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Kinetic-Catalytic Spectrophotometric Determination of Ruthenium(III) Using the Oxidation of Neutral Red by Metaperiodate in Cationic Micellar Medium

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A simple, selective catalytic method has been developed for determination of ruthenium(III) based on its catalytic effect on the oxidation of neutral red by metaperiodate in micellar medium. The reaction rate was controlled specrophotometrically by controlling the dye absorbance at 523 nm. The optimized conditions made it possible to determine ruthenium(III) in the range of 0.001-0.14 μg/mL ($\Delta A = 3.2044C_{Ru} + 0.001$) and with a detection limit of 0.77 ng/mL. The relative standard deviation of 0.020 and 0.06 mg/mL Ru(III) was 2.3 and 1.4 %, respectively. The proposed method has been successfully applied for analysis of trace amounts of ruthenium(III) in real samples.

Key Words: Ruthenium(III), Spectrophotometry, Neutral red, Catalytic.

INTRODUCTION

Ruthenium is situated in the middle of the second row of the transition metal series and lives at the heart of the periodic table. Different studies have been carried out regarding the application of materials containing Ru compounds. Due to their electrochemical and thermoelectric properties, such types of materials showed potential catalytic, pharmaceutical, analytical and theoretical applications[1-4]. The success of *cis*-platin as an anticancer agent has stimulated the search for other organometallic cytotoxic compounds with more acceptable toxicity profile and, if possible, an increase of antitumor activity. In the last three decades, a wide range of ruthenium agents has been synthesized and tested for anti-tumor properties. Despite of their low cytotoxic potential *in vitro*, many ruthenium compounds increase the life time expectancy of tumor-bearing hosts. Thus the increasing importance of the use of ruthenium in widely different fields, particularly in pharmacology[5-9], metallurgy[10-12] and in high technology components[13-15], had made it necessity to develop simple, inexpensive and selective methods for the determination of traces of ruthenium(III) in various samples.

Different methods have been reported for detecting this metal such as voltammetry[16], atomic absorption spectrometry[17], fluorimetry[18] and spectrophotometry[19-22]. The availability of spectrophotometric instruments and the simplicity of analytical procedure make the procedure attractive for a wide range of applications. Many spectrophotometric methods have been used for determination of Ru(III) *via* its catalytic effect on the oxidation of dyes, such as benzylamine[23], indigocarmine[24], hematoxilyin[25], thymolblue[26], rhodamine B[27,28] and Ce(IV)-As(III) system[29] by some oxidants. All of these methods have interference effect or high limit of detection (> 5.0 ng/mL). The availability of spectrophotometry apparatus and the simplicity of analytical procedures make the technique attractive for a wide range of application.

In this paper a rapid, selective, sensitive and simple method is described for the determination of Ru(III) based on its catalytic effect on the oxidation of neutral red by metaperiodate. Neutral red is a maroon colour in the water solution with high molar absorbtivity (10^4 L mol^{-1} cm^{-1}) that Ru(III) has suitable catalytic effect on the oxidation of this reagent.

EXPERIMENTAL

Neutral red solution of 1.0×10^{-3} mol L^{-1} was prepared by dissolving 0.0288 g of neutral red (Merck) in water and diluting it in a 100 mL volumetric flask. Metaperiodate stock solution of 0.01 mol L^{-1} was prepared by dissolving 0.5750 g potassium metaperiodate (Merck) in water and diluting it in a 250 mL volumetric flask. A 100 µg/mL stock solution of Ru(III) was prepared by dissolving 0.0128 g, of $RuCl_3$ (Lobachem), in ethanol in a 100 mL volumetric flask.

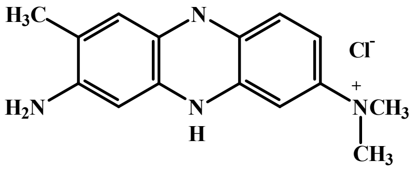
All glassware were cleaned with a detergent solution, rinsed with tap water, soaked in dilute HNO_3 solution (2 % v/v), rinsed with water and dried.

Absorption spectra were recorded with a CECIL model 7500 spectrophotometer with a 1.0 cm quartz cell. A model 2501 CECIL Spectrophotometer with 1.0 cm glass cuvettes was used to measure the absorbance at a fixed wavelength of 521 nm. A thermostat water batch was used to keep the reaction temperature at 30 ºC.

Recommended procedure: All the solutions and distilled water were kept in a thermo stated water batch at 30 °C for 20 min for equilibration before starting the experiment. An aliquot of the solution containing 1.0×10^{-2}–1.4 µg/mL Ru(III) was transferred into a 10 mL volumetric flask and then 1 mL of sulfuric acid solution (2 M), 1 mL of 0.013 M cetyl trimethylammonium bromide and 0.8 mL 0.001 M neutral red solution were added to the flask. The solution was diluted to *ca.* 8 mL with water, then 2 mL of 0.001 M metaperiodate solution was added and the solution was diluted to the mark with water. The solution was mixed and a portion of the solution was transferred to the spectrophotometer cell. The reaction was followed by measuring the decrease in absorbance of the solution against water at 523 nm for 0.5-4.5 min from initiation of the reaction. This signal (sample signal) was labeled as ΔA_s. The same procedure was repeated without addition of Ru(III) solution and the signal (blank signal) was labeled as ΔA_b. Time was measured just after the addition of last drop of metaperiodate.

