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Derivative Spectrophotometric Determination of Ruthenium(III) using Cinnamaldehyde Isonicotinoylhydrazone (CINH)

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Ruthenium(III) forms a brownish yellow coloured water soluble complex with cinnamaldehyde isonicotinoylhydrazone (CINH) reagent in acidic buffer pH 3.0 with λ_{max} at 402 nm. The molar absorpitivity and Sandell's sensitivity is 1.25 $\times 10^4$ L mol^{-1} cm^{-1} and 0.00809 μg/cm^2, respectively. The Beers law validity range is 0.202 to 4.04 μg/mL. Ruthenium(III) forms (M:L) 1:1 complex with CINH and stability constant of the complex is 4.56×10^5. The developed derivative spectrophotomrtic method was employed for the determination of ruthenium(III) in synthetic samples of alloy and river water samples. The effect of various diverse ions have also been studied.

Key Words: Cinnamaldehyde isonicotinoylhydrazone, Derivative spectrophotometry, Ruthenium(III).

INTRODUCTION

The potential application of hydrazone derivatives for the spectrophotometric determination of metal ions has been reviewed by Singh *et al.*[1]. Few hydrazone reagents[2-4] were used for the spectrophotometric determination of ruthenium(III). In the light of good analytical characteristic of hydrazones, herein we report zero and first order derivative spectrophotometric determination of Ru(III) in aqueous medium. Derivative spectrophotometric methods for the determination of metal ions[5-8] are not exploited much.

EXPERIMENTAL

Spectrophotometric measurements were made in an Shimadzu 160A microcomputer based UV-Visible spectrophotometer equipped with 1.0 cm quartz cells, an ELICO LI-120 digital pH meter was used for pH adjustments.

All reagents used were of AR grade unless otherwise stated. All solutions were prepared with distilled water. The standard Ru(III) solution (0.01 M) was prepared by dissolving 0.2076 g of ruthenium chloride ($RuCl_3$ AR Loba) in minimum amount of dilute hydrochloric acid and diluted up to the mark using distilled water in a 100 mL standard flask.

The reagent cinnamaldehyde isonicotinoylhydrazone (CINH) was prepared by simple condensation of 1 mol of Cinnamaldehyde with 1 mol of isonicotinoylhydrazide and its structure is given in Fig. 1.

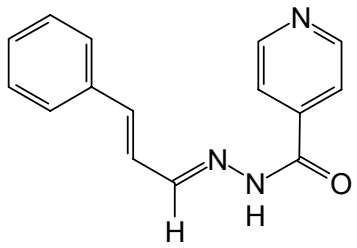

Fig. 1. Structure of cinnamaldehyde isonicotinoylhydrazone

The reagent solution (0.01 M) was prepared by dissolving 0.2512 g of CINH in 100 mL of dimethyl formamide. The reagent is stable for 48 h.

Buffer solutions were prepared by 1 M hydrochloric acid-1 M sodium acetate (pH 0.5-3.5); 0.2 M acetic acid 0.2 M sodium acetate (pH 4.5-7.0); 2 M ammonium chloride - 2 M Ammonium hydroxide (pH 7.5-12.0).

Reaction with metal ions: 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 (pH, 1.0-11.0), metal ion (1 mL of 1×10^{-3} M) and 1 mL of 1×10^{-2} M CINH solutions. The solution mixture was diluted up to the mark with distilled water. The absorbance was measured in 350- 600 nm range against reagent blank. The results are summarized in Table-1.

