for determining minute quantities of substances. The method is highly sensitive , selective and precise and hence could be used for the determination of all the elements except noble gases . The importance of uv - visible spectrophotometry in inorganic analysis is due to the determination of metal using a variety of complexes with organic and inorganic ligands which absorb in the visible region of spectrum . Ruthenium is a rare and polyvalent hard white transition metal . Small amounts of Ru can increase the hardness of platinum and palladium . The corrosion resistance of titanium is increased markedly by the addition of a small amount of ruthenium [1] . Ruthenium is a versatile catalyst . This is used to remove H_2S from oil refineries[2]. Ruthenium was also suggested as a possible material for microelectronics because its use is compatible with semiconductor processing techniques[3] . Organometallic ruthenium carbene and allenylidene complexes are efficient catalysts for olefin metathesis[4] . Ruthenium complexes shows greater resistance to hydrolysis and has more selective action on tumors. This paper examines the analytical usefulness of 4 - benzylideneamino - 3 - mercapto -6 -methyl 1,2, 4 - triazine (4H) - 5 - one as a spectrophotometric reagent for the determination of ruthenium(III) .

A large number of reagents and various types of spectrophotometric methods were adopted for the microlevel determination of ruthenium. R . P Yaffe and A.F.Viogt [5] conducted the spectrophotometric investigations of some complexes of ruthenium with thiosemicarbazide , 4 - phenylthio semicarbazide and diphenyl thiocarbazide . William .D. Jacobs [6] reported an experiment for the spectrophotometric determination of Ru with N, N' -bis (3 -dimethyl - aminopropyl) dithiooxamide .T. Hara[7] proposed a simple method for the spectrophotometric determination of ruthenium with 1,4- diphenyl thiosemicarbazide and the Beer's law range was 0.5 to 15 ppm . W.L. Belew [8] suggested a method for the spectrophotometric determination of Ru using thiocyanate . Spectrophotometric determination of Ru was done simultaneously with osmium by Eugine .W. Berg [9] . The absorption maxima was at 620nm and the molar absorptivity was 2.47 x 10^{3} Lmol $^{-1}$ cm^{-1} and the method works over the range of 5 to 30 ppm .

P. J Lingane [10] proposed a method for the spectrophotometric determination of ruthenium with dithio oxamide . Molar absorptivity was found to be 1.11 x 10^{4} L mol $^{-1}$ cm^{-1} at 654 nm . The experiment gave good result at pH10. H. Rizvi [11] made use of solvent extraction for the spectrophotometric determination of Ru(III) with tropolone . Ru(III) reacts with tropolone at pH 4.5 to 6 and has an absorption maxima at 415 nm . Beer's law was obeyed in the range 0 to 5.7 ppm . S.C Shone [12] proposed o-hydroxy thiobenzhydrazide as a selective reagent for the spectrophotometric determination of ruthenium .

Nitin Kohli [13] proposed another selective reagent 3- Nitroso -4- hydroxy - 5,6 - benzocoumarian for the spectrophotometric determination of ruthenium . The absorbance maxima was at 520 nm and molar absorptivity value was 1.04 x 10^{4} Lmol^{-1} cm^{-1} . Rapid spectrophotometric determination of ruthenium with diethazene hydrochloride was done by H.S. Gowda [14] at 515nm and the Beer's law was obeyed in the range 1 to 10.4 ppm.

Propericiazine was used as a reagent for spectrophotometric determination of Ru(III) by A . Thimme Gowda [15] . The maximum absorption was found at 511 nm . Spectrophotometric determination of ruthenium after soild phase extraction with 3 - hydroxy -2- methyl -1,4- naphthoquinone - 4 -oxime into microcrystalline P- dichlorobenzene was done by Rakesh Kumar Sharma [16] . Absorbance was measured at 450nm and Beer's law obeyed upto 10.1 ppm of Ru. Molar absorptivity and Sandell sensitivity were 2.7 x 10^{4} dm^{3} mol^{-1} cm^{1} and 0.0037 gcm^{-2} respectively. Another method was developed by M.S.E.I - Shahawi[17] for the detection , semiquantitative and spectrophotometric determination of Ru(III) by solid phase extraction with 3 - hydroxy - 2- methyl -1,4 - naphthoquinone - 4- oxime - loaded polyurethane foam columns . Microamounts of ruthenium was determined by Xingguo [18]. Spectrophotometric determination of ruthenium after soild phase extraction. with some quinoxaline dyes into microcrystalline p-dichlorobenzene was done by Alaa .S. Amin [19] . Beer's law is obeyed upto 2.5 g ml-1 of Ru. Spectrophotometric determination of ruthenium in solutions of nitroso and sulfate complexes using microwave radiation was done by A.V. Bashilov [20].

