



Microgram determination of iridium (III) by kinetic spectrophotometric method

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ABSTRACT

A method for the determination of iridium is based on the Ir(III) catalyzed oxidation of alanine by hexacyanoferrate(III) in aqueous alkaline medium by kinetic - spectrophotometric analysis. By this method Beer's law is obeyed in the range of 2.99 to 19.98 $\mu\text{g cm}^{-3}$ of Ir(III). The molar absorptivity & sandell's sensitivity are found 1.0×10^3 to $1.3 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ and 0.145 to 0.192 $\mu\text{g cm}^{-2}$ respectively. The value of correlation coefficient lies between 0.999 to 0.985. 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 results show that the present method is more simple and sensitive than the reported methods and especially useful in absence of the expected interfering ions. The standard deviations estimated from six independent determinations in sample of Ir(III) are 0.0588 to 0.115.

Key Words: Microgram determination, Oxidation, Hexacyanoferrate, Alanine, Ir(III).

1. INTRODUCTION

Iridium an important member of platinum group metals is used as an effective catalyst. The global demand for Iridium in 2007 was 119,000 troy ounces (3700 Kg) out of which 24000 troy ounces (750 Kg) were used for catalysis (1). It is a minor constituent of most platinum metal deposits. Therefore, high selective, sensitive, rapid and economical methods are needed for its trace determination. Some instrumental methods are reported for this purpose (2-4). However, the necessary instruments are expensive, day to day maintenance costs are high and the methods are not free from various types of interferences (5-7). Some researchers also reported the kinetic spectrometry methods for the determination of trace iridium based on the catalytic effect of iridium in the oxidation reaction of rhodamine-B (8) and ethylrhodamine (9-19) by potassium periodate. 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 alanine by hexacyanoferrate (III) catalyzed by iridium (III) in aqueous alkaline medium.

2. EXPERIMENTAL SECTION

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 oxidation of alanine. [Alanine] = $3.00 \times 10^{-3} \text{ mol dm}^{-3}$, [HCF(III)] = $3.00 \times 10^{-4} \text{ mol dm}^{-3}$, [NaOH] = 0.40 mol dm^{-3} , $\mu = 0.50 \text{ mol dm}^{-3}$, Temp. = $35 \pm 0.1^\circ \text{C}$, $\lambda_{\text{max}} = 420 \text{ nm}$. For this purpose following procedure was adopted for preparation of calibration curve. A definite volume of stock solution of hexacyanoferrate abbreviated as (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 the pipette. The reaction mixture and stock solution of alanine was then clamped in a thermostat at $35 \pm 0.1^\circ \text{C}$. After 30 min, a required amount of alanine solution was added to the reaction mixture and stirred to start the reaction. All the additions were made in amounts calculated for maintaining the concentration of different reagents as mentioned above. Different sets were prepared in a similar manner varying the Ir(III) concentration. Aliquots were withdrawn from the reaction mixture after repeated intervals of 5 min and absorbance was recorded. The absorbance of reaction mixture goes on decreasing with the passage of time. The absorbances vs. time plots were made for all the sets. Initial rates $[dA/dt]_i$ were evaluated after 5 min from the start of the reaction by using plane mirror method. The pseudo first order rate constant (k_1) were calculated by Guggenheim's method.

3. RESULTS AND DISCUSSION

The study deals with the kinetic spectrophotometric studies on the microgram determination of Ir(III), while it catalyses the alanine and hexacyanoferrate(III) redox system in aqueous alkaline medium. The reaction was followed by noting the absorbance of the reaction mixture after 5, 10, 15, 20 min from the start of the reaction. Linear calibration curves were obtained in terms of type 'A', type 'B', type 'C', type 'D', type 'E', type 'F' and type 'G', i.e. A_5 or A_{10} or A_{15} or A_{20} or A_{25} or $[dA/dt]_i$ or k_1 vs. [Ir(III)] plots respectively. (where A_5 , A_{10} , A_{15} , A_{20} , A_{25} are the absorbance values after 5, 10, 15, 20, 25 min from the start of the reaction respectively. The stoichiometry of the reaction was studied by estimating the amount of hexacyanoferrate(II) ions produced after definite interval of time with standard solution of ceric(IV) sulphate using ferroin as redox indicator. The studies show that two moles of hexacyanoferrate(III) are used for the oxidation of one mole of alanine. Based on the experimental results, it can be proposed that reaction proceeds through complex formation between anion of alanine and Ir(III) which slowly disproportionate into Ir(I) and intermediate product. Ir(I) reoxidized by two moles of hexacyanoferrate(III) ions to Ir(III) through electron transfer mechanism & the intermediate product decomposes to final product (10,11).

