

Determination of ruthenium(III) in the presence of micellar medium by derivative spectrophotometric technique

M. RAMESWARA RAO^{1*}, K.B. CHANDRASEKHAR², N. DEVANNA³

¹ Department of Quality Control, Chemical Technical Operations Unit-1, Dr. Reddy's Laboratories Pvt. Ltd, Bollaram, Jinnaram, Medak (Dist) -502325, India

² Department of Chemistry, Jawaharlal Nehru Technological University Anantapur, College of Engineering, Anantapur-515002, Andhrapradesh, India

³ Oil Technological Research Institute, Jawaharlal Nehru Technological University Anantapur, Anantapur-515002, Andhrapradesh, India

* Corresponding author. Tel.: +91-9885282328; e-mail: raamesh_1120@yahoo.co.in

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A sensitive spectrophotometric method has been developed for the determination of ruthenium(III) using 3,5-dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH) in presence of neutral micellar medium of Triton X-100. The metal ion forms a brownish yellow coloured water soluble complex with the DMHBIH reagent in acidic buffer pH 4.25. Spectral data shows the formation of an 1:1 (M:L) complex with a stability constant 1.82×10^6 . Beer's law is obeyed over a concentration range of 0.202 to 4.043 $\mu\text{g/mL}$ of Ru(III) at 390 nm. The molar absorptivity and Sandell's sensitivity are calculated to be $1.7 \times 10^4 \text{ L.mol}^{-1}.\text{cm}^{-1}$ and $0.006 \mu\text{g.cm}^{-2}$ Ru(III) respectively. The developed derivative spectrophotometric method was employed for the determination of Ru(III) in synthetic alloy samples and real water samples. The effect of various diverse ions has also been studied.

Derivative spectrophotometry / Ruthenium(III) / 3,5-dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH) / Synthetic alloy samples / Real water samples

Introduction

Ruthenium is a hard white metal. It does not transit at room temperature, but oxidizes explosively at high temperatures. The metal is not attacked by hot or cold acids or aqua-regia. The oxidation states of ruthenium range from +1 to +8, though oxidation states of +2, +3 and +4 are most common. The chief source of ruthenium is osmiridium, in which it ranges from 0.2% to about 20%. Ruthenium has highly effective ability to harden platinum and palladium and it is alloyed with these metals to make electrical contacts for severe wear resistance. The corrosion resistance of titanium is improved a hundred-fold by addition of 0.1% ruthenium. Ruthenium is used as a catalyst in some platinum alloys. The compound rutheniumtetroxide (RuO_4) is highly toxic similar to osmiumtetroxide (OsO_4) and may explode. Ruthenium does strongly stain human skin, may be carcinogenic and bio-accumulates in bone.

Hydrazones are important organic analytical reagents for the determination of metal ions in

microgram quantities. They react with metal ions forming colour complexes and act as chelating agents. The potential applications of hydrazone derivatives for the spectrophotometric determination of metal ions have been reviewed by Singh *et al.* [1]. Few hydrazone reagents were used for the spectrophotometric determination of ruthenium(III) [2-5]. The great interest towards derivative spectrophotometry is due to the increased resolution of spectral bands, allowing the detection and location of the wavelengths of poorly resolved components of complex spectra and reducing the effect of spectral background interferences. Derivative spectrophotometric methods for the determination of metal ions are not exploited much [6-9]. In the light of the good analytical characteristics of hydrazones, herein we report zero, first and second order derivative spectrophotometric determination of Ru(III) using 3,5-dimethoxy-4-hydroxybenzaldehydeisonicotinoyl-hydrazone (DMHBIH) in presence of Triton X-100, a neutral (nonionic) surfactant medium.

Experimental

Apparatus

A Shimadzu 160A, microcomputer-based UV-VIS spectrophotometer equipped with 1.0 cm quartz cells was used for all spectral measurements. The instrumental parameters were optimized and the best results were obtained with a scan speed of 145 nm/min, slit width of 1.0 nm and $\Delta\lambda = 2$ nm for the first order derivative mode in the wavelength range 350 nm to 650 nm. An ELICO LI-120 digital pH-meter was used for the pH adjustments. The reproducibility of the measurements is within 0.01 pH. Sartorius BS/BT 2245 model (Germany make) electronic analytical balance having maximum capacity of 220 g and sensitivity of ± 0.1 mg was used for weighing purpose.

