Asian Journal of Chemistry Vol. 14, No. 2 (2002), 799–806

Development and Validation of Catalytic Spectrophotometric Method for Trace Determination of Ruthenium

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This paper describes highly sensitive, selective and rapid catalytic spectrophotometric method for the determination of trace amounts Ru(III). The method is based on the catalytic effect of Ru(III) on oxidation of benzylamine by alkaline hexacyanoferrate(III). The progress of reaction is followed by measuring the absorbance of the reaction mixture, *i.e.*, disappearance of hexacyanoferrate(III) at 420 nm. The calibration curves are linear in the range of 10 to 121 ng mL^{-1} of [Ru(III)] with detection limit 6.9 ng mL^{-1}. The standard deviations and percentage errors for the determination of Ru[III] in the range of 10 to 121 ng mL^{-1} have been calculated. The influence of many interferents on the determination of Ru(III) has been examined. The method has been applied to the analysis of Ru(III) in synthetic samples. Recovery was found to be quantitative. The method is convenient and reliable with sort analysis time. The developed method permits the determination of Ru(III) concentrations down to 10 ng mL^{-1} with good accuracy and reproducibility.

Key Words: Catalytic, Spectrophotometry, Trace, Determination, Ruthenium.

INTRODUCTION

The development of convenient, responsive and cost effective techniques for trace level determination of metals in biological, environmental, geological and industrial samples has been a challenging task before analytical chemists. This has greatly stimulated the interest in research, aimed at determination of such species in trace levels, in a variety of complex matrices. Thus the instrumental methods for trace analysis have undergone spectacular development in recent past. However, the much less expensive 'kinetic methods of analysis' is superior to many other techniques because of its sensitivity, simplicity, reproducibility and easy adoptability[1]. The catalytic kinetic methods continue to be the most popular method in the literature of kinetic methods of analysisis[1].

Ruthenium with other oxidants, catalyses the oxidation of several organic

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compounds in acidic as well as in alkaline media[2]. Thus ruthenium and its complexes, particularly in lower oxidation states, have generated a great deal of interest because of their use as homogeneous catalysts[2,3], anti-fungal[4] and antibacterial[5] activities. The catalytic effect of ruthenium, usually in one of the higher oxidation states, have been utilised for its determination. In recent years, few catalytic spectrophotometric methods have been developed for determination of ruthenium(III). However, most of these methods[6–9] require the use of expensive as well as rarely available chemicals as substrates. The most recent method for determination of Ru(III) was developed by Chen *et al.*[10] However, for high sensitivity, the reaction has been carried out at a very high temperature of 90°C and also the calibration curve is found to be linear in a very small range up to 5.4 ng mL^{-1}.

In the present investigation an attempt has been made to develop a catalytic spectrophotometric method for the determination of Ru(III) based on the Ru(III) catalysed oxidation of inexpensive and easily available benzylamine by alkaline hexacyanoferrate(III). The method has also been applied for determination of Ru(III) in synthetic samples. The method is proved to be highly sensitive, selective and rapid for ruthenium(III) determination in wide range of concentration.

EXPERIMENTAL

All reagents used were of analytical reagent grade. Triple distilled deionised water was used throughout in this investigation. Working solutions in all cases were prepared just before use by dilution as required. A stock solution of 4.0×10^{-2} M benzylamine (Sigma) was prepared after its purification by distillation at reduced pressure. Stock solution of 4.0×10^{-2} M potassium hexacyanoferrate(III) (SDS) was prepared and its strength was checked iodometrically[11]. The solution was stored in dark amber-colour volumetric flask. Sodium hydroxide and perchloric acid were used to maintain the pH at any desired value. Standard BDH buffers was used for standardization of pH meter. Sodium perchlorate (Purum, Fluka) was used to maintain a constant ionic strength at 0.5 M.

A stock solution of ruthenium(III), 5.0×10^{-3} M, was prepared by dissolving the appropriate amount of $RuCl_3 \cdot 3H_2O$ (Johnson Mathey Inc.) in 1 M hydrochloric acid. The possibility of oxidation of ruthenium(III) in hydrochloric acid[12] was checked by an oxygen absorption method using a manometeric set up. There was no absorption of O_2 by ruthenium(III) solution; thus the formation of ruthenium(IV) by aerial oxidation was excluded. The solution was also tested with potassium iodide solution to detect the presence of any ruthenium(IV) in the stock solution[12].

