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Spectrophotometric Determination of Osmium (Viii) using 2,4-Dimethoxybenzaldehyde Isonicotinoyl Hydrazone (Dmbih) in presence of Surfactant Triton X-100.

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ABSTRACT

A simple and sensitive spectrophotometric method has been developed for the determination of Osmium(VIII) using 2,4-Dimethoxy benzaldehyde isonicotinoyl hydrazone (DMBIH). Osmium (VIII) forms a yellow coloured water soluble complex in acidic medium (pH 5.0) in presence of surfactant Triton X-100(5%). The molar absorptivity and Sandell's sensitivity of coloured species are 1.48×10^4 L.mol^{-1} cm^{-1} and 0.0068 μg/cm^2 respectively. Beer's law is obeyed in the range 0. 951 -11.412 μg/ml of Osmium (VIII) at 393 nm(λ_{max}). Osmium (VIII) forms a 1:2 complex and stability constant of the complex is 3.13×10^{11}. The developed spectrophotometric method has been satisfactorily applied for the determination of Osmium (VIII) in synthetic mixture and Osmium ores and interference ions also studied systematically.

Keywords: Osmium(VIII),2,4-dimethoxy benzaldehyde isonicotinoyl hydrazone (DMBIH), synthetic mixture and Osmium ores, derivative spectrophotometry .

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INTRODUCTION

The potential analytical applications of hydrazone derivatives have been reviewed [1].Hydrazones are important class of known analytical reagents [2-8] .These reagents are formed by the condensation of hydrazides and a carbonyl compound. Hydrazones are also found to have biological activity. These compounds contain an azomethine nitrogen atom and this is responsible for their reactivity with number of transition metal ions which form coloured complexes. Analytical application of hydrazone were reported here in spectrophotometric determination of Osmium(VIII) using 2,4-dimethoxy benzaldehyde isonicotinoyl hydrazone (DMBIH).

EXPERIMENTAL

A shimadzu 160A, microcomputer based UV-VIS spectrophotometer equipped with 1.0cm quartz cells was used for all spectral measurements. The instrumental parameters are optimized and the best results were obtained with scan speed fast, slit width of 1nm and $\Delta\lambda$=2nm for first order derivative mode in the wavelength range 350-650nm. ELICO L1-120 digital pH meter was used for the pH adjustments and Sartorius electronic balance was used for weighing. All chemicals used were of A.R grade stated. All solutions were prepared with doubly distilled water. The standard Osmium(VIII) solution was prepared by dissolving 0.2542g of OsO_4 in few drops 5M sulphuric acid and diluted up to the mark using doubly distilled water and made up to the mark in a 100-ml of volumetric flask. The stock solution was standardized by the method of Klobbie [9]. Aqueous solution of 5% Triton X-100 was prepared by diluting 5gm of Triton X-100 to 100ml with doubly distilled water. Buffer solutions (phosphate buffers) were prepared by using 0.1M HCl, 0.1M NaOH, 0.1M disodium hydrogen phosphate and 0.1M potassium dihydrogen phosphate. Solutions of various ions of suitable concentrations were prepared using AR grade chemicals.

The reagent 2,4-dimethoxy benzaldehyde isonicotinoyl hydrazone (DMBIH) was synthesized by refluxing equimolar amounts of 2,4-dimethoxy benzaldehyde and Isonicotinoyl hydrazide. In a 250 ml round bottomed flask hot ethanolic solution of 2,4-dimethoxy benzaldehyde (1.6617g, 0.01 mole) and hot ethanolic solution of Isonicotinoyl hydrazide(1.3714g, 0.01mole) were mixed and refluxed using water condenser for 3 hours. On cooling the reaction mixture, an yellow coloured product separated out, which was collected by filtration and washed with double distilled water. The resulting hydrazone was recrystalized using 50% ethanol (yield 86%, mp 115^{0}C) and the structure of DMBIH shown in figure -1.

The reagent solution (0.01 M) was prepared by dissolving 0.28531 g of DMBIH in 100 ml of Dimethylformamide (DMF). The reagent solution is stable for 48 hours. The reaction of some important metal ions were tested at different pH values. The samples were prepared in 10ml

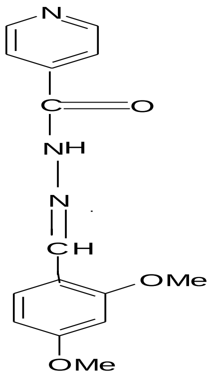

Fig.1. Structure of 2,4-Dimethoxy benzaldehyde isonicotinoyl hydrazone(DMBIH)

Volumetric flasks by adding buffer solution 3.0 ml (pH 3-6), metal ion 0.5 ml of 1x10^{-3}M, Triton X-100 (5%) 0.5ml and DMBIH 0.5 ml of 1x10^{-2}M solution. The mixture was diluted up to the mark with distilled water. The absorbance was measured in 300-700nm range against reagent blank.