Reagents

All chemicals used were of A.R. grade unless stated. All solutions were prepared with distilled water.

Ruthenium(III) stock solution

The standard ruthenium(III) solution (1×10^{-2} M) was prepared by dissolving 0.2076 g of ruthenium chloride (RuCl_3 , A.R. LOBA) in minimum amount of dilute hydrochloric acid and diluted up to the mark using distilled water in a 100-mL standard flask. The stock solution was standardized spectrophotometrically [10].

Triton X-100 solution

Aqueous solution of 5% Triton X-100 was prepared by diluting 5.0 mL of Triton X-100 (GR Merck) to 100 mL with distilled water.

Buffer Solutions

Buffer solutions were prepared by 1.0 M hydrochloric acid – 1.0 M sodium acetate (pH 0.5-3.5); 0.2 M acetic acid – 0.2 M sodium acetate (pH 4.5-7.0); 0.25 M sodium tetraborate decahydrate – 0.1 M hydrochloric acid (pH 8.0-9.1); 0.25 M sodium tetraborate decahydrate – 0.1 M sodium hydroxide (pH 9.2-10.8). Solutions of various diverse ions of suitable concentrations were prepared using A.R. grade chemicals.

Synthesis of 3,5-dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH)

The reagent 3,5-dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH) was synthesized by refluxing equimolar amounts of 3,5-dimethoxy-4-hydroxy benzaldehyde and isonicotinoylhydrazide. In a 250-mL round bottom flask hot ethanolic solutions of 3,5-dimethoxy-4-hydroxybenzaldehyde (1.8218 g, 0.01 mole) and isonicotinoylhydrazide (1.3714 g, 0.01 mole) are mixed and refluxed using a water condenser for 5 h. On cooling the reaction mixture, a light greenish coloured crystalline product was separated out, collected by filtration and washed

several times with (20%) ethanol in water and dried in vacuo. The resulting hydrazone was re-crystallized by using ethanol (yield, 76%; mp 221°C).

The infrared spectrum of the reagent shows bands at ν (cm^{-1}) 3429.03 (NH), 2924.16 (OH), 1658.62 ($>\text{C}=\text{O}$), 1578.92 (C=N), 1514.12 (C=N pyridine ring), 1372.71 (N-H primary amide). The ^1H NMR (200 MHz) spectrum of the reagent was recorded in DMSO solvent. It shows signals corresponding to δ 11.9 (s, 1H, NH), 8.97 (s, 1H, OH phenolic), 8.78 (d, 2H, ArH pyridine ring), 8.34 (s, 1H, N=C-H), 7.8 (d, 2H, ArH pyridine ring), 7.01 (s, 2H, ArH aldehydic), 3.8 (s, 6H, $-\text{OCH}_3$ (2 methoxy)), 3.3 (s, 2H, water in solvent), 2.5 (s, 6H, DMSO solvent). The mass spectrum shows a molecular ion peak at m/z 302.2 (M+1). The structure of DMHBIH was confirmed based upon above IR, NMR and mass spectral data, given in Fig. 1. The product is sparingly soluble in methanol but easily soluble in dimethylformamide (DMF) and dimethylsulfoxide (DMSO). Hence, reagent stock solution (0.01 M) was prepared by dissolving 301.30 mg of DMHBIH in 100 mL of DMF. The reagent solution is stable for 48 h.

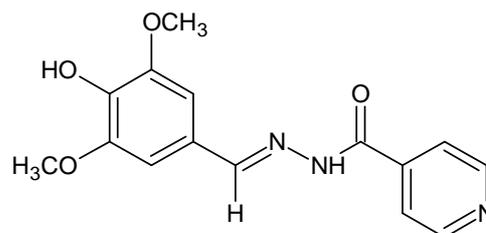


Fig. 1 Structure of 3,5-dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH).