A double beam spectrophotometer Shimadzu, Model UV-240, equipped with 10 mm silica cells and an automatic digital recorder was used for recording spectral changes as well as absorbance measurements. The constant temperature 35.0 ± 0.1°C of the cell compartment was maintained by circulating water from a Remi ultracryostat Model C-702 thermostatic bath. All pH measurements were made on an Elico digital pH meter Model LI-120 fitted with an Elico C-51 combined electrode (glass electrode plus saturated calomel electrode).

The glassware used for this work was cleaned scrupulously by rinsing with 10^{-2} M EDTA, de-ionised water, 10^{-3} M EDTA and finally with triple distilled water in order to eliminate any trace of metal ions coming from the glass surface. Cells were cleaned after use by immersion in nitric acid (1 : 1) for 15 minutes to remove traces of ruthenium adsorbed.

Procedure

In order to establish the maximum catalytic effect of ruthenium and therefore the sensitivity is at the maximum, the concentrations and other conditions were selected after a critical examination of data given in a previous study of the influence of reaction variables on the rate of chosen indicator reaction[13]. All the solutions after adjustment to pH 10.50 ± 0.02 were brought to the same temperature by immersion in a thermostat at 35.0 ± 0.1°C for 30 minutes.

To a 10 mL glass stopper standard volumetric flask kept in the thermostat, 2.0 mL each of 1.6×10^{-3} M $[Fe(CN)_6]^{3-}$ and 4.0×10^{-2} M NaOH were added in order. This was followed by the addition of 2.0 mL of $4.0 \times 10^{-7} - 4.8 \times 10^{-6}$ M solution of ruthenium(III) salt immediately before the run to avoid any interaction among these reagents. The reaction was initiated by injecting 2.0 mL of 4.0×10^{-3} M benzylamine solution. The reaction mixture was shaken and a portion transferred to a 10 mm path length spectrophotometric cell kept in a temperature controlled cell compartment at 35.0 ± 0.1°C. The progress of the reaction was monitored using the "fixed-time procedure" as a measure of 'initial rate' from the change (decrease) in the absorbance of hexacyanoferrate(III) at 420 nm ($\varepsilon = 1020\ M^{-1}\ cm^{-1}$) for fixed intervals. The data obtained were used to plot the calibration graph for change in absorbance after a fixed time, *i.e.*, ΔA_t *versus* Ru(III) concentration as shown in Fig. 1.

RESULTS AND DISCUSSION

A plot of ΔA_t, *i.e.* the absorbance changes after t min (t = 4, 5 and 7) of mixing of the reagents *versus* ruthenium(III) concentration in the reaction mixture are linear from 10 to 121 ng mL^{-1} of [Ru(III)]. The calibration lines do not pass through the origin (Fig. 1) and give small values of the intercepts, which are equal to corresponding absorbance changes for the uncatalysed reaction after t minute. The linear regression equations relating ΔA_t to $[Ru^{3+}]$ between 1.0×10^{-7} M and 1.2×10^{-6} M are given in equations (1) to (3). The relationship at higher concentration of ruthenium is more complicated.

$$\Delta A_4 = 1.70 \times 10^5\ [Ru^{3+}] + 0.003 \quad \ldots (1)$$

$$\Delta A_5 = 1.98 \times 10^5\ [Ru^{3+}] + 0.006 \quad \ldots (2)$$

$$\Delta A_7 = 2.27 \times 10^5\ [Ru^{3+}] + 0.016 \quad \ldots (3)$$

Using these three calibration curves, the recovery experiments were performed

for the determination of Ru(III) in the range of 10–121 ng mL^{-1}. The accuracy and the reproducibility in determination of ruthenium(III) are presented in Table-1. The standard deviations and percentage errors, from the least square fit plots, corresponding to the each determination in the range of 10–121 ng mL^{-1} were also calculated and are given in Table-1. It is observed that the relative errors in case of calibration curve for ΔA_7 are higher than that of ΔA_5 as shown in Table-1. This is understandable because ΔA_5 is a closer measure of initial rate and gives sufficient and convenient absorbance changes. Although smaller fixed-times, *i.e.*, ΔA_4, ΔA_2 (ΔA_2 not shown in Fig. 1) have been tested, the absorbance