For the spectrophotometric determination of Osmium(VIII) ,an aliquot of the solution containing 0.951-11.412µg/ml of Osmium(VIII) ,3.0ml of buffer solution (pH 5.0), 0.5ml of 5% Triton X-100 and 0.5ml of 1x10^{-2}M DMBIH reagent solution were taken in 10 ml volumetric flask and the solution was diluted up to the mark with doubly distilled water. The measured absorbance was used to compute the amount of Osmium(VIII) from the predetermined calibration curve.

The first-order derivative spectrum was recorded with scan speed fast having a degree of freedom 9, in the wave length range from 350-650nm. The first-order derivative peak height was measured at 449 nm is shown in figure - 2. The peak height was plotted against the amount of Osmium (VIII) to obtain the calibration curve. The second order derivative spectrum of [Os (VIII)-DMBIH] system was recorded peak height at 466 nm. Calibration plot was constructed by plotting the derivative amplitude against the amount of Os (VIII).

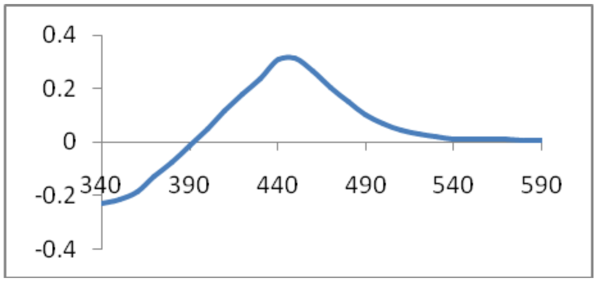

Fig.2. First order derivative spectrum of [Os(VIII)-DMBIH] complex

RESULTS AND DISCUSSION

The reagent 2,4-dimethoxy- benzaldehyde isonicotinoyl hydrazone (DMBIH) was easily synthesized as any other Schiff base reagent. The new chromogenic reagent DMBIH was used for the spectrophotometric determination of then Osmium (VIII) .The colour reactions of some important metal ions with DMBIH are summarized in Table-1. The absorption spectrum of DMBIH and its Osmium(VIII) complex under the optimum conditions are shown in Figure-3. The [Os(VIII)-DMBIH] complex shows the maximum absorbance at 393 nm, where the reagent blank does not absorb appreciably.

Metal ion	P^H	λ_{max} (nm)	Molar absorptivity (ε) ($L.mol^{-1}cm^{-1}$)
Ru(III)	5	395	$1.6 \times 10^{4*}$
Os(VIII)	5	393	1.48×10^{4}

*Present work

Table-1: The colour reactions of some important metal ions with DMBIH .

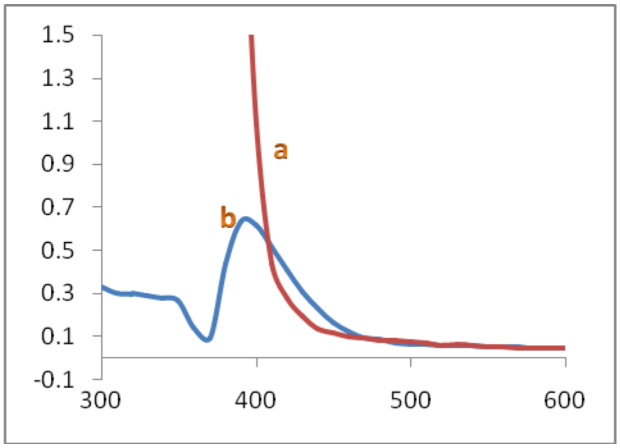

Fig.3. Zero order Absorption spectra
(a) Reagent (DMBIH) Vs DMF blank (b) [Os(VIII)-DMBIH] complex

Osmium (VIII) reacts with DMBIH in acidic buffer to give yellow coloured water soluble complex . The colour reaction between Osmium (VIII) and DMBIH was instantaneous even at room temperature in pH range 3-6, the maximum colour intensity was observed at pH 5 in presence of surfactant Triton X-100 (5%).

A slow decrease in absorbance was observed for the coloured species after 15 min. The stability of the complex was increased by adding surfactant Triton X-100(5%). The absorbance of [Os(VIII) – DMBIH] remain constant for more than 2 hours. The effect of surfactants such as Tritonx-100, Sodium dodecyl benzene sulphonate (SDBS) and Cetyl trimethyl ammonium bromide (C-TAB) on the absorption profiles of the system has been investigated and presented in Table-2. In presence of Triton X- (5%) the complex is more stable and exhibited maximum absorbance. Hence Triton X-100 (5%) has been selected for further studies.