Analytical properties of DMHBIH

The reactions of some important metal ions were tested at different pH values. The samples were prepared in 25-mL volumetric flasks by adding 10 mL of buffer solution (pH 1.0-11.0), 0.5 mL of 1×10^{-3} M metal ion, 1.0 mL of Triton X-100 (5%) and 0.5 mL of 1×10^{-2} M DMHBIH reagent solution. The mixture was diluted up to the mark with distilled water. The absorbance was measured in the 350-700 nm range against reagent blank. The results are summarized in Table 1.

Recommended procedures

Determination of ruthenium(III) (zero order)

An aliquot of the solution containing 0.202 to 4.043 $\mu\text{g/mL}$ of Ru(III), 10 mL of buffer pH 4.25, 1.0 mL of Triton X-100 (5%) and 1.0 mL of DMHBIH reagent 1×10^{-2} M were taken in a 25-mL volumetric flask and the solution was diluted up to the mark with distilled water. The absorbance of the solution was recorded at 390 nm in a 1.0-cm cell

against reagent blank prepared in the same way but without metal ion. The measured absorbance was used to compute the amount of ruthenium(III) from the calibration plot.

Determination of Ru(III) by first order derivative spectrophotometry

For the above solution of Ru(III)-DMHBIH a first order derivative spectrum was recorded with a scan speed having degrees of freedom 9 in the wavelength range 350 nm to 600 nm. The first order derivative peak height (*h*) was measured by the peak-zero method at 426 nm. The peak height was plotted against the amount of Ru(III) to obtain the calibration curve.

Determination of Ru(III) by second order derivative spectrophotometry

For the above solution, second order derivative spectrum of Ru(III)-DMHBIH system was recorded with reference to reagent blank in the wavelength range 350 nm to 600 nm. In the second order derivative spectrum the peak height at 438 nm was measured from the zero line of the spectrum. Calibration plots were constructed by plotting the derivative amplitude against the amounts of ruthenium(III).

Analysis of alloy samples

0.5 g sample of alloy was digested in 15 mL of aqua-regia by warming and the solution was evaporated to dryness. The residue was dissolved in 10 mL of

diluted HCl and the resulting solution concentrated to 5.0 mL, diluted to 50 mL with distilled water, filtered and made up to the mark in a 100-mL volumetric flask.

Real water samples

Each filtered (with whatman No. 40) river water sample (250 mL) was mixed with 10 mL of concentrated nitric acid in a 500-mL distillation flask. The sample was digested in the presence of excess potassium permanganate solution according to the method recommended by Fifield *et al.* [11]. The solution was cooled and neutralized with a dilute NH₄OH solution. The digest was transferred into a 25-mL standard flask and diluted up to the mark with distilled water.

Results and discussion

The reagent DMHBIH was easily synthesized as any other Schiff base reagent. So far the new chromogenic reagent DMHBIH was not used for the determination of Ru(III). The de-protonation constants of DMHBIH have been determined by recording UV-Visible spectra of μM ($1.2 \times 10^{-6} \text{ M}$) at various pH values [12] and by taking the arithmetic mean of the values obtained from the measurements at five different wavelengths. The values of de-protonation of the ligand are 5.1 (pK_1) and 8.2 (pK_2). The possible species that may be formed at different pH values are shown in Fig. 2.

