



Kinetic Spectrophotometric Method for The Determination of Ir(III) by Its Catalytic Effect on The Oxidation of Sulphur Containing Amino Acid by HCF(III) in Aqueous Alkaline Medium

Dr. Anjali Goel¹, Dr. Savita Garg²

¹Deparment of Chemistry, Kanya Gurukul Mahavidyalaya, Gurukul Kangri University Haridwar, Uttarakhand,

India

²Deparment of Chemistry, SEA college of Arts, Science and Commerce, K.R.Puram, Bangalore, Karnataka, India

ABSTRACT

A simple kinetic spectrophotometric method has been developed for the determination of ultra trace amount of Ir(III). The method is based on the Ir(III) catalysed oxidation of sulphur containing amino acid by HCF(III) in aqueous alkaline medium. Under the optimum experimental conditions Ir (III) can be determined in the range 0.258 -8.37µg ml⁻¹ for cystine and methionine with an maximum average error of 99.5% and maximum relative standard deviation of 1.702%. The effect of few interfering ions have been worked out .For developing the calibration curves in terms of absorbance or reaction rate or pseudo first order rate constant vs. [Ir (III)] plot, absorbance was noted at λ max of 420 nm. The molar absorptivity and sandell's sensitivity are found for cystine 2.83 x 10³ – 4.11 x 10³ l mol⁻¹ cm⁻¹ & 0.0680 – 0.0467µgcm⁻² and for methoinine 2.31 x 10³ – 3.27 x10³ l mol⁻¹ cm⁻¹ k 0.0680 – 0.0467µgcm⁻² and for methoinine 2.31 x 10³ – 3.27 x10³ l mol⁻¹ cm⁻¹ k 0.0680 – 0.0467µgcm⁻² and for methoinine 2.31 x 10³ – 3.27 x10³ l mol⁻¹ cm⁻¹ k 0.0680 – 0.0467µgcm⁻² and for methoinine 2.31 x 10³ – 3.27 x10³ l mol⁻¹ cm⁻¹ k 0.0680 – 0.0467µgcm⁻² and for methoinine 2.31 x 10³ – 3.27 x10³ l mol⁻¹ cm⁻¹ k 0.0680 – 0.0467µgcm⁻² and for methoinine 2.31 x 10³ – 3.27 x10³ l mol⁻¹ cm⁻¹ k 0.0680 – 0.0467µgcm⁻² and for methoinine 2.31 x 10³ – 3.27 x10³ l mol⁻¹ cm⁻¹ k 0.0680 – 0.0467µgcm⁻² and for methoinine 2.31 x 10³ – 3.27 x10³ l mol⁻¹ cm⁻¹ k 0.0680 – 0.0467µgcm⁻² and for methoinine 2.31 x 10³ – 3.27 x10³ l mol⁻¹ cm⁻¹ k 0.0680 – 0.0467µgcm⁻² and for methoinine 2.31 x 10³ – 3.27 x10³ l mol⁻¹ cm⁻¹ k 0.0680 – 0.0588µgcm⁻² respectively. The results show that the present method is more simple and sensitive than the reported methods and especially useful in absence of expected interfering ions.

Keywords - Microgram determination, Ir (III), Hexacyanoferrate (III), Oxidation, Cystine and Methoinine

I. INTRODUCTION

In recent year with the increasing interst in the geochemistry of iridium and other platinum group eles. ments higher sensitivity and precision for the analysis of these elements have been required. Iridium is a minor constituent of most platinum metal deposits. Therefore high selective sensitivity, rapid ,economical methods are needed for its trace determination. Some instrumental methods are reported for this purpose^{1-5.} However the necessary instruments are expensive day to day and maintenance costs are high and the methods are not from various types of interferences.⁶⁻¹⁰. Anjali et al also reported the kinetic spectrometry methods for the determination of trace iridium based on the catalytic effect of the iridium in the oxidation reaction of alanine¹¹, Cystine ¹² & Isoleucine¹³.

Thus in the present study an attempt has been made to determine Ir (III) concentration in micrograms in aqueous alkaline medium by kinetic – spectrophotometric method. The method is based on the oxidation of amino acids like cystine, methionine by hexacyanoferrate (III) catalyzed by Ir (III) in aqueous alkaline medium.



II. METHODS AND MATERIAL

All chemical used were of A.R. grade. HCF (III) was used after recrystallisation. All the solution and reaction mixtures were prepared by using double distilled water. Absorbance was recorded on Sys. UV-Vis spectrophotometer -117, λ max for the reaction mixture observed was 420nm.IrCl₃10H₂O (SRL) was prepared by dissolving the sample in dil HCl¹⁴. In order to optimize the variable effect of concentration of each reagent, the rate of reaction was studied.

The condition worked out for estimation of Ir(III)

Following are the finally worked out conditions for running the kinetic sets for the purpose of determination of [Ir(III)] in aqueous alkaline medium based upon the hexacyanoferrate(III) oxidation of amino acids.