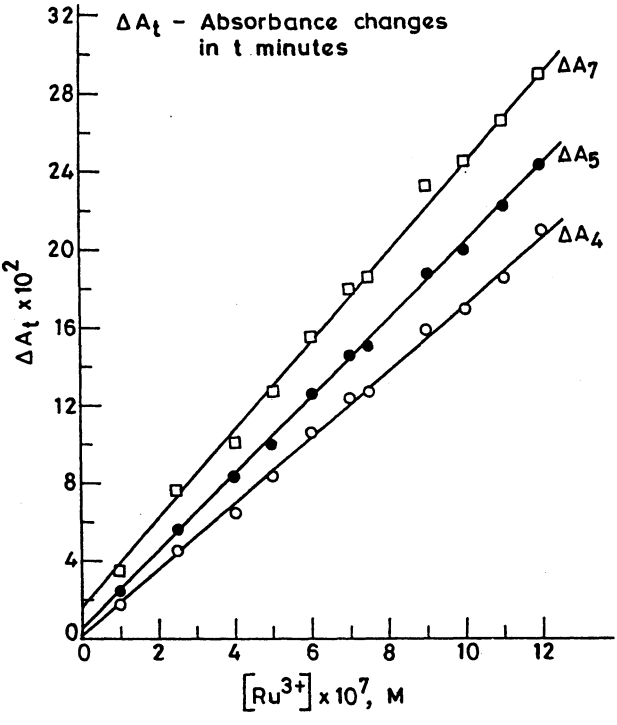

Fig. 1. Plots of absorbance changes in t min, ΔA_t *vs.* [Ru(III)] as calibration graphs. Conditions are given in Table-1.

changes are rather small and the measurements entail larger relative error. Thus the linear regression eqn. (2) corresponding to ΔA_5 was utilised for further validation, *i.e.*, statistical and application study.

The oxidation of benzylamine by alkaline hexacyanoferrate(III) is a slow process but it is strongly catalysed by ruthenium(III). The mechanism of this indicator reaction reported in literature[13] is reproduced in equation (4) to (7).

$$[Ru(H_2O)_6]^{3+} + OH^- \underset{}{\overset{K_1}{\rightleftharpoons}} \underset{\text{(Reactive species)}}{[Ru(H_2O)_5OH]^{2+}} + H_2O \qquad \ldots (4)$$

$$[Ru(H_2O)_5OH]^{2+} + \underset{\text{(substrate)}}{\text{Benzylamine}} \overset{K_2}{\rightleftharpoons} [\text{Intermediate complex}] \quad \ldots (5)$$

$$[\text{Intermediate complex}] \xrightarrow[\text{slow}]{k} \text{Oxidation Product} + \underset{\text{(Hydride species)}}{[Ru(H_2O)_5H]^{2+}} \quad \ldots (6)$$

$$[Ru(H_2O)_5H]^{2+} + 2OH^- + 2[Fe(CN)_6]^{3-} \longrightarrow [Ru(H_2O)_5OH]^{2+} + 2[Fe(CN)_6]^{3-} + H_2O \quad \ldots (7)$$

After resorting to some valid approximations a rate expression for the catalysed reaction has been given as

$$\frac{-d[Fe(CN)_6^{3-}]}{dt} = \frac{kK_1K_2[\text{Substrate}][OH^-][Ru]_T^{3+}}{1 + K_1[OH^-]\{1 + K_2[\text{Substrate}]\}} \quad \ldots (8)$$

At low concentrations of the substrate, *i.e.*, $1 \gg K_2[\text{Substrate}]$, the rate expression reduces to eqn. (9).

$$\frac{-d[Fe(CN)_6^{3-}]}{dt} = \frac{kK_1K_2[\text{Substrate}][OH^-][Ru^{3+}]_T}{1 + K_1[OH^-]} \quad \ldots (9)$$

TABLE-1
ACCURACY AND PRECISION OF Ru(III) DETERMINATION IN AQUEOUS SOLUTION IN THE PROPOSED KINETIC METHOD AT $[Fe(CN)_6^{3-}] = 4.0 \times 10^{-4}$ M, [BENZYLAMINE] = 1.0×10^{-3} M, pH = 10.50 ± 0.02, TEMP. = 35.0 ± 0.1°C AND I = 0.5 M ($NaClO_4$)