Surfactant	Type	Absorbance at 380 nm
None		0.529
Tritonx-100(5%)	Neutral	0.642
CTAB(5%)	Cationic	0.490
SDBS(5%)	Anionic	0.243

Table-2. Influence of different surfactants on the [Os (VIII)-DMBIH] complex

Characteristics	Results
Colour	Yellow
λ_{max}(nm)	393
p^H range (optimum)	5
Mole of reagent required per mole of metal ion for full colour development	10 folds
Molar absorptivity(L.mol $^{-1}$cm^{-1}) (ε)	$1.48x10^4$
Sandell's sensitivity(µg/cm^2)	0.0068
Beer's law validity range(µg/ml)	0.951-11.412
Optimum concentration range(µg/ml)	1.902-10.461
Composition of complex(M:L) obtained in Job's and mole ratio methods	1:2
Stability constant of the complex	$3.13x10^{11}$
Standard deviation	0.002
Relative standard deviation(%)	0.2

Table-3: Physico-Chemical and Analytical Characteristics of [Os (VIII)-DMBIH]

When varying amounts of 5% Triton X-100 solution from 0.5ml to 4.0 ml, the constant absorbance was obtained from 0.5ml. The absorbance remains constant up to 4.0ml of 5% Triton X-100. Hence 0.5ml of 5% Triton X-100 was sufficient in all analytical studies. Triton X-100 serves to stabilize and sensitize the metal complex. Similarly when varying the volume of reagent DMBIH from 0.5ml to 4.0ml, the constant absorbance was obtained from 0.5 ml. therefore a 10 fold molar excess of reagent is adequate for full colour development.

The order of addition of buffer solution, metal ion, Triton X-100 and reagent has no adverse effect on the absorbance of [Os(VIII)-DMBIH] complex. Beer's law obeyed in the range 0.951-11.412 µg/ml. The Molar absorptivity and Sandell's sensitivity is 1.48 x10^{4}L.mol $^{-1}$cm^{-1} and 0.0068 µg/cm^2. [Os(VIII)-DMBIH] complex was obtained from the Beer's law. The linear regression analysis of absorbance at 393 λ_{max} of the complex against metal ion (µg/ml) shows a linear fit shown in figure-4. The various important analytical characteristics of [Os (VIII)-DMBIH] complex are summarized in Table-3. The first order beers law graph was shown in Figure-5. This shows that the derivative amplitudes measured at 449 nm for first order were found to be proportional to the amount of Osmium(VIII) .The stoichiometry of the complex was found to be

1:2 (metal : ligand) investigated by Job's continuous variation method and molar ratio method, with a stability constant 3.13x10^{11}.

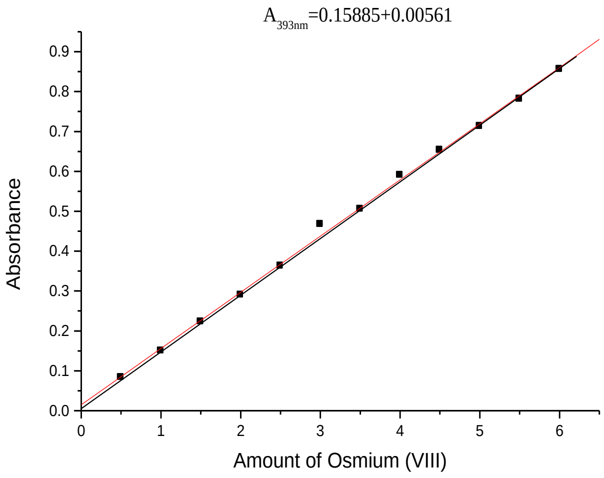

Fig.4. Zero order Beer's law plot of [Os(VIII)-DMBIH]

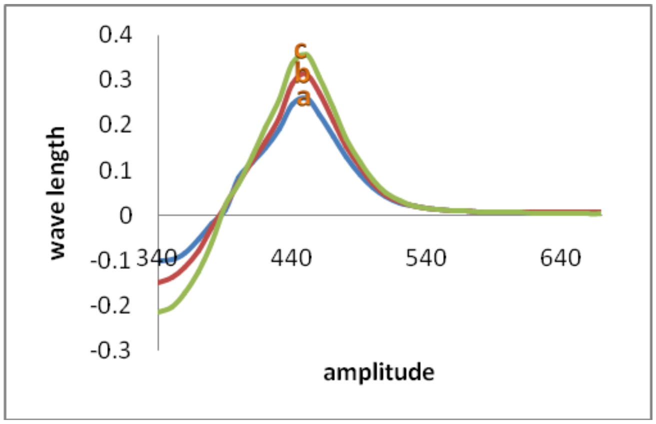

Fig.5. First order derivative Beers law of [Os(VIII)-DMBIH] complex

(a) 5.706 µg/ml of Os(VIII)
(b) 7.608 µg/ml of Os(VIII)
(c) 9.510 µg/ml of Os(VIII)

The effect of various diverse ions in the determination of 4.755 µg/ml Osmium(VIII) and tolerance limit of foreign ions was studied 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-4.