 $[Cystine & Methionine] = 3.00 \quad x \quad 10^{-3} \text{ mol } dm^{-3}, \text{ HCF (III)} = 3.00 \ x \quad 10^{-3} \text{ mol } dm^{-3}, \text{ NaOH} = 0.4 \text{ mol } dm^{-3} \text{ Temp.} = 35 \pm 0.1^{\circ}\text{C}, \quad \lambda max = 420 \text{ nm}, \\ \mu = 0.5 \text{ mol } dm^{-3} \text{ mol } dm^{-3$

Preparation of calibration curve

A definite volume of stock solution of HCF (III) was mixed with calculated volume of a stock solution of Ir(III) ,Sodium hydroxide, Potassium chloride and water and stirred a little with the help of pipette. The reaction mixture and stock solution of amino acids like cystine and methionine were then clamped in a thermostat at 35 ± 0.1 °C. After 30 min. a required amount of amino acid solution was added to the reaction mixture and stirred to start the reaction. Aliquots were withdrawn from the reaction mixture after repeated intervals of 5 min and the absorbance was recorded on systronic UV- Vis. Spectrophotometer 117. The absorbance of reaction mixture goes on decreasing with the passage of time. Absorbances vs. time plots were made for all the sets. Initial rates (dA / dt) were evaluated after 5 min. from the start of the reaction by using plane mirror method. The first order rate constant (K₁) were calculated by Guggenheim's method. Different sets were prepared in a similar manner varying the [Ir(III)] between 0.258 – 8.37 µgml⁻¹ for cystine and methionine. All the additions were made in amounts calculated for maintaining the concentration of different reagents as mentioned above.

The stoichiometry of the reaction was studied by estimating the standard solution of ceric(IV)sulphate using ferrion as redox indicator. The studies shows that eight moles of hexacyanoferrate (III) are used for the oxidation of one mole of cystine and four moles of hexacyanoferrate (III) are used for the oxidation of one mole of methionine. Based on the experimental results, it can be proposed that reaction proceeds through complex formation between anion of (cystine and methionine) and Ir(III) which slowly disproportionate into Ir(I) and intermediate product. Ir(I) deoxidized by two moles of HCF(III) ions to Ir(III) through electron transfer mechanism and the intermediate product decomposes to final product ^{15–17}.

III. RESULTS AND DISCUSSION

The proposed method was tested for many reaction mixture containing known amounts of [Ir(III)] in the range of the detection limits. The results were found to be reproducible with reasonable standard deviation and low range of errors as calculated from six determinations. **(Table – 1)**

Validity of Beer's law and other characteristics of the method

The range of Ir(III) in which the Beer's law is obeyed, Molar absorptivity, Sandell's sensitivity, Correlation coefficient and coefficient of determination, relative standard deviation and % error for the estimation of[Ir(III)] in μ gml⁻¹ by using oxidation of cystine and methionine is given in **Table -1** for HCF(III) in alkaline medium.

The amounts of Ir(III) in the range of the detection limit were tested for the above proposed method. The results were found to be reproducible with reasonable standard deviation and low range of errors as calculated from six determinations. A comparison of the data presented in **Table -1** reveals that the Beer's law limit for the estimation of [Ir(III)] using amino acids- cystine and methionine are the same i.e. $0.258 - 8.37\mu$ gml⁻¹. The value of slope of the calibration curves, molar absorptivity and sandell's sensitivity indicated that the sensitivity of the method is good. A change in absorbance by 0.001 unit is expected on changing the concentration of [Ir(III)] by $0.0345 - 0.0983\mu$ g cm⁻³. The detection limits are also good for the trace determination of [Ir(III)]. The correlation coefficient (r) is in the range 0.9996 - 0.9866 which indicate the high precision involved in the determination and almost perfect correlation of the data. The negative sign shows decrease in absorbance with time. The value of coefficient of determination (r²) suggests that 0.9994 - 0.9734 change in the value of A₅ or A₁₀ or A₁₅ or A₂₀ or (dA /dt)_i or K₁ is caused by Ir(III). The standard deviation is within reasonable limits. Percentage recovery on the basis of six parallel determinations is 98.8 - 95.5. The values of the molar absorptivity and sandell's sensitivity calculated from the graph lies in the range of $2.83 \times 10^3 - 3.27 \times 10^3$ l mol⁻ cm⁻¹ and $0.0680 - 0.0588\mu$ gcm⁻² respectively.

Procedure for estimation of [Ir(III)] curves

For the estimation of [Ir(III)], the calibration curves should be prepared first as described above in the range of $0.258 - 8.37\mu$ gml⁻¹ concentration of[Ir(III)]. Then [Ir(III)] may be determined in aqueous calculated quantity of HCF(III) and starting the reaction by adding amino acid solution followed by noting the absorbance of reaction mixture at different desired time as described above or evaluating initial rate in terms of (dA/dt)_i after 5 min. or evaluating (K₁) by the methods discussed above. Then by using these different calibration curves [Ir(III)] in μ gml⁻¹ may be determined. (fig 1-4)