Table 1 [HCF(III)] = $3.00 \times 10^{-4} \text{ mol dm}^{-3}$, [Alanine] = $3.00 \times 10^{-3} \text{ mol dm}^{-3}$, [NaOH] = 0.40 mol dm^{-3} , $\mu = 0.50 \text{ mol dm}^{-3}$, Temp. = $35 \pm 0.1^\circ \text{C}$, $\lambda_{\text{max}} = 420 \text{ nm}$

Parameters	A	B	C	D	E	F	G
Beer's law limit ($\mu\text{g cm}^{-3}$)	2.99-19.98	2.99-19.98	2.99-19.98	2.99-19.98	2.99-19.98	2.99-19.98	2.99-19.98
Molar absorptivity $\times 10^{-3}$ ($\text{l mol}^{-1} \text{cm}^{-1}$)	1.000	1.150	1.225	1.275	1.325	-	-
Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	0.192	0.167	0.157	0.151	0.145	-	-
Slope $\times 10^3$ absorbance unit. $\mu\text{g}^{-1} \text{cm}^3$	-5.500	-6.100	-6.500	-6.800	-7.000	0.101	0.022
Intercept (abs. Unit) from regression eq.	0.254	0.252	0.250	0.248	0.245	0.0004	0.00021
Correlation coefficient (r)	-0.9990	-0.9988	-0.9994	-0.9984	-0.9924	0.9832	0.9934
Coefficient of determination (r^2)	0.9980	0.9976	0.9989	0.9868	0.9850	0.9865	0.9848
Std deviation (%) (From six determination)	0.1155	0.1154	0.0588	0.1220	0.0000	0.0000	0.0000
Recovery %	100.00	99.99	99.99	99.26	100.00	100.00	100.00
% error	0.950	0.966	0.500	0.740	0.000	0.000	0.000

Table 2 Comparison of present method for iridium(III) determination with some of the reported methods in literature

S. No	Reagents	Medium	Heating Temp. ($^\circ \text{C}$) Time (min)	Molar absorptivity ($\text{l mol}^{-1} \text{cm}^{-1}$)	Linear range ($\mu\text{g cm}^{-3}$)	Ref. No.
1	Phenanthrenequinone Monoxime	CHCl_3	85- 90°C (30 min)	2.3×10^4	3.2-38.6	12
2	2-Methyl-1,4 naphthoquinone 4-Oxime	Butanol	2 hour (in water bath)	1.26×10^4	1.6-11.5	13
3	3 hydroxy-2-Methyl 1,4 naphthoquinone 4-Oxime	Ethanol	3 hour (in water bath)	1.27×10^4	1.51-15.9	14
4	1-(2-Pyridylazo)-2-naphthol	Ethanol	No heating	1.03×10^4	0.25-75.0	15
5	Diphenylcarbazone	Ethanol	45 min (in water bath)	1.76×10^4	0.8-10.0	16
6	2-Mercapto-4-methyl-5-phenylazopyrimidine (MFAP)	CHCl_3	No heating	9.5×10^3	0.6-9.0	17
7	Bis(thiopheno-2-aldehydo)-thiocarbohydrazone (BTATCH)	Ethyl acetate	100°C (30 min)	3.2×10^4	1.2-4.2	18
8	Difurfuryl thiocarbohydrazone (DCE)	Ethyl acetate	No heating	4.15×10^4	0.93-3.73	19
9	HCF(III)	Aqueous	35°C	1.0×10^3 - 1.325×10^3	2.99 - 19.98	Present method