TABLE-1
ANALYTICAL CHARECTERISTICS OF CINNAMALDEHYDE ISONICOTINOYLHYDRAZONE (CINH)

Metal ion	pH	λ_{max} (nm)	Molar absorptivity ($L\ mol^{-1}\ cm^{-1}$) $\times 10^4$
Cu(II)	2.0	412	0.65
Ru(III)	3.0	402	1.25
V(V)	3.0	404	0.75
Mo(VI)	3.0	394	3.10

Recommended procedure

Determination of Ru(III) (zero order spectrophotometry): An aliquot of the solution containing 0.202-4.04 µg/mL of Ru(III), 10 mL of buffer solution pH 3.0 and 1 mL of 0.01 M CINH reagent 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 402 nm in a 1.0 cm cell against reagent blank prepared in the same way but without Ru(III) metal solution. The measured absorbance was used to compute the amount of Ru(III) from the calibration plot.

Determination of Ru(III) by first order derivative spectrophotometry: For the above solution of Ru(III)-CINH first order derivative spectrum was recorded with a scan speed having degrees of freedom 9 in a wavelength range 350 to 600 nm. The derivative spectrum was measured by peak height (h) method at 446 nm. The peak height (h) at 446 nm is proportional to the concentration of ruthenium(III). Therefore, the peak heights were measured at this wavelength for the construction of calibration plots.

RESULTS AND DISCUSSION

Cinnamaldehyde isonicotinoylhydrazone (CINH) reagent is easily obtained as any other Schiff base reagent. So far the new chromogenic reagent (CINH) was not used for the spectrophotometric determination of Ru(III).

The colour reactions of some important metal ions with CINH are summarized in Table-1. The colour reaction are mainly due to the complex formation of CINH with divalent, trivalent, pentavalent and hexavalent metal ions such as Cu(II), Ru(III), V(V) and Mo(VI) in acidic buffer medium to give intense coloured complexes. In acidic medium, the ligand presumably co-ordinates the metal ions as di-anion to give a neutral complexes.

Determination of Ru(III) using CINH: Ru(III) reacts with CINH in acidic medium to give brownish yellow water-soluble species. The colour reactions between Ru(III) and CINH are instantaneous even at room temperature in the pH range 1.0-6.0. The absorbance of the brownish yellow coloured species remains constant for more than 1 h. The maximum colour intensity is observed at pH 3.0.

A 5-fold molar excess of reagent is adequate for full colour development. The order of addition of metal ion, reagent and buffer solution has no adverse effect on the absorbance. The complex formation reaction between Ru(III) and CINH has been studied in detail based on the composition of the complex as determined by using Job's and molar ratio methods. Important physico-chemical and analytical characteristics of Ru(III) and CINH are summarized in Table-2.

TABLE-2
PHYSICO-CHEMICAL AND ANALYTICAL CHARECTERISTICS OF Ru(III) - CINH COMPLEX

Characteristics	Results
λ_{max} (nm)	402
pH range (optimum)	2.0-4.0
Mole of reagent required per mole of metal ion for full colour development	5 folds
Molar absorptivity (L mol^{-1} cm^{-1})	1.25×10^4
Sandell's sensitivity (μg/cm^2)	0.00809
Beer's law validity range (μg/mL)	0.202-3.638
Optimum concentration range (μg/mL)	0.81-3.64
Composition of complex (M:L) obtained in jobs and mole ratio method	1:1
Stability constant of the complex	4.56×10^5
Standard deviation in the determination of 1.47 μg/mL of Ru (III) for ten determinations	0.0003
Relative standard deviation (%)	0.2
Regression coefficient	0.99

Derivative spectrophotometry is a useful technique because it decreases the interference *i.e.*, increase the tolerance limit value of the foreign ions and may be advantageously used for the determination of metal ions having overlapping spectra. The recommended procedure has been employed for the determination of Ru(III).

The zero order and first order derivative spectra of Ru(III) complex of CINH are given in Figs. 2 and 3, respectively.