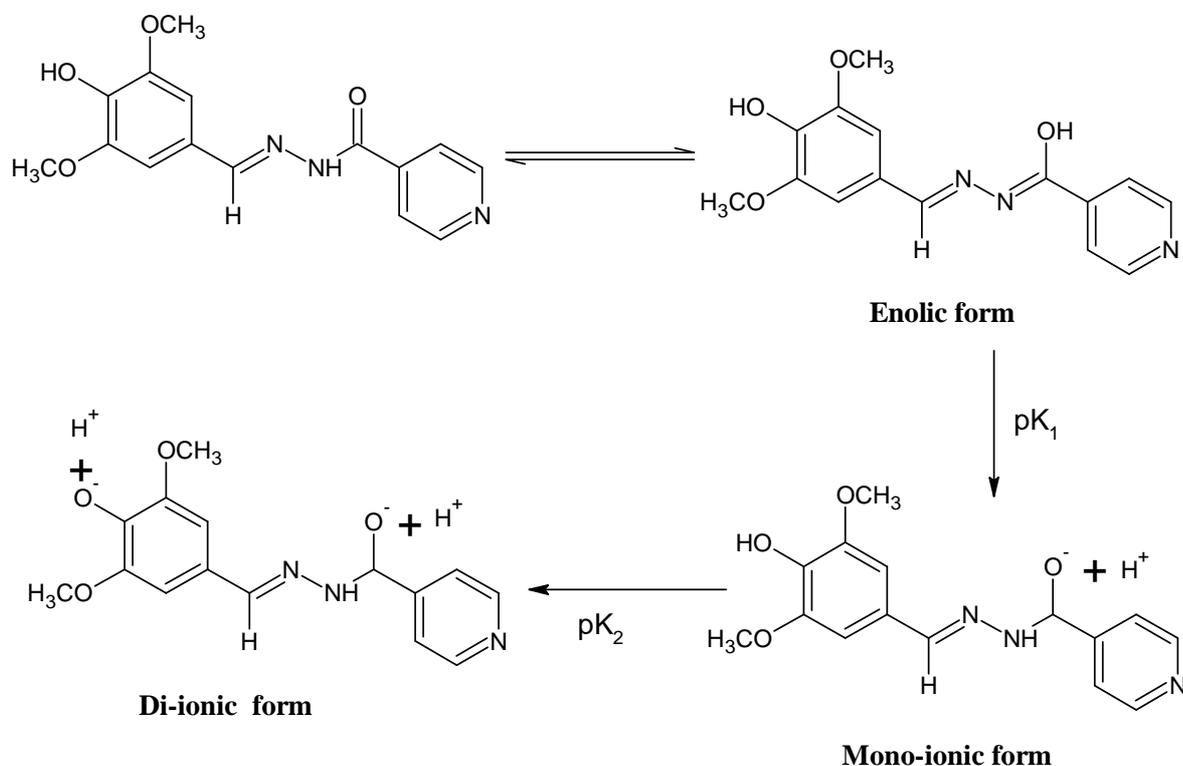


Fig. 2 Different species of DMHBIH at different pH values.

In acidic medium, the ligand presumably exists in enolic form and co-ordinates the metal ion as mono-anion to give neutral complexes. The colour reactions of some important metal ions with DMHBIH are summarized in Table 1. The colour reactions are mainly due to complex formation of DMHBIH with divalent, trivalent metal ions such as Pd(II), Cu(II) Au(III) and Ru(III) in acidic medium to give intense coloured complexes.

Absorption spectra

The absorption spectra of the DMHBIH reagent and [Ru(III)-DMHBIH] complex recorded in optimum conditions against buffer solution and reagent blank, respectively, are shown in Fig. 3. The complex shows absorption maximum at an analytical wavelength of 390 nm, where the reagent does not show appreciable absorbance. Therefore, analytical wavelength 390 nm was used for all measurements.

Effect of pH

The effect of pH on the colour reaction was studied and the optimum pH was established for the reaction mixture by employing the recommended procedure. A plot was made between pH and absorbance of the complex at 390 nm and shown in Fig. 4.

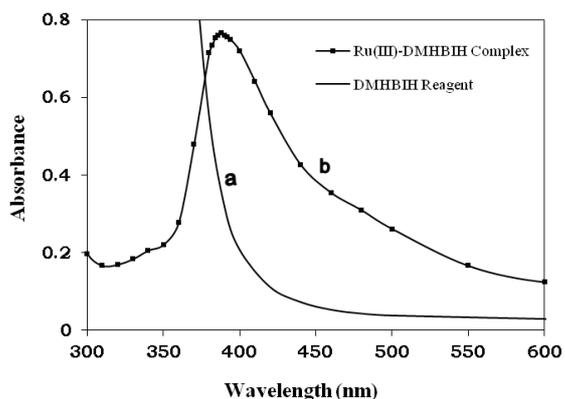


Fig. 3 Zero order absorption spectra.