According to table 1, the Beer's law limit is 2.99 - 19.98 $\mu\text{g cm}^{-3}$ for the estimation of Ir(III). The value of slope of the calibration curve, molar absorptivity and sandell's sensitivity indicated that the sensitivity of the method is good. Molar absorptivity and sandell's sensitivity of the method ranges from 1.00×10^3 to $1.33 \times 10^3 \text{ l mol}^{-1} \text{cm}^{-1}$ and 0.145 to 0.192 $\mu\text{g cm}^{-2}$ respectively. The value of slope lies between 7.00×10^{-3} to $0.101 \times 10^{-3} \mu\text{g}^{-1} \text{cm}^3$. The intercept and correlation coefficient are also calculated. The high value of correlation coefficient (r) and low value of intercept on the ordinate validates the linearity of the calibration graphs. The standard deviations evaluated from six determinations in sample of 2.99 to 19.98 $\mu\text{g cm}^{-3}$ of Ir (III) were 0.0588 to 0.1220 which are considerably

low. These are good for the trace determination of Ir(III). The correlation coefficient lies between (-) 0.999 to 0.993 and coefficient of determination (r^2) 0.9848 to 0.999 indicates high precision involved in the determination and good correlation of the data. Percentage recovery on the basis of six determinations is 99.26 to 100%.

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- Na^+ , K^+ , NH_4^+ , As^{3+} , Mn^{2+} , Ca^{2+} , Cr^{2+} , Li^+ , Sr^{2+} and anions- CO_3^{2-} , PO_4^{3-} , F^- , Cl^- , tartrate ion, citrate ion, CH_3COO^- , NO_3^- , SCN^- , EDTA, oxide, $\text{C}_2\text{O}_4^{2-}$, IO_4^- do not interfere in the estimation of [Ir(III)]. The metals like Ag, As, Co, Cd, Cr, Cu, Mo, Ni, Pb, Sb and Zn interfere in this method. Therefore, a pretreatment is required for separating / precipitating / masking these ions before undertaking the proposed method. For this purpose, H_2S may be passed in presence of 0.3 M H^+ solution, followed by filtration and boiling of H_2S . Thereafter, the solution should be neutralized and the present method be applied. In absence of the above given interferences, the proposed method may successfully be used for the determination of microgram quantities of Ir(III) in aqueous media.

The results of the present method are compared with other reported spectrophotometric methods in table 2. From the data it can be revealed that the reported methods are time consuming, occurs at very high temperature and in the organic solvents like chloroform, ether etc. As compared with these methods, the present methods is considerably less complicated, occurs at room temperature and in aqueous alkaline medium. The linear range of detection for the present method is quite good i.e 2.99 to 19.98 μgcm^{-3} as compared to reported methods. The absorptivity value ranges from 1.00×10^3 to $1.33 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ which is lower than the reported methods.

4. CONCLUSION

The results of the above method show that molar absorptivity and sandell sensitivity of the method are good. The linear range of estimation lies between 2.99 to 19.98 μgcm^{-3} . The estimation can be carried out in presence of some interfering ions. The comparison of the present method with the earlier reported methods reveals that present method is relatively simple, inexpensive and sensitive which require low reagent concentration and can be used at room temperature without heating, in aqueous alkaline medium.

SUMMARY OF RESEARCH

1. Estimation of iridium(III) has been carried out by studying the oxidation of alanine by hexacyanoferrate(III) ions in aqueous alkaline medium in presence of iridium(III) as catalyst.
2. For estimation the kinetic study has been carried out spectrophotometrically.
3. Linear calibration curves were obtained in terms of type 'A', type 'B', type 'C', type 'D', type 'E', type 'F' and type 'G', i.e A_5 or A_{10} or A_{15} or A_{20} or A_{25} or $[dA/dt]$ or k_1 vs. $[\text{Ir(III)}]$ plots respectively. (where A_5 , A_{10} , A_{15} , A_{20} , A_{25} are the absorbance values after 5, 10, 15, 20, 25 min from the start of the reaction respectively).
4. The results show that Beer's law is obeyed in the range of 2.99 to 19.98 $\mu\text{g cm}^{-3}$ of Ir(III).
5. The molar absorptivity & sandell's sensitivity are found 1.0×10^3 to $1.3 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ and 0.145 to 0.192 $\mu\text{g cm}^{-2}$ respectively

FUTURE ISSUES

The method may be used to determine the iridium(III) concentration in micrograms even then in presence of some interfering ions. The study will also contribute to the literature of chemical kinetics and analytical methods.

DISCLOSURE STATEMENT

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