

Direct and Derivative Spectrophotometric Determination of Ruthenium(III)

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Abstract: A spectrophotometric method has been developed for the determination of ruthenium (Ru) (III) in an aqueous dimethyl formamide using 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATC) as a chromophoric reagent. The metal ion reacts with HMBATC forming a dark brown colored water soluble complex in the acidic medium. The Ru-HMBATSC complex shows the absorption maximum at 375 nm. However, at this wave length, the reagent shows considerable absorbance. At 390 nm, the complex shows large absorbance while the reagent blank shows negligible absorbance. Hence the analytical studies were carried out at 390 nm. Beer's law is obeyed in the range of 0.50–8.10 $\mu\text{g ml}^{-1}$. The molar absorptivity and Sandell's sensitivity were $0.964 \times 10^4 \text{ lit mol}^{-1} \text{ cm}^{-1}$ and $0.01 \mu\text{g cm}^{-2}$ respectively. The interference effect of various foreign ions has been studied. The complex has 1:1 [Ru(III)-HMBATSC] stoichiometry with a stability constant of 5.8×10^7 . The relative standard deviation of the method is found to be 1.56% (n=10). A first order derivative spectroscopic method is developed for the determination of Ru (III), which is more sensitive than the zero order method. The developed method has been employed for the determination of Ru (III) in synthetic mixtures and water samples.

Key words: Spectrophotometry, HMBATSC, Determination of Ruthenium (III), Applications.

Introduction

Ruthenium is a rare transition metal of the platinum group and is associated with platinum ores. Because of its highly effective ability to harden platinum and palladium, ruthenium is used in platinum and palladium alloys to make severe wear-resistant electrical contacts. It is a versatile catalyst^{1,2} and very recently ruthenium complexes have been used in the detection of proteins³ and chlorpheniramine⁴ and investigated as anticancer drugs⁵. Ruthenium plays no biological role but does strongly stain human skin, may be carcinogenic and bio-accumulates in bone. Ruthenium complexes show greater resistance to hydrolysis and have more selective action on tumors.

Beamish and McBryde^{6,7} are critically reviewed the spectrophotometric methods for determination of ruthenium. Some of the recently developed spectrophotometric methods indicate for the proposal of more new selective spectrophotometric methods⁸⁻¹¹ for determination of ruthenium. The present paper describes a simple, rapid, selective and sensitive method for the determination of micro amounts of ruthenium (Ru-III) in aqueous medium by complexing with 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATC) which has been used for determination of vanadium¹², cobalt¹³, molybdenum¹⁴ and nickel¹⁵ by us.

Experimental

Apparatus

The absorbance and pH measurements were made on a Shimadzu UV-visible spectrophotometer (model UV-160A) fitted with 1-cm quartz cells and Philips digital pH meter (model L1 613) respectively. The pH meter has temperature compensation arrangement and has reproducibility of measurements within ± 0.01 pH.

Reagents and Chemicals

The 2-hydroxy-3-methoxy benzaldehyde and thiosemicarbazide were purchased from SD Fine Chemicals, India. Ruthenium trichloride ($\text{RuCl}_3 \cdot \text{XH}_2\text{O}$) was obtained from (AR, Loba), India. All chemicals and solvents used were of analytical reagent grade, and doubly distilled water was used for preparation of all solutions and experiments.

The preparation and characterization (by IR and NMR spectral data) of the reagent, 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC), has been reported Praveen Kumar *et al.*¹⁶ A 0.01 M solution of the reagent was prepared by dissolving 0.2250 g of HMBATSC in dimethyl formamide (DMF) and diluting to 100 mL with DMF. Lower concentrations were prepared by diluting the appropriate volume of 0.01 M reagent solution.

Ruthenium(III) Solution

Stock solution of Ru(III) chloride (50 mg mL^{-1}) was prepared by dissolving 0.0128 g of ruthenium trichloride in 0.5 M hydrochloric acid and diluting it to 100 mL and the solution was standardized spectrophotometrically¹⁷. The possibility of oxidation of Ru(III) in hydrochloric acid was checked by potassium iodide solution.

