Asian Journal of Chemistry Vol. 19, No. 5 (2007), 3431-3434

Kinetic Spectrophotometric Determination of Ir(III) in Alkaline Medium

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A simple and sensitive spectrophotometric method has been developed for the determination of trace amount of Ir(III). The method is based on the Ir(III) catalyzed oxidation of glycine by hexacyanoferrate (III) in aqueous alkaline medium. Beer's law is obeyed in the range of 1.99 to 39.98 μgcm^{-3} of Ir(III). The molar absorptivity and sandell's sensitivity are found 0.50×10^3 to 1.1×10^3 L mol^{-1} cm^{-1} and 0.384 to 0.174 μg cm^{-2}, correlation coefficient 0.9873 to 0.9968 and effect of few interfering ions have been worked out for developing the calibration curves in terms of absorbance or initial rates or pseudo first order rate constant *vs.* Ir(III) plot, λ_{max} was 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.

Key Words: Determination, Oxidation, Hexacyanoferrate, Glycine, Ir(III).

INTRODUCTION

Owing to their corrosion resistant nature, iridium alloys have found a wide rnage of applications in both the chemical industry and manufacture. Iridium is also a minor constituent of most platinum metal deposits. Therefore, high selective, sensitive, rapid and economical methods are needed for its trace determination. Neutron activation analysis, atomic absorption spectrometry or inductively coupled plasma, atomic emission spectrometry may be used for this purpose. However, the necessary instruments are expensive, day to day maintenance costs are high and the methods are not free from various types of interferences.

A wide variety of reagents such as 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol[1], 3-hydroxy-2-methyl-1-phenyl-4-pyridone or 3-hydroxy-2-methyl-1-(4-tolyl)-4-pyridone[2] have been used for the spectrophotometric determination of iridium. Estimation of Mn(II) by kinetic spectrophotometric method is reported in literature[3]. But the estimation of Ir(III) by kinetic spectrophotometric method has not been yet reported. Thus, in the present paper the kinetic spectrophotometric estimation of Ir(III) based on oxidation of glycine by hexacyanoferrate in aqueous alkaline medium has been carried out. The study deals with the kinetic spectrophotometric studies on the microgram estimation of Ir(III) while it catalyses the amino acid hexacyanoferrate redox system in aqueous alkaline medium.

EXPERIMENTAL

All chemicals used were of AR grade. Hexacyanoferrate(III) was used after recrystallization. All the solutions and reaction mixtures were prepared by using double distilled water. Absorbance was recorded on Sys. UV Visible spectrophotometer-118. λ_{max} for the reaction mixture were 420 nm at which the absorbance was noted only in the period in which the λ_{max} did not change and no precipitate/turbidity appeared. $IrCl_3 \cdot 10H_2O$ (SRL) was prepared by dissolving the sample in dil. HCl[4]. Following were the finally worked out conditions for running the kinetic sets for the purpose of determination of Ir(III) in aqueous alkaline medium: [glycine]-3 × 10^{-3} M; [HCF(III)]-3 × 10^{-4} M; [OH^-]-4 × 10^{-1} M; μ-0.5 M; λ_{max} = 420 nm, Temp. = 35 ± 0.1ºC. Following procedure was adopted for preparation of the calibration curves.

A definite volume of stock solution of hexacyanoferrate(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 mixture and stock solution of glycine was then clamped in a thermostat at 35 ± 0.1ºC After 0.5 h, a required amount of glycine solution was added to the mixture and stirred to start the reaction. All the additions were made in amounts calculated for maintaining the concentrations of different reagents as mentioned above. Different sets were prepared in a similar manner varying the Ir(III). Aliquots were withdrawn from the reaction mixture after repeated intervals of 5 min and the absorbance was recorded and absorbance *vs.* time plots were made for all the sets. Initial rates $(dA/dt)_5$ 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. Linear calibration curves were obtained in terms of type A-G *i.e.* A_5 or A_{10} or A_{15} or A_{20} or A_{25} or $(dA/dt)_5$ 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.

RESULTS AND DISCUSSION

Ir(III) may be determined in aqueous solution by mixing the sample with calculated quantity of hexacyanoferrate(III), sodium hydroxide, potassium chloride and starting the reaction by adding glycine followed by noting the A_5 or A_{10} or A_{15} or A_{20} or A_{25} evaluating (dA/dt) or k_1 by the

TABLE-1
CHARACTERISTICS OF VARIOUS TYPES OF CALIBRATION CURVES FOR THE PROPOSED METHOD
[glycine]-3 × 10^{-3} M; [HCF(III)]-3 × 10^{-4} M; [OH^-]-4 × 10^{-1} M; μ-0.5 M; λ_{max} = 420 nm, Temp. = 35 ± 0.1ºC

Parameters	A	B	C	D	E	F	G
Beer's law limit (μgcm^{-3})	1.99-39.98	1.99-39.98	1.99-39.98	1.99-39.98	1.99-39.98	1.99-39.98	1.99-39.98
Molar absorptivity × 10^{-3} (L mol^{-1} cm^{-1})	0.50	0.60	0.70	0.80	1.1	–	–
Sandell's sensitivity (μgcm^{-2})	0.384	0.320	0.275	0.240	0.174	–	–
Slope × 10^3 absorbance unit (μgcm^{-3}) (from regression equation)	-1.8386	-2.1563	-2.5135	-2.7483	-3.0000	-0.0776	0.0071
Intercept (abs. unit) (from regression equation)	0.2983	0.2952	0.2929	0.2882	0.2874	0.0003	0.0001
Correlation coefficient (r)	-0.9953	-0.9934	-0.9937	-0.9885	-0.9907	0.9968	0.9873
Coefficient of determination (r^2)	0.9907	0.9869	0.9875	0.9771	0.9815	0.9937	0.9748
Standard deviation (%) (from 6 determinations)	0.4082	0.2828	0.2121	0.2121	0.2449	0.4898	0.7348
Recovery (%)	100.00	99.52	98.97	99.67	99.34	98.48	97.46
Error (%)	2.3933	1.4388	1.0273	0.9868	1.3245	0.0151	0.0254

method discussed above. After this different calibration curves were used for the determination of Ir(III) in μgcm^{-3}. Methods of least squares[5] was used for obtaining the linear calibration curves with characteristics as given in Table-1.

The values of the molar absorptivity and sandell's sensitivity calculated from the graph were 0.50×10^{-3}-1.1×10^{3} L mol^{-1} cm^{-1} and 0.384-0.174 μg cm^{-2}, respectively. The detection limits 1.99 to 39.98 μg cm^{-3} are considerably low and these are very good for the trace determination of Ir(III). The correlation coefficient (r) and the coefficient of determination (r^2) indicate the high precision involved in the determination and good correlation of the data.

The results were found to be reproducible with good relative standard deviations and reasonable range of errors calculated on the basis of 6 determinations (Table-1). The method may be used in presence of the cations like Na^+, K^+, NH_4^+, As^+, Mn^{2+}, Ca^{2+}, Cr^{2+}, Li^+ and anions CO_3^{2-}, PO_4^{3-}, F^-, Cl^-, NO_3^-, SCN^-, EDTA, $C_2O_4^{2-}$, IO_4^{2-}, tartrate ion, citrate ion, as they do not interfere in the present case.

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(*Received*: 6 February 2006; *Accepted*: 19 February 2007) AJC-5425