$[Ru^{3+}]$ added ng mL^{-1}	ΔA_4		ΔA_5		ΔA_7	
	$[Ru^{3+}]$ found* ng mL^{-1}	%Error	$[Ru^{3+}]$ found* ng mL^{-1}	%Error	$[Ru^{3+}]$ found* ng mL^{-1}	%Error
10.10	9.60 ± 0.09	−4.95	9.70 ± 0.08	−3.96	9.54 ± 0.12	−5.54
25.26	26.27 ± 0.11	+3.99	25.67 ± 0.12	+1.62	25.87 ± 0.10	+2.41
40.43	37.90 ± 0.10	−6.25	39.42 ± 0.07	−2.50	38.20 ± 0.08	−5.51
50.53	48.71 ± 0.71	−3.60	48.51 ± 0.62	−3.99	49.32 ± 0.64	−2.39
60.64	61.75 ± 0.32	+1.83	61.15 ± 0.26	+0.84	61.85 ± 0.24	+1.99
70.75	71.86 ± 0.50	+1.56	71.25 ± 0.45	+0.70	72.36 ± 0.45	+2.27
75.80	74.79 ± 0.85	−1.33	74.80 ± 1.00	−1.32	75.40 ± 1.04	−0.53
90.96	93.99 ± 0.21	+3.33	92.48 ± 0.18	+1.67	95.51 ± 0.20	+5.00
101.07	100.46 ± 0.38	−0.60	99.05 ± 0.39	−1.99	103.39 ± 0.40	+2.29
111.17	109.66 ± 0.82	−1.36	110.67 ± 0.79	−0.45	111.58 ± 0.80	+0.36
121.28	123.60 ± 0.23	+1.91	121.28 ± 0.15	0.00	120.27 ± 0.14	−0.83
		Av. = ±2.79		Av. = ±1.73		Av. = ±2.65

*Average of triplicate runs.

Thus, other concentrations and experimental conditions remaining fixed, the rate of disappearance of hexacyanoferrate(III) is linearly related to the total (T) concentration of Ru(III) and this has been verified by us (vide infra, Fig. 1).

The spectral changes during a kinetic run have been recorded and the results are produced in Fig. 2. There are a continuous decrease of absorbance at 420 nm band (broad) and a corresponding decrease in the peak height at 303 nm (sharp) and 325 nm (shoulder) as well. The $[Fe(CN)_6]^{3-}$ is being consumed in the reaction because of its reduction to $[Fe(CN)_6]^{4-}$ by benzylamine, so the height of all the peaks assigned to $[Fe(CN)_6]^{3-}$ show a decrease with time due to its eventual conversion to $[Fe(CN)_6]^{4-}$. $[Fe(CN)_6]^{4-}$ has a weak absorption band near 325 nm but is not observed because it gets lost in the shoulder of $[Fe(CN)_6]^{3-}$ at 325 nm. An isosbestic point at 282 nm is also observed in the above spectrum which points out to the coexistence of two species, *viz*, $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ as assumed in eqn. (7) of the proposed mechanism[13]. The statistical detection limit P defined by Kaiser[14] was calculated from the standard deviation (S_0) and the background signal (P_0) using expression:

$$P = P_0 + 3\sqrt{2}\, S_0 \qquad \ldots(10)$$

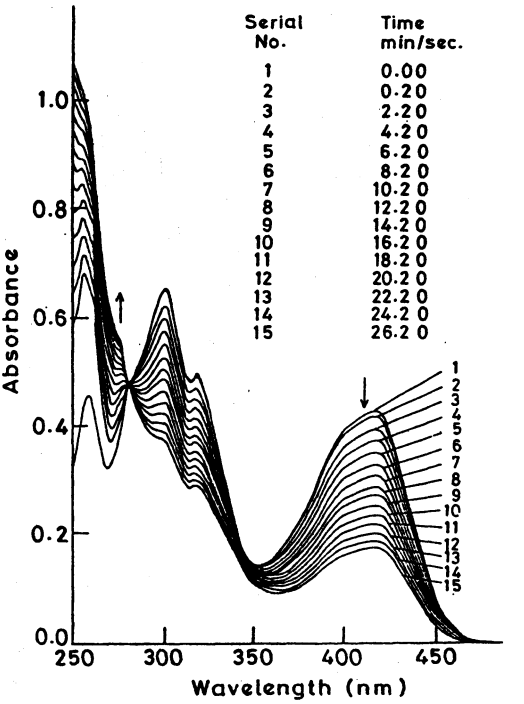

Fig. 2. Repetitive scan of the reaction mixture during a typical kinetic run at $[Ru^{3+}] = 1.0 \times 10^{-6}$M and other conditions given in Table-1