- a) Reagent DMHBIH vs. water blank.
b) Ru(III)-DMHBIH complex vs. reagent blank. Ru(III) = 4.043 $\mu\text{g/mL}$, DMHBIH = 4×10^{-4} M, buffer pH = 4.25, Triton X-100 = 0.2%.

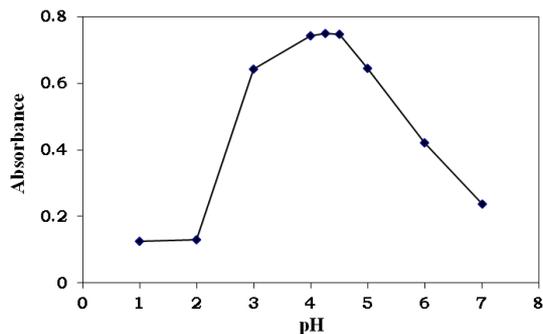


Fig. 4 Effect of pH on the absorbance of the Ru(III)-DMHBIH complex. Ru(III) = 4.043 $\mu\text{g/mL}$, DMHBIH = 4×10^{-4} M, buffer pH = 1.0 - 7.0, Triton X-100 = 0.2%, wavelength = 390 nm.

Ruthenium(III) reacts with DMHBIH in acidic buffer to give a brownish yellow coloured water soluble complex. The colour reaction between ruthenium(III) and DMHBIH was instantaneous even at room temperature in the pH range 2.0 to 6.0, the maximum colour intensity is observed at pH 4.25. Hence, pH 4.25 was kept constant throughout the experiment.

Effect of time

The absorbance of the solution was measured at different time intervals to ascertain the stability of the coloured complex. The colour reaction between Ru(III) and DMHBIH is instantaneous at room temperature. A slow decrease in absorbance of the coloured species is observed after 20 minutes. The stability of the complex was increased by adding neutral surfactant. The absorbance of the Ru(III)-DMHBIH complex remains constant more than 3 h in presence of the neutral surfactant Triton X-100.

Effect of surfactants

The effect of various surfactants such as Triton X-100, sodium dodecyl benzene sulphonate (SDBS) and cetyl trimethyl ammonium bromide (CTAB) on the absorption profiles of the Ru(III)-DMHBIH system has been investigated and presented in Table 2. In presence of Triton X-100 the complex is more stable and exhibited maximum absorbance. Hence, Triton X-100 is selected for further studies.

Table 1 Characteristics of DMHBIH complexes in solution.

Metal ion	λ_{max} (nm)	pH	Surfactant used	Colour of the complex	Molar absorptivity ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)
Pd(II)	382	5.5	Triton X-100	Bright yellow	2.44×10^4
Cu(II)	400	8.0	Triton X-100	Bright yellow	1.08×10^4
Au(III)	384	4.0	SDBS	Yellow	2.9×10^4
Ru(III)	390	4.25	Triton X-100	Brownish yellow	1.7×10^4

Effect of Triton X-100

A study on the effect of volume of Triton X-100 on the absorbance of the complex indicates that absorbance of the metal complex remains constant over a range of 1.0 mL to 4.0 mL of Triton X-100 (5%). Therefore, 1.0 mL of Triton X-100 (5%) was sufficient in all analytical studies. Triton X-100 serves to stabilize and sensitize the metal complex.

Effect of DMHBIH concentration

On varying the volume of reagent DMHBIH (1×10^{-2} M) from 0.5 mL to 4.0 mL, constant absorbance was obtained from 1.0 mL to 4.0 mL. Therefore, a 10-fold molar excess of DMHBIH reagent is essential for complete and constant colour development. Excess of reagent has no effect on the absorption of the complex.

Order of addition of reactants

The order of addition of metal ion, DMHBIH reagent, buffer solution and surfactant has no adverse effect on the absorbance of the Ru(III)-DMHBIH coloured complex.