Ion added	Tolerance limit µg/mL	Ion added	Tolerance limit µg/mL
Ascorbic acid	528	Bromide	16
Acetate	339	Sodium tetra bromide	10
Thiosulphate	202	Sr^{2+}	438
Phosphate	199	Se^{3+}	237
Thiocyanide	116	Cu^{2+}	190
Thio urea	114	Ba^{2+}	137
Citrate	67	Ca^{2+}	100
Urea	60	Sb^{2+}	24
Chloride	35	Cd^{2+}	22
Iodide	26	Zn^{2+}	20
Oxalate	25	Ni^{2+}	12
Sulphate	24	Co^{2+}	8
Fluoride	19	NH$_4^+$	4
Nitrate	18	Mn^{2+}	3

Table 4. Tolerance limit of foreign ions in the determination 4.755 µg/ml Osmium(VIII).

Composition of mixture and amounts taken /mg	Osmium found (mg/l)	Error (%)
Os(VIII),0.2; Ir(III),1.5; Pd(II),0.1; Pt(IV),0.1	0.19	+ 5.0
Os(VIII),0.180; Ir(III),0.2; Pt(IV),0.5; Mn(II),0.5; Sb(V),0.2	0.178	**+** 1.11
Os(VIII),0.180; Zn(II),5.0; Pb(II),2.0; Mn(II),2.0; Ni(II),1.0	0.183	+1.67

* Average of best three among five determinations

Table 5. Determination of Os(VIII) in synthetic mixtures

APPLICATIONS

The developed method was applied for the determination of Osmium (VIII) in synthetic mixture and Osmium ores.

Determination of Osmium(VIII) in synthetic mixture.

As compared to the cost of platinum group metals, this working place cannot afford to purchase real samples containing osmium. The applicability of the method was tested by analyzing synthetic samples containing added osmium and the osmium content was determined by following the method described under standard procedure. Therefore this method is used successfully for the estimation of Osmium in microgram in alloy samples. The results are presented in Table-5

Determination of Osmium (VIII) in ores.

Certified samples of syserkite or osmiridium were not available. Therefore, synthetic mixtures whose composition correspond to syserkite or osmiridium were prepared and osmium content was determined by following the method described under standard procedure. The results are presented in Table-6.

Osmium taken (mg/l)	Iridium added (mg/l)	Ruthenium added (mg/l)	Platinum Added (mg/l)	Osmium found * (mg/l)	Error (%)
0.30	0.075	0.045	0.015	0.28	+ 6.67
0.60	0.150	0.090	0.030	0.62	- 3.33
0.90	0.225	0.135	0.045	0.89	+ 1.11
1.20	0.300	0.180	0.060	1.19	+ 0.83

* Average of best three among five determinations.

Table 6. Determination of synthetic Osmium ores corresponding to Osmiridium or Syserkite

CONCLUSION

The present method using 2,4-dimethoxy benzaldehyde isonicotinoyl hydrazone (DMBIH) as spectrophotometric reagent for the determination of Osmium(VIII) in aqueous medium in presence of Triton X-100 surfactant is sensitive and simple. Many of the methods involve either heating at a specific temperature or extraction of the reaction mixture. However heating at a specific temperature for a long time is laborious and time consuming. The determination of Osmium(VIII) using DMBIH is not laborious and there is no need of heating or extraction of the components. Further the reagent is easy to synthesize using available chemicals. More over the present method is simple, rapid, selective and more precise for the determination of Osmium(VIII) when compared with other reagent [9-13]given in the Table - 7.

Reagents	λ_{max}	pH	Molar absorbtivity(Є) (L/mol/cm)	Ref. No.
1,3-Cyclohexanedione bisthiosemicarbazone monohydrochloride	510	3.0-6.0	0.92 X 10^4	10
β - Mercapto resorcylic acid	570	0.5M HCl	1.38 X 10^4	11
1-Phenyl-4,4,6-trimethl(1H,4H)-2-pyrimidinethiol	520	-	1.33 X 10^4	12
Phthalimide dithiosemicarbazone	450	3.3-4.5	1.30 X 10^4	13
Thiopyrogallol	640	9.0	1.01 X 10^4	11
N-4-(methoxyphenyl)-α- thiopicolinamide	440	0.3-0.8M HCl	0.83 X 10^4	14
N-(4-methyl) -α- thiopicolinamide	430	1.0-1.6M HCl	0.65 X 10^4	14
2,4-dimethoxy benzaldehyde isonicotinoyl hydrazone	393	3.0-5.0	1.48 X10^4	Present work

Table-7. Comparisons of spectrophotometric methods for the determination of Osmium(VIII) using various regents.

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