Mohsen Keyvanfard [21] developed spectrophotometric reaction rate method for the determination of ultra trace amounts of Ru(III) by its catalytic effects on the oxidation of safranin 0 by metaperiodate . The experiment was carried out at pH - 4 . Maximum absorbance was obtained at 521 nm. Catalytic and kinetic spectrophotometric determination of trace amounts of Ru(III) with acridine red and potassium periodate was done by Yang Z.Y. Guo[22] . Derivative Spectrophotometric determination of Ru(III) using cinnamaldehyde isonicotinoyl hydrazone (CINH) was done by Kumar V.K [23].

A method for the catalytic spectrophotometric determination of ruthenium was proposed by Radhey .M.Naik [24] . Maximum abosrbance was at 526 nm . Extractive separation and spectrophotometric determination of traces of from mixtures containing excess Pt group metals was done by Shakuntala S.Sawant [25] . It was determined in the range 1.2 - 4.5 ppm . The molar absorptivity was calculated and was 1.516 x 10^{4} L mol^{-1} cm^{-1}..

MATERIALS AND METHODS

Apparatus

A Systronics uv-visible spectrophotometer -117 with 10mm quartz cell was used for the absorbance and transmittance measurements .For pH measurments Elico pH meter was used.

Reagents and Solutions

All chemicals used were of AR grade.

Ruthenium(III) Stock Solution

A stock solution of ruthenium(III) was prepared by dissolving $RuCl_3$ xH_2O in distilled water along with KCl . The stock solution was standardised using standard methods [26] and working solutions were prepared by suitable and accurate dilutions of the stock solution.

Reagent Solution

The reagent 4 -benzylideneamino-3-mercapto-6-methyl-1,2,4-triazine(4H)- 5-one was prepared by using benzaldehyde and 4 amino - 3 mercapto -6 - methyl- 1,2,4 - triazine (4H)-5-one by the reported procedure[27] . The reagent solution was prepared using doubly recrystallised reagent dissolved in alcohol to make 0.1 % solution.

Buffer Solutions

Buffer solutions of suitable pH were prepared by mixing KCl , HCl , NaOH , Potassium hydrogen phthalate , potassium hydrogen phosphate , borax , $NaHCO_3$ in proper proportions [28] .

Foreign Ion Solutions

Various metal ion solutions were prepared by dissolving Analar grade salts in distilled water or dilute hydrochloric acid . The anion solutions were prepared by dissolving alkali metal salts in distilled water.

PROCEDURE

An aliquot of the Ru(III) solution containing 2-20 ppm was transferred quantitatively into 25 ml standard flask . Excess of 0.1 % alcoholic solution of 4 - benzylideneamino - 3 - mercapto - 6-

methyl - 1, 2, 4 - triazine (4H) - 5 - one was added to the flask and made upto the mark using buffer solution of pH 9 . The solution was mixed very well and the absorbance of the solution was measured at 410 nm, using 10mm matched cells against the reagent blank.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of ruthenium(III) - BMMT complex was studied for a wavelength range of 390nm to 520nm and shown in figure 1 . The coloured Ru(III) - BMMT complex had a maximum absorption at 410nm and at this wavelength the reagent has very small absorbance. At pH 9, ruthenium(III) forms a light yellow coloured complex with BMMT reagent. The complex formation reaction between Ru(III) and the reagent BMMT was found to be fast and the maximum colour was developed instantaneously at room temperature . The colour remains stable for atleast 24 hours and the absorption value has no considerable change.

Effect of pH

Buffer solutions of pH ranging from 1 to 13 were prepared [28] and with these solutions the absorbance of Ru(III) - BMMT complex were studied . It was observed that the absorbance value was maximum for the coloured complex at a pH 9 . Hence for all studies , the pH was maintained at 9.

Effect of metal concentration

Ruthenium(III) solution was treated with various amounts of the reagent to study the effect of metal concentration on the intensity of the colour developed with the reagent. When 2.0 ml of 0.1 % solution was used for 6ppm of ruthenium(III), maximum and constant absorbance was observed.