Calibration graphs and analytical characteristics

The system obeyed Beer's law in the range 0.202 to 4.043 $\mu\text{g/mL}$ of Ru(III) with excellent linearity in terms of correlation coefficient value ($r = 0.99$). However, the practical range of determination of Ru(III) obtained from Ringbom's curve is 0.809 to 3.639 $\mu\text{g/mL}$ at 390 nm. The molar absorptivity and Sandell's sensitivity of the Ru(III)-DMHBIH complex

are $1.7 \times 10^4 \text{ L.mol}^{-1}.\text{cm}^{-1}$ and $0.006 \mu\text{g.cm}^{-2}$, respectively. The specific absorptivity of the complex is $0.17 \text{ mL.g}^{-1}.\text{cm}^{-1}$. The precision of the method in terms of relative standard deviation ($n = 10$) for the determination of 2.021 $\mu\text{g/mL}$ of Ru(III) is 0.03%. Important analytical parameters of Ru(III)-DMHBIH are summarized in Table 3.

Composition and stability of the complex

The composition of the complex is determined by Job's continuous variation method and mole ratio method and found to be 1:1 [Ru(III): DMHBIH]. The stability constant of the complex is determined as 1.82×10^6 by Job's method.

Derivative spectrophotometry is a useful technique because it decreases the interference, *i.e.* increases the tolerance limit value of foreign ions and may be advantageously used for the determination of metal ion having overlapping spectra. The conceptual simplicity, relatively quick and easy realization, increased selectivity in the analysis of minor components, are the main reasons why the interest in derivative spectra is constantly growing for practical applications. The recommended derivative procedure has been employed for the determination of Ru(III) using DMHBIH.

The first order and second order derivative spectral graphs are shown in Fig. 5 and Fig. 6, respectively. This shows that, the derivative amplitude measured at 426 nm for first order and 438 nm for second order were found to be proportional to the amount of ruthenium(III).

Table 2 Effect of various surfactants on the Ru(III)-DMHBIH complex.

Surfactant (5%)	Nature of surfactant	Absorbance at 390 nm
None	–	0.685
Triton X-100	Neutral	0.760
CTAB	Cationic	0.628
SDBS	Anionic	0.470

Table 3 Important analytical parameters of the Ru(III)-DMHBIH complex.

Parameter	Results		
	Zero order	First order derivative	Second order derivative
λ_{max} (nm)	390	426	438
Detection limit ($\mu\text{g/mL}$)	0.0846	–	–
Limit of quantization ($\mu\text{g/mL}$)	0.2537	–	–
Beer's law range ($\mu\text{g/mL}$)	0.202-4.043	0.202-4.447	0.202-4.447
Regression equation $Y = a + bx$			
Slope (b)	0.1631	0.0398	0.0218
Intercept (a)	0.0791	0.0296	0.0191
Correlation coefficient (r)	0.9988	0.9981	0.9971

Effect of diverse ions

The effect of various diverse ions in the determination of Ru(III) was studied 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 required to cause an error $\pm 2\%$ in the absorbance or amplitude. The results are given in Table 4.

The data obtained in the derivative method is also incorporated. The data suggests that larger amounts of many anions such as bromide, iodide and urea do not interfere when they present more than 1000 $\mu\text{g/mL}$.

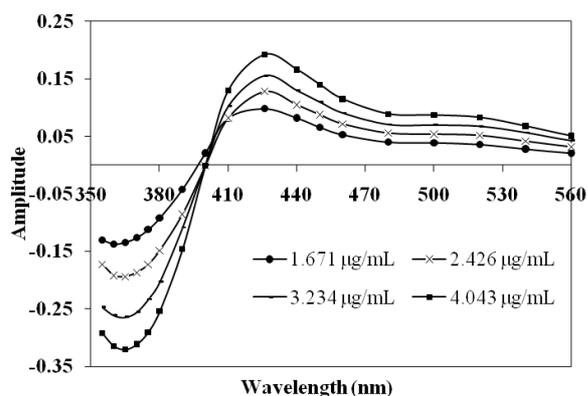


Fig. 5 Typical first order derivative spectra of Ru(III)-DMHBIH complex vs. reagent as blank. Ru(III) = 1.671, 2.426, 3.234, 4.043 $\mu\text{g/mL}$, DMHBIH = 4×10^{-4} M, buffer pH = 4.25, Triton X-100 = 0.2%.