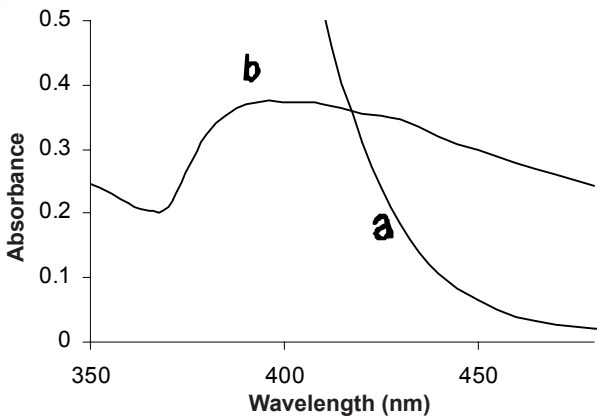

Fig. 2. Zero order absorption spectra of (a) Reagent CINH 4×10^{-4} M *vs.* Water blank at pH = 3.0. (b) Ru(III)-CINH Complex *vs.* Reagent blank at pH = 3.0, Ru(III) = 3×10^{-5} M, CINH = 4×10^{-4} M

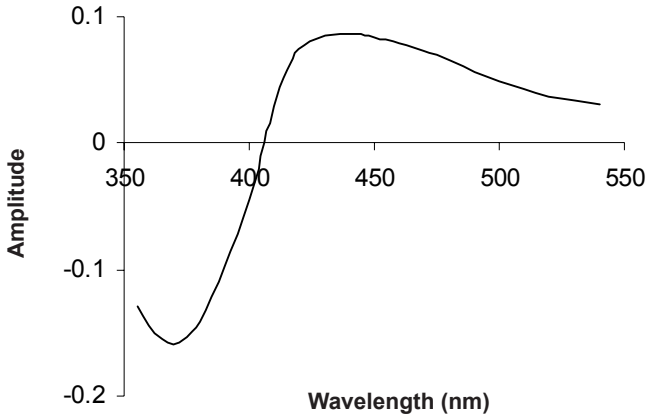

Fig. 3. First order derivative spectrum of Ru(III)-CINH complex *vs.* reagent blank at pH = 3.0, Ru(III) = 3×10^{-5} M, CINH = 4×10^{-4} M

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 of ± 2 % in the absorbance or amplitude. The results are given in Table-3. The data obtained in the derivative method is also incorporated. The data suggest that several associated anions and cations do not interfere when they are present in large excess. Such as phosphate, bromide, sulphate, iodide, urea, U(VI), Ba(II), Mn(II), Sn(II), Se(IV) and Ca(II). The tolerance limit values for many anions and cations are more in derivative method. The interference of associated metal ions such as Fe(III) and Cu(II) is decreased with masking agents fluoride and thiouera, respectively.

Applications: The proposed method was applied for determination of ruthenium(III) in various synthetic samples of alloy and river water samples.

Analysis of synthetic alloy sample: 0.5 g sample of the synthetic alloy was digested in 15 mL of 2:1 ratio mixture of conc. HCl and conc. HNO_3. It was heated until it is dissolved and final volume reduced to 5 mL. 5 mL of 5 M 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.

TABLE-3
TOLERENCE LIMIT OF FOREIGN IONS IN THE DETERMINATION OF 1.47 µg/mL Ru(III)

Ion added	Tolerance limit (µg/mL)		Ion added	Tolerance limit (µg/mL)	
	Zero order	First derivative		Zero order	First derivative
Phosphate	1330	1330	Ba^{2+}	55	55
Bromide	1279	1439	Mn^{2+}	44	44
Sulphate	1159	1159	Sn^{2+}	38	38
Iodide	761	1015	Se^{4+}	32	32
Urea	603	603	La^{3+}	28	28
Nitrate	248	248	Ca^{2+}	24	24
Fluoride	152	152	Bi^{3+}	8.0	8.0
Ascorbic	141	141	Hg^{2+}	8.0	40
acid			Pb^{2+}	7.0	7.0
Acetate	118	118	W^{6+}	6.0	6.0
Tetraborate	98	98	Ce^{4+}	5.0	5.0
Tartarate	59	59	Zr^{4+}	4.0	4.0
Thiocyanide	23	23	Sr^{2+}	4.0	4.0
Citrate	4.0	4.0	Fe^{3+}†	2.0	2.0
Thiourea	0.06	0.06	Ti^{4+}	2.0	38
U^{6+}	95	95	Cu^{2+}‡	1.0	1.0
Na^{+}	92	92	Cd^{2+}	1.0	22