Beer's law and optimum range

The adherence of Beer's law to the Ru(III) – BMMT system was studied by measuring the absorbance of varying concentrations of Ru(III) solution. A straight line graph was obtained when absorbance was plotted against concentration of metal ion , which passed through the orgin . From the plot, it was found that at 410 nm the Beer's law was valid upto 18 ppm of ruthenium(III). Figure – 2 . The optimum concentration range for maximum precision was deduced from Ringbom's plot [29] . The percentage transmittance was plotted against the logarithm of metal concentration . the linear portion of the curve indicates that the range was 4-16 ppm of Ru (III) Figure -3

Molar absorptivity and sensitivity

The molar absorptivity was calculated from the absorbance of solutions at different concentrations of Ru(III) . The mean value was found to be 1.6545 x 10^3 L mol $^{-1}$ cm $^{-1}$ the Sandell's sensitivity[30] was found to be 6.143 x 10^{-7} g /cm^2

Effect of foreign ions

The absorbance of Ru(III) - BMMT complex was studied in presence of some foreign ions . To a series of same concentration of metal ion and BMMT solutions , ppm solutions of different foreign ions are added . The solutions are made upto the mark using buffer solution of pH 9 in 25ml standard flask . The absorbance was measured and noted against reagent blank solution .

Mn(II), Ce(IV), Zr(IV), Cu(II), V(VI) Mg(II), and Li(I) offered serious interference even at 10 ppm level.