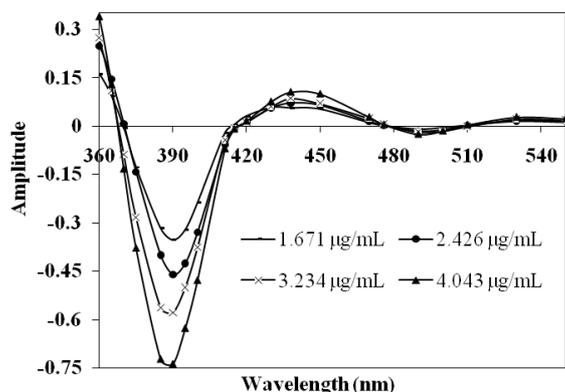


Fig. 6 Typical second order derivative spectra of Ru(III)-DMHBIH complex vs. reagent as blank. Ru(III) = 1.671, 2.426, 3.234, 4.043 $\mu\text{g/mL}$, DMHBIH = 4×10^{-4} M, buffer pH = 4.25, Triton X-100 = 0.2%.

Table 4 Tolerance limit of foreign ion in the determination of 2.021 $\mu\text{g/mL}$ of Ru(III).

Ion added	Tolerance limit ($\mu\text{g/mL}$)		
	Zero order	First order	Second order
Bromide	3196	3196	3196
Iodide	1523	2030	2030
Urea	1086	1207	1207
Sulphate	576	1537	1537
Nitrate	248	496	496
Tetraborate	246	491	491
Phosphate	152	760	760
Thiocyanide	93	465	465
Ascorbic acid	71	141	141
Fluoride	61	152	152
Tartarate	53	60	60
oxalate	25	352	352
Thiourea	3.0	3.0	3.0
Ba(II)	192	275	275
Mg(II)	150	150	200
Zn(II)	131	157	157
Mn(II)	101	132	132
La(III)	83	111	111
W(VI)	74	74	110
Co(II)	71	94	94
Pb(II)	66	83	90
Rh(II)	60	60	84
Sr(II)	53	70	70
Bi(III)	42	42	42
Zr(IV)	37	55	55
Cd(II)	36	54	54
Hg(II)	16	80	80
Sn(II)	14	95	95
U(VI)	10	48	48
Ni(II)	9.0	14	14
Ag(I)	9.0	22	22
Os(VIII)	6.0	6.0	10
Se(IV)	6.0	32	32
Pd(II)	6.0	6.0	6.0
Li(I)	4.0	7.0	7.0
Mo(VI)	4.0	15	23
Cu(II)	0.3, 4.0 ^a	1.0, 5.0 ^a	1.0, 5.0 ^a
Al(III)	3.0	5.0	5.0
Ti(IV)	3.0	4.0	4.0
Ce(IV)	2.2	11	11
Fe(III)	2.2 ^b	4.0 ^b	4.0 ^b
V(V)	1.0	1.0	2.0
Cr(VI)	0.4	1.0	1.0
Sb(III)	0.2	0.4	2.0
As(III)	0.2	1.0	1.0

^a masked with 3.0 $\mu\text{g/mL}$ of thiourea

^b masked with 61 $\mu\text{g/mL}$ of fluoride

Sulphate, nitrate, tetraborate and phosphate were tolerable more than 150 $\mu\text{g/mL}$. Cations such as barium(II), magnesium(II), zinc(II) and manganese(II) do not interfere when they are present up to 100 $\mu\text{g/mL}$. Lanthanum(III), tungsten(VI), cobalt(II), lead(II), rhodium(II) and strontium(II) were tolerable

more than 50 µg/mL in the determination of ruthenium(III) using DMHBIH. However, metals like vanadium(V), chromium(VI), antimony(III) and arsenic(III) are seriously interfered. The interference of associated metal ions such as copper(II) and iron(III) was decreased with masking agents thiourea and fluoride respectively.