†Masked by fluoride 152 µg/mL; ‡Masked by thiourea 0.06 µg/mL

TABLE-4
ESTIMATION OF RUTHENIUM(III) (µg/mL) IN SYNTHETIC ALLOY SAMPLES

Sample (µg/mL)	Amount of Ru(III) (µg/mL)		Error (%)
	Amount added	Amount found*	
Pb(II) (0.8) + Co(II) (20.0) +	0.850	0.826	+2.8
Os(VIII) (8.0) + Rh(III) (100)	2.0	1.95	+2.5

*Average of best three determinations among five determinations.

TABLE-5
ESTIMATION OF Ru(III) (µg/mL) IN RIVER WATER SAMPLES

Sample	Amount of Ru(III) (µg/mL)		Error (%)
	Amount added	Amount found*	
River water	0.450	0.438	+2.6
	0.610	0.598	+1.9

*Average of best three determinations among five determinations.

TABLE-6
COMPARISON OF SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF Ru(III)

Reagent	λ_{max} (nm)	pH	Molar absorptivity (ε) (L mol^{-1} cm^{-1})	Extraction/ heating	Beers law range	Ref
Tropolone	415	4.5-6.0	1.87×10^4	Extn. $CHCl_3$ heated 10 min at 100 ºC	0-5.7 ppm	9
4-5-Diamino-6-hydroxy pyrimidine sulphate	530	Acidic medium	6.5×10^3	Heated	–	10
3-Nitroso-4-hydroxy 5,6-benzocoumarin	520	5.5-8.0	1.04×10^4	Extn. BtOH heated 20 min at 100ºC	1-7.4 ppm	11
2,2´,2´´-Terpyridine	690	3.0-4.5	8.3×10^3	Heated 0.5 h at 85 ºC	2-10 ppm	12
3-(2-Pyridyl)-5,6-diphynyl 1,2,4-triazine	485	5.0	2.1×10^4	Extracted microcrystalline *p*-dichlorobenzene	0.5-3.4 ppm	13
3-Hydroxy-2-methyl-1,4-napthaquinone-4-oxime	450	5.7	2.7×10^4	–	0-10.1 ppm	14
Res-acetophenone guanylhydrazone	375	1.5	0.7469×10^4	–	0-35.0 ppm	4
Cinnamaldehyde isonicotinoyl hydrazone (CINH)	402	3.0	1.25×10^4		0.4 to 4.04 (µg/mL)	Present method

Analysis of river water sample: A known aliquot river water sample was added to a 10 mL buffer (pH 3.0) solution in a 25 mL volumetric flask and 1 mL of (1×10^{-2} M) reagent solution is added, made up to the mark with distilled water. The absorption at 402 nm is recorded against reagent blank. The amount of ruthenium(III) present was determined from a pre determined calibration plot and results presented in Table-5.

Conclusion

The present method using CINH as spectrophotometric reagent for the determination of ruthenium(III) in aqueous medium is sensitive and simple. This method was favourably compared with previously reported spectrophotometric methods[4,9-14] presented in Table-6. Most of the spectrophotometric methods involve both extraction and heating of the reaction mixture[9-12] or only extraction[13]. However heating at a specific temperature and for a long time is laborious and time consuming. The determination of ruthenium(III) using CINH is not laborious and there is no need of heating the components or extraction. Further, the reagent is easy to synthesize using available chemicals. Moreover, the present method is simple, rapid, reasonably sensitive and selective for the determination of ruthenium(III).

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