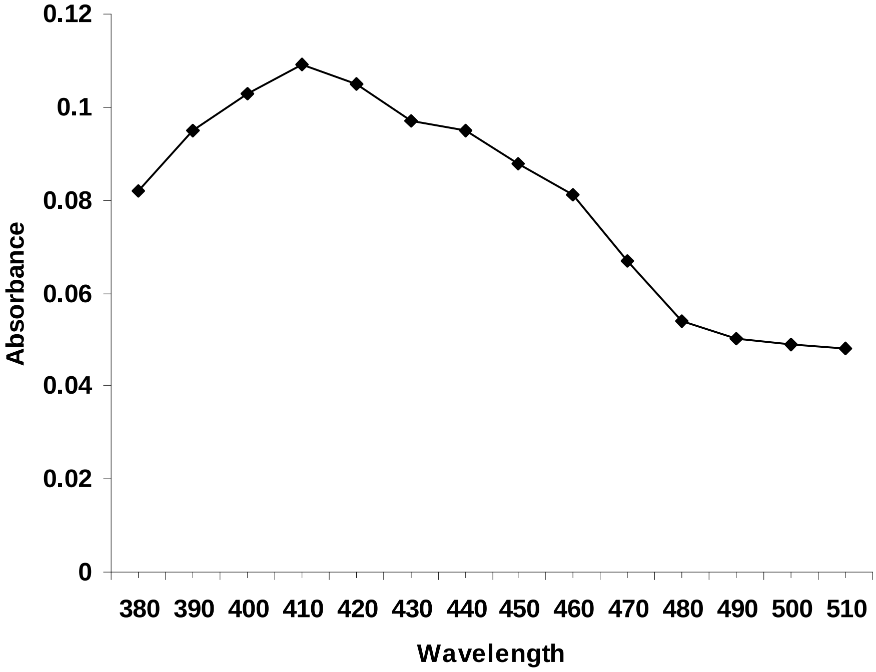

Figure 1 . Absorbtion Spectra of Ru(III) - BMMT System

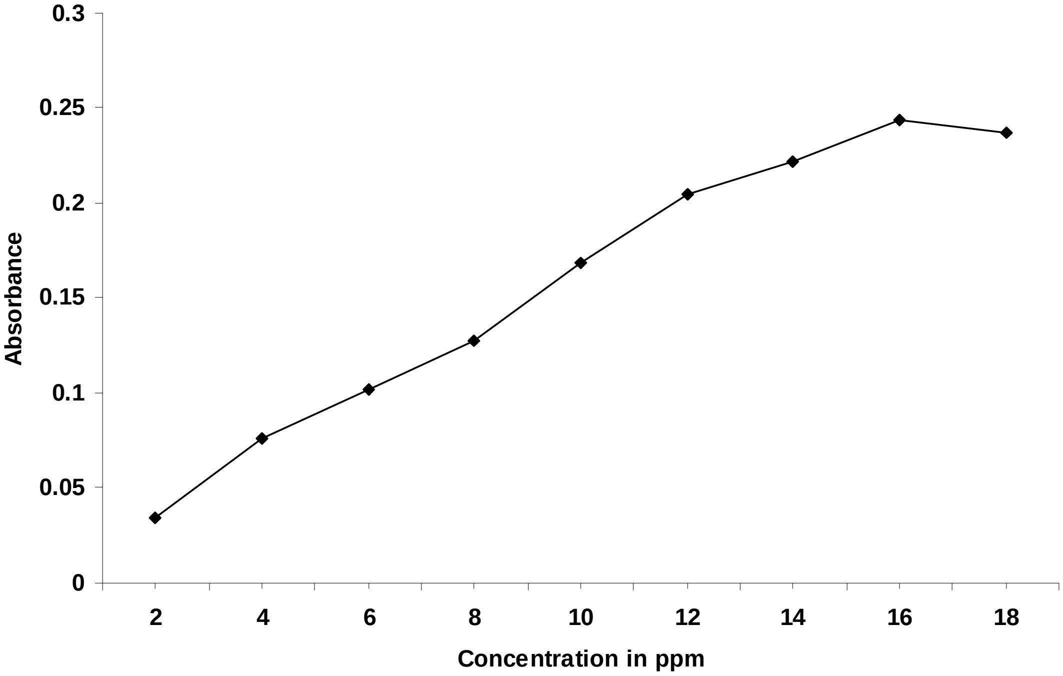

Figure 2 . Verification of Beer's Law for Ru(III) - BMMT System

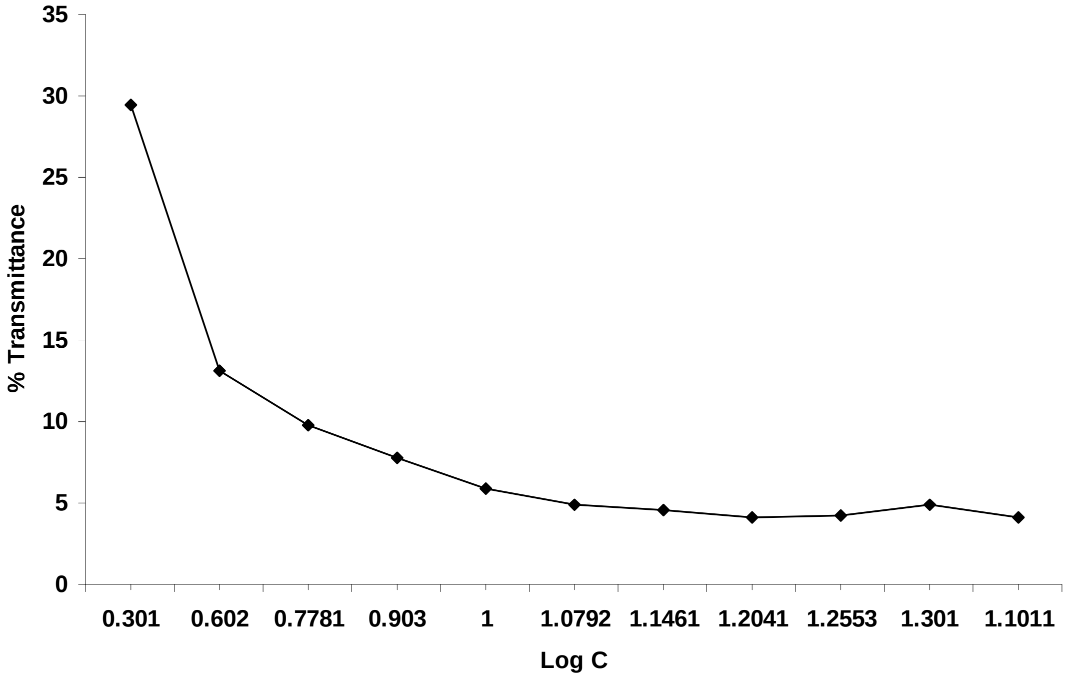

Figure 3 . Ringbom's Plot for Ru(III) - BMMT System