Applications

The spectrophotometric determination of Ru(III) in synthetic alloy samples and real water samples were carried out by employing the recommended procedure. A known aliquot of the sample solution was taken in a 25-mL volumetric flask containing 10 mL of buffer pH 4.25, 1.0 mL of Triton X-100 (5%) and 1.0 mL of DMHBIH reagent 1×10^{-2} M reagent solutions. The contents in the flask were made up to the mark with distilled water. The amount of ruthenium(III) present in these samples was computed from a pre-determined calibration plot and results are summarized in Table 5.

Conclusions

The present method, using DMHBIH as spectrophotometric reagent for the determination of Ru(III) in presence of Triton X-100 was considerably superior to other spectrophotometric methods, when comparing analytical parameters *viz.* linear range and molar absorptivity (see Table 6).

Most of the spectrophotometric methods involve both extraction and heating of the reaction mixture [13-15] or only heating [16,17]. The organic solvents used for the extraction process, such as benzene and chloroform, are often carcinogenic, toxic and cause environmental pollution. Heating at a specific temperature for a long time is laborious and time consuming. The present method is not laborious and there is no need of heating the components or pre-extraction. Further, the Triton X-100 enhances the stability of the metal complex. Moreover, the present method is simple, rapid, reasonably sensitive and selective for the determination of ruthenium(III).

Table 5 Determination of Ru(III) in synthetic alloy samples and real water samples by present method.

Sample	Amount of Ru(III) added (µg/mL)	Amount of Ru(III) found ^b (µg/mL)			RSD (%)		
		Zero order	First order	Second order	Zero order	First order	Second order
Zn-Mg alloy sample (Zn,50 mg + Mg,50 mg)	5.0	5.14	5.11	5.12	-2.8	-2.2	-2.4
Zn-Mg alloy sample (Zn,20 mg + Mg,20 mg)	3.5	3.36	3.39	3.45	+4.0	+3.1	+1.4
Synthetic alloy sample (µg/g) ^a	2.2	2.28	2.26	2.25	-3.6	-2.7	-2.2
River water sample	0.61	0.62	0.63	0.62	+1.6	-3.2	-1.6
Pond water sample	0.61	0.63	0.60	0.62	+3.2	+1.6	-1.6

^a Pb(II), (0.8) + Co(II), (20.0) + Os(VIII), (0.8) + Rh(II), (100);

^b average of best three among five determinations

Table 6 Comparison of spectrophotometric methods for the determination of ruthenium(III).

Reagent	λ_{\max} (nm)	pH	Beer's law range	Molar absorptivity ($L \cdot mol^{-1} \cdot cm^{-1}$)	Extraction / heating	Ref.
Res-acetophenone guanylhydrazone	375	1.5	0-35.0 ppm	0.74×10^4	Aqueous	[5]
Tropolone	415	4.0	0-5.7 ppm	1.87×10^4	Extn. $CHCl_3$, heated at 100 °C	[13]
3-Nitroso-4-hydroxy-5,6-benzocoumarin	520	5.5-8.0	1-7.4 ppm	1.04×10^4	Extn. BtOH 20 min, heated at 100°C	[14]
3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine	485	5.0	0.5-3.4 ppm	2.1×10^4	Heated 30 min at 85°C, extracted	[15]
4-5-diamino-6-hydroxy pyrimidine sulphate	530	Acidic medium	–	6.5×10^3	Heated	[16]
2,2',2''-terpyridine	690	3.0-4.5	2-10 ppm	8.3×10^3	Heated 2 min at 80°C	[17]
3-Hydroxy-2-methyl- sodium isoamylxantahte	350	4.5-7.0	3.5-7.7 µg/mL	1.18×10^4	Aqueous	[18]
3,5-dimethoxy-4-hydroxybenzaldehyde isonicotinoyl hydrazone	390	4.25	0.202-4.043 µg/mL	1.07×10^4	Aqueous	Present method

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