Buffer Solutions

The buffer solutions were prepared by mixing 1 M hydrochloric acid and 1M sodium acetate (pH 1.0–3.0), 0.2 M acetic acid and 0.2 M sodium acetate (pH 3.5–7.0).

The working solutions were prepared daily by diluting the stock solution to an appropriate volume. Solutions of the studied interfering ions of suitable concentrations were prepared using analytical grade reagents.

General procedure

Direct spectrophotometry

In each of a set of different 10 mL standard flasks, 5 mL buffer solution (pH 2.5), varying volumes of 1×10^{-3} M Ru(III) solution and 1 mL of HMBATSC (1×10^{-2} M) were taken and the volume was made up to the mark with doubly distilled water. The absorbance was measured at 390 nm against the reagent blank. The calibration curve was constructed by plotting the absorbance against the amount of Ru(III). The calibration graph follows the straight line equation $Y = a c + b$; where c was the concentration of the solution, Y was measured absorbance or peak height and a and b were constants.

First order derivative method

For the above solutions, first order derivative spectra were recorded with a scan speed of fast (nearly 2400 nm min^{-1}); slit width of 1 nm with one degree of freedom, in the wavelength range 370–430 nm. The derivative peak height was measured by the peak-zero method at 382 nm. The peak height was plotted against the amount of Ru(III) to obtain the calibration.

Results And Discussion

Direct spectrophotometry

Ru(III) reacts with HMBATSC in acidic buffer medium forming a dark brown colored water soluble complex. The effect of pH on the intensity of color formation was studied to optimize the pH of Ru(III) complex. The results indicate the absorbance was maximum and constant in the pH range of 2.0–3.0. Hence the pH 2.5 was chosen for further studies.

The absorption spectra of the solution containing Ru(III) complex against the reagent blank and that of the reagent solution against the corresponding buffer blank were recorded in the wavelength region 340–600 nm. The Ru(III) complex has an absorption maximum at 375 nm. However, at this wave length, the reagent shows

considerable absorbance. At 390 nm, the complex shows large absorbance while the reagent blank shows negligible absorbance. Hence the analytical studies were carried out at 390 nm.

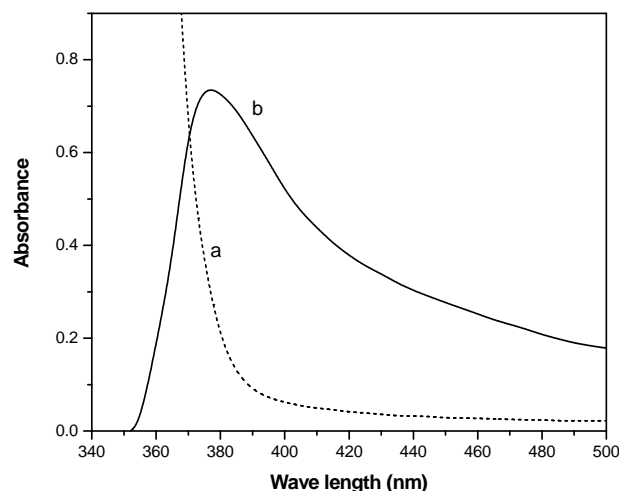


Fig. 1. Absorption spectra of (a) HMBATSC Vs Buffer blank; (b) [Ru(III) - HMBATSC] Vs reagent blank; [Ru(III)] = 1×10^{-4} M; [HMBATSC] = 1×10^{-3} M; pH = 2.5

A 10 fold molar excess of HMBATSC was necessary for Ru(III) complex and constant color development. Excess of the reagent has no effect on the absorbance of the complex. The color reaction between Ru(III) and HMBATSC was instantaneous at room temperature. The absorbance of the complex was found to be constant for more than 72 hours.