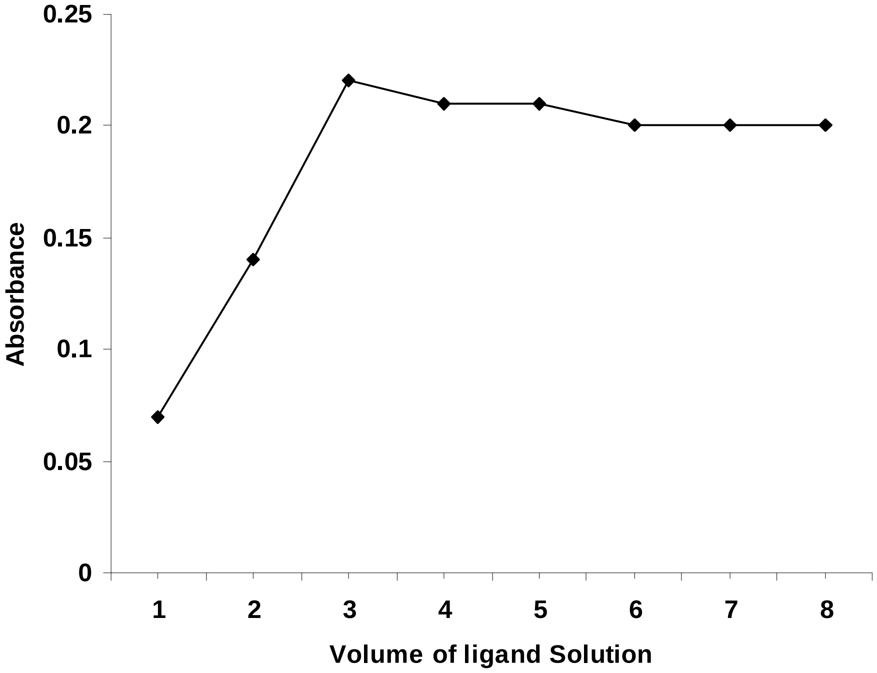

Figure 4 .Mole Ratio Graph for Ru(III) - SMMT System

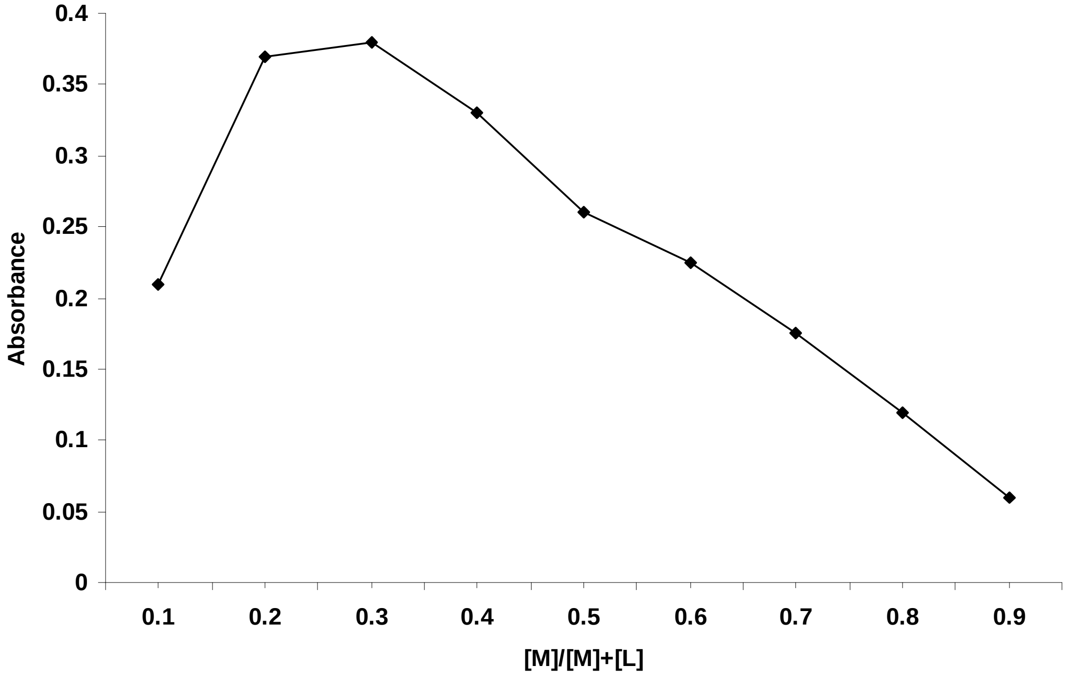

Figure 5 . Continous Variation Graph for Ru(III) - SMMT System

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