The standard deviation for the background signal was evaluated from three separate kinetic runs corresponding to ΔA_5 for the uncatalysed reaction. The

detection limit calculated for the proposed method, under optimum experimental conditions, using ΔA_5 data was found to be 6.9 ng mL^{-1} ruthenium in the test sample. The sensitivity expressed as the slope of the calibration function corresponding to ΔA_5 was sufficiently high, (1.98×10^5 L $mole^{-1}$). Improvement can be achieved by increasing the time interval to seven minutes or more but this would increase the total analysis time and error correspondingly.

To test the selectivity of the developed method, interference study by many cations and anions on the kinetic determination of 70.75 ng mL^{-1} ruthenium(III) was carried out using ΔA_5 regression equation. Table-2 shows the tolerance concentration ratio to ruthenium. The tolerance limit is taken as the concentration, which causes an error of not more than ±4% in ruthenium determination.

TABLE-2
EFFECT OF DIVERSE IONS ON THE DETERMINATION OF 7.0×10^{-7} M (70.75 ng mL^{-1}) OF RUTHENIUM(III) USING ΔA_5 REGRESSION EQUATION OTHER CONDITIONS APPLIED, AS GIVEN IN TABLE-1

Ions added	Limiting concentration ratio, ([Interfering ion]/[Ru(III)])
NO_3^-, SO_3^{2-}, acetate, tartarate, oxalate, citrate, $S_2O_3^{2-}$, Cr(III), La(III), Bi(III), Mg(II), K(I), Mo(VI)	1200*
Cu(II), Co(II), Ni(II), Cd(II), Zn(II), Mn(II), Hg(II), Pd(II)	570
Fe(III), Ce(III), Rh(III)	200
Br^-, BrO_3^-, CN^-	50
Ce(IV), Ag(I)	20
EDTA as Na_2 salt, Os(VIII), Ir(III), I^-	10

*Maximum ratio tested.

Determination of Ruthenium(III) in Synthetic Samples

In order to validate the analytical capability, *i.e.*, to establish the reliability and applicability of the developed method, it was applied to the determination of Ru(III) in different synthetic samples. This was done because authentic samples containing trace amounts of ruthenium were not available. The results shown in Table-3 indicate that the recoveries are very quantitative. Thus ruthenium can be determined in the specified concentration range in mixtures containing many metal ions in relatively high concentrations. The higher recovery in each case may be attributed to synergistic effect due to presence of other cations, which is not uncommon.

TABLE-3
APPLICATION OF THE METHOD TO SYNTHETIC SAMPLES USING ΔA_5 REGRESSION EQUATION UNDER CONDITIONS GIVEN IN TABLE-1

Synthetic samples (SS)	Composition of the synthetic mixture ng mL^{-1}	Ruthenium found* ng mL^{-1}	Recovery %
SS-1	Ru(III) 15.76 + Mo(IV) 7580 + Pd(II) 303 + Rh(III) 758	15.76	104
SS-2	Ru(III) 20.21 + Rh(III) 2021 + Fe(III) 1000 + OS(VIII) 101	21.02	104
SS-3	Ru(III) 30.21 + Ir(III) 151 + Ag(I) 240 + Os(VIII) 151 + Ru(III) 1027	31.10	103
SS-4	Ru(III) 80.85 + Os(VIII) 243 Ir(III) 243 + Pd(II) 404 + Rh(III) 1617	84.90	105

*Average of triplicate runs.

CONCLUSION

In conclusion, trace determination of Ru(III) at levels down to 7 ng mL^{-1} is feasible by the use of ruthenium(III) catalysed, $[Fe(CN)_6]^{3-}$-benzylamine redox reaction, without the need of pre-concentration. Thus the method reported here is simple, sensitive, reproducible and easy adoptable in comparison to the methods reported in literature.

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(*Received:* 21 November 2001; *Accepted*: 5 February 2002) AJC-2590