For the possible determination of ruthenium at micro levels, the absorbance of the solutions containing different amounts of metal ion was measured. The linear plot between the absorbance and the amount of Ru(III) gives the straight line which obeys the equation $A = 0.4850C + 0.0100$. From the calibration plot, it is observed that in the present method, Beer's law is obeyed in the range of $0.50\text{--}8.10 \mu\text{g ml}^{-1}$. The molar absorptivity and Sandell's sensitivity were $0.964 \times 10^4 \text{ lit mol}^{-1} \text{ cm}^{-1}$ and $0.01 \mu\text{g cm}^{-2}$ respectively.

The effect of various foreign ions that are generally associated with ruthenium ion on its determination under optimum conditions developed was studied and the results are presented in **Table 1**.

From the Table 1, it was observed that many of anions and some cations do not interfere even they are present in more than 50 fold excess. Chloride was tolerable up to 20-fold excess. The metal ions Pt(IV), Au(II) and Cu(II) interfere in 4-fold excess. Ag(I), Pd(II) and V(V) interfere in 2-fold excess. However, in presence of $1760 \mu\text{g ml}^{-1}$ of ascorbic acid, V(V) and Au(III) were tolerable up to 30-fold excess. In the presence of $1400 \mu\text{g ml}^{-1}$ of tartrate Pt(IV) and Cu(II) were tolerable in 20-fold excess and 14-fold excess respectively. Ag(I) and Pd(II) were tolerable up to 24-fold and 16-fold respectively in presence of $1200 \mu\text{g ml}^{-1}$ of citrate.

The composition of the complex was determined using Job's method and confirmed by molar ratio method. The results indicate a 1:1 stoichiometry between the metal ion and the reagent under the experimental conditions. Molar ratio method results confirm a 1:1 complex formation between the metal ion and the reagent. The stability constant of the complex was calculated from Job's method and obtained as 5.8×10^7 .

Table 1. Tolerance limits of foreign ions

Diverse ion	Tolerance limit (~gml ⁻¹)	Diverse ion	Tolerance limit (~gml ⁻¹)
Ascorbic acid	1760	U (VI)	600
Tartrate	1400	Cd (II)	560
Citrate	1200	K (I)	410
EDTA	1150	Ce (IV)	340
Sulphate	960	Mg (II)	280
Bromide	800	Mo (VI)	250
Nitrate	620	Ti (IV)	240
Urea	570	V (V)	10, 150 ^a
Thiosulphate	560	Al (III)	135
Iodide	500	Zn (II)	130
Formate	450	Ag (I)	10, 120 ^c
Bromate	420	Au (III)	20, 100 ^a
Thiourea	380	Pb (II)	105
Fluoride	320	Pt (IV)	20, 100 ^b
Phosphate	250	Pd (II)	10, 80 ^c
Oxalate	220	Cu (II)	20, 68 ^b
Acetate	150	Ni (II)	60
Chloride	100	Co (II)	60
	V (IV)	50	
	Fe (II)	44	

^aIn the presence of) 1760 μgml^{-1} of ascorbic acid; ^b1400 μgml^{-1} of tartrate; ^c1200 μgml^{-1} of citrate.

First order derivative method

The first derivative spectra of experimental solutions containing different amounts of Ru(III) were recorded in the wavelength region 370–430 nm (Fig. 1). The derivative curve shows a peak at 382 nm. At this wavelength, the derivative amplitudes were proportional to the amount of Ru(III) in the range 0.25–16.2 $\mu\text{g ml}^{-1}$. The standard deviation of the method for ten determinations of 1.01 $\mu\text{g ml}^{-1}$ of Ru(III) was ± 0.0019 .