Interference Effect of Cations and Anions

The effect of various ions on the determination of [Ir(III)] By this method has also been studied. It has been observed that the presence of cations like Na⁺, K⁺, NH₄⁺, AS₃⁺, Mn₂⁺, Ca₂⁺, Cr₃⁺, Li⁺, Sr²⁺ and anions like CO₃²⁻ PO₄³⁻, F⁻, Cl⁻, Tartrate ion, Citrate ion, NO₃⁻, SCN⁻, EDTA, Oxide, C₂O₄²⁻, IO₄⁻ do not interfere in the estimation of [Ir(III)]. The metals like Ag, Al, Co, Cd, Bi, Cu, Mo, Ni, Pb, Sb and Zn interfere in this method. Therefore a pretreatment is required for separation/ precipitating/masking these ions before undertaking the proposed method for this purpose, H₂S may be passed in presence of 0.3 MH⁺ solutions, followed by filtration and boiling of H₂S. After it a dilute alkaline solution of α – nitroso – β – naphthol is added and precipitates are filtered¹⁷. Thereafter the solution is neutralized and the present method is applied. In absence of the above given

interferrants, the proposed method is applied. In absence of the above given interferrants, the proposed method may successfully be used for the determination of microgram quantities of[Ir(III)] in aqueous media.

Comparison with other methods

The result of the present method is compared with other reported spectrophotometric methods in **Table -2**. From the data it can be revealed that the reported methods are consuming, occurs at very high temperature and in the organic solvents like chloroform, ether etc. As compared with these methods, the present method is considerably less complicated occurs at room temperature and in aqueous alkaline medium. The method is also sensitive and requires low reagent concentration. The linear range of detection for the present method is quite good i.e. $0.258 - 8.37\mu$ gml⁻¹ as compared to reported methods. The absorptivity value ranges from 2.37 x $10^3 - 3.27 \times 10^3$ lmol⁻¹cm⁻¹ which lies in the range of reported methods in ethyl acetate medium. But the absorptivity value is lower than the reported in chloroform medium.

IV.CONCLUSION

Thus from the above results it can be concluded that the proposed method is relatively simple, inexpensive and sensitivity which require low reagent concentration and can be used at room temperature without heating in aqueous alkaline medium. In the present work a simple, sensitive, selective and inexpensive method with sulphur containing amino acid like cystine and methionine, HCF (III) redox system has been developed for the determination of iridium. The method avoids the use of hazardous solvent as the reaction occurs in aqueous medium. The method requires low reagent concentration and can be used at room temperature without heating. Thus the present method is simple, sensitive cost effective and more environments friendly. **Table -1**

Characteristics of various types of calibration curves for the proposed method [HCF (III)] = 3.00 X 10 ⁻⁴ mol dm⁻³, [Cystine] or [Methionine] = 3.00 X 10 ⁻⁴ mol dm⁻³ [NaOH] = 0.4 mol dm⁻³, μ =0.5 mol dm⁻³, Temp. =35 ± 0.1 °C, λ max = 420nm

Parameters	Cystine	Methionine	
Beer's law limit	0.258 -8.37	0.258 - 8.37	
Molar absorptivity x 10 ⁻³	2.83 - 4.11	2.31 - 3.27	
$(lmol^{-1}cm^{-1})$			
Sandell's sensitivity	0.0680 - 0.0467	0.0834 - 0.0588	
(µgcm ⁻²)			
Slope x 10 ²	(-) 1.47 – 0.0254	(-) 0.120 - 0.003	
Absorbance unit(µg ⁻¹ cm ³)			
Intercept	0.3388 - 0.00008	0.3810 - 0.00025	
(Absorbance unit)(µg ⁻¹ cm ³)			
Correlation coefficient(r)	(-) 0.9996 - 0.9995	(-) 0.9994 - 0.9866	
Coefficient of determination(r ²)	0.9994 - 0.9989	0.9988 - 0.9734	
Standard Deviation (%)	0.0406 - 6.786	0.0318 - 1.702	
(From six determination)			
Recovery	98.8 - 96.2	99.5 – 95.5	

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Table -2

Comparison of the present method for iridium determination with some of methods reported in literature

Reagent	Medium	Heating	Molar	Linear	Reference
		T®C	absorptivity	range	
		(T/min.)		(µg cm⁻³)	
		No heating			
Difurfuryl –	Ethyleacetate	No heating	4.15 x 10 ⁴	0.93 - 3.73	18
thiocarbohydrazone				[Ir(III)]	
(DCE)					
1phenyl -4,4 -6 – trimethyl –	CHCl ₃	60®C	3.38 x 10 ³	3.8 - 42.0	19
(1H,4H)-Pyrimidine -2 –		5 min.		[Ir(III)]	
Thiolate(PTPT)					
2 –Mercapto -4,methyl – 5-	CHCl ₃	No heating	9.5 x 10 ³	0.6 - 9.0	20
phenylazopyrimidine(MFAP)				[Ir(III)]	
Bis(thiopheno -2 –aldehydo)-	Ethyleacetate	100®C	3.2 x 10 ⁴	1.2 -4.2	21
thiocarbohydarzone (BTATCH)		30 min.		[Ir(III)]	
Present Method	Aqueous	35®C	2.37 X 10 ³ –	0.258 –	
	alkaline		3.27 X 10 ³	8.37	
				[Ir(III)]	

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