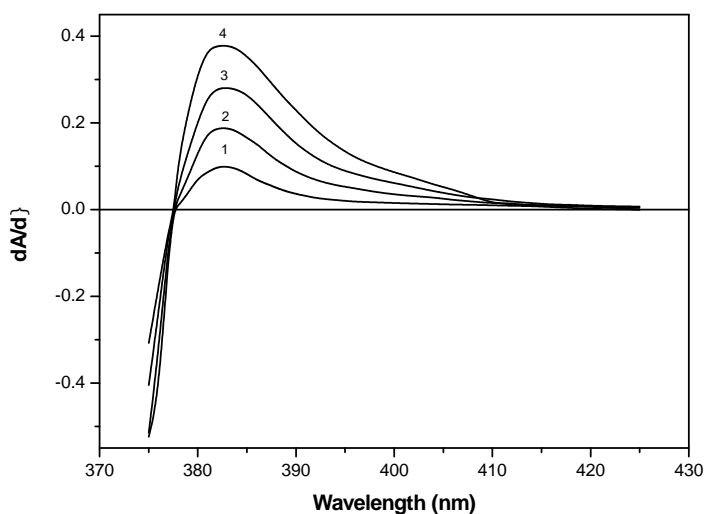


Fig. 2. First derivative spectra of Ru(III) – HMBATSC Vs reagent blank; Ru(III) ($\mu\text{g ml}^{-1}$) = (1) 1.01; (2) 2.02; (3) 3.03; (4) 4.04

The effect of various cations and anions on the derivative amplitude was studied and noticed that all the ions that did not interfere in the zero order determinations of Ru(III) (Table 1) also did not interfere in the first order

derivative method. The metal ions Pt(IV) and Cu(II) interfere in all the derivative spectrophotometric methods. Ag(I), Pd(II) and Au(III) which interfered in 2-fold and 4-fold excess respectively in zero order method, were tolerable in 10-fold excess in the second and third order derivative methods.

Applications

Determination of Ru(III) in synthetic mixtures

Molten Zinc and Zn-Mg alloy are used as solvents in the separation of Uranium from ruthenium and other fission products in experimental Breeder-reactor-II (EBR-II). Hence, determination of ruthenium in the presence of zinc and magnesium forms an important method. The present method was applied for the determination of ruthenium in the synthetic mixture of Zn-Mg alloy which was prepared by mixing the specified amounts of the metal salts¹⁷. Ru(III) contents in these mixtures were determined by the present method and from predetermined calibration plot and results are presented in Table 2.

Table 2. Determination of ruthenium in Zn-Mg alloy

Zinc added (mg)	Magnesium added (mg)	Amount of ruthenium (~g)		Relative error (%)
		Added	Found*	
50	-	6.00	6.04	+0.67
-	50	6.00	5.98	-0.34
20	20	4.00	3.97	-0.75
20	20	2.00	2.03	+1.5

* Average of five determinations.

Determination of Ru(III) in synthetic mixtures and water samples

The water samples were collected in a clean 2 L beaker and slowly evaporated to about 25 mL. Five mL of H₂O₂ were added and evaporated to dryness¹⁸. It was then dissolved in 2 mL of water and filtered to remove the insoluble substance. The filtrate was collected in a 100 mL volumetric flask quantitatively added a known amount of Ru(III) and diluted to the mark with distilled water. The amounts of Ru(III) were evaluated using the proposed first order derivative method by measuring the first derivative amplitude at 382 nm. The results are presented in Tables 3 and indicate good recoveries of Ru(III) in all samples.

Table 3. Determination of Ru(III) in water samples

Samples (drinking water)	Amount of ruthenium (~g ml ⁻¹)		Recovery(%)
	Added	Found*	
1	0.303	0.311	102.64
2	0.606	0.612	100.99
3	1.212	1.205	99.42
4	1.818	1.824	100.34

* Average of five determinations.

Conclusions

A simple and sensitive spectrophotometric method was developed for the determination of Ru(III). The proposed method can be used for the determination of trace amounts of Ru(III) in synthetic mixtures and water samples as the most of the metal ions do not interfere with the determination. The first order derivative method for the determination of trace amounts of Ru(III) was more sensitive than zero order method.

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