RESULTS AND DISCUSSION

Neutral red undergoes a oxidation reaction with metaperiodate to form a colourless product at very slow rate. It is found that this reaction rate is sharply increased by addition of trace amount of Ru(III). Fig. 1 shows the absorption spectra of neutral red-IO_4^- Ru(III) system at different time. The absorbance of the solution decreased with time at 523 nm. Neutral red has the following structure:



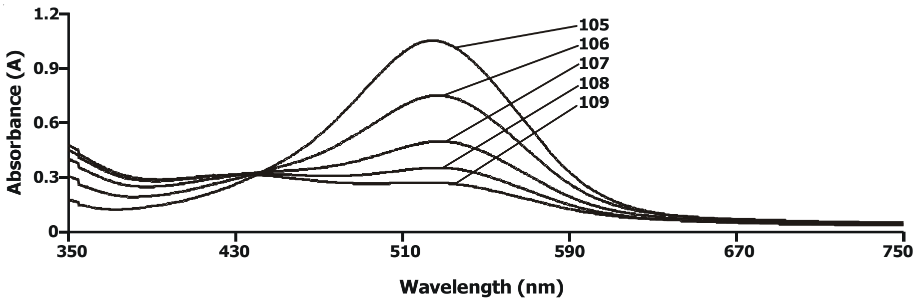


Fig. 1. Variation of the neutral red -IO_4^--Ru(III) system with time, condition: sulfuric acid concentration, 0.12 M; neutral red 8.0×10^{-5} mol L^{-1}; IO_4^- 2.0×10^{-4} mol L^{-1}; cetyltrimethyl amonium bromide concentration, 6.5×10^{-3} M, Ru(III), 100.0 ng/mL; temperature, 30 ºC; Time interval for each scan, 60 s

The mechanism of this process probably is equal with the mechanism of nil blue-IO_4-Ru(III) catalytic system[30]. This mechanism could be represented as follows:

$$\text{Ru(III)} + IO_4^- \longrightarrow \text{Ru(VIII)} + IO_3^-$$

$$\text{Ru(VIII)} + \text{Periodate} \longrightarrow \text{Ru(VIII) - Periodate complex}$$

$$\text{Ru(VIII) - Periodate complex} + NR_{(Red)} \longrightarrow NR_{(Ox)} + \text{Ru(III)} + IO_3^-$$

The total catalytic reaction could be expressed as follows:

$$NR_{(Red)} + \text{Periodate} \xrightarrow{\text{Ru(VIII)}} NR_{(Ox)} + IO_3^-$$

The mechanism led to the rate law as:

$$R = -d[NR]/dt = k[\text{Ru(VIII)-periodate complex}]\,[NR] \qquad (1)$$

Considered that the rate of the uncatalytic reactions was very slow and [Ru(VIII)] was equal to [Ru(III)], the rate law (1) was rewritten as:

$$R = -d[NR]/dt = k'[\text{Ru(III)}]\,[\text{periodate}]\,[NR] \qquad (2)$$

Considering that neutral red and KIO_4 were present in such excess that their concentration could be regarded as constant, the reaction became pseudo first-order for Ru(III) and the rate equation was further simplified as:

$$R = k'[\text{Ru(III)}] \qquad (3)$$

The equation (3) was the quantitative basis for the determination of trace Ru(III) by the proposed methods.

Influence of variables: In order to optimize the reaction to get the best sensitivity the variables affect the sensitivity such as acid concentration, concentration of neutral red and metaperiodate, the effect of deferent kinds of surfactant concentration and temperature were studied in terms of their effect on the sensitivity of determination of Ru(III).

The influence of sulfuric acid concentration on the sensitivity was studied in the range 0.04-0.2 M. Fig. 2 shows that the net reaction rate increases with sulfuric concentration up to 0.12 M and decreases at higher concentration values. This phenomenon is due to the fact that, in sulfuric acid concentration < 0.12 M, neutral red is protonated and thus the rate of reaction decreases. On the other hand at higher sulfuric acid concentration values (> 0.12), the ability of periodate to oxide neutral red increases with increasing hydroxide ions, thus, decreases the catalytic role of Ru(III). Therefore, a sulfuric acid concentration of 0.12 M was selected as the optimum sulfuric acid concentration value.

Fig. 3 shows the effect of the neutral red concentration on the sensitivity for the range of 0.4×10^{-4}–1.2×10^{-4} M. This sensitivity (net reaction rate) increases with increasing neutral red concentration up to 8×10^{-5} M and decreases at higher concentration. This may be due to the aggregation of the dye at higher concentrations. Therefore, a final concentration of to 8×10^{-5} M of neutral red was selected as the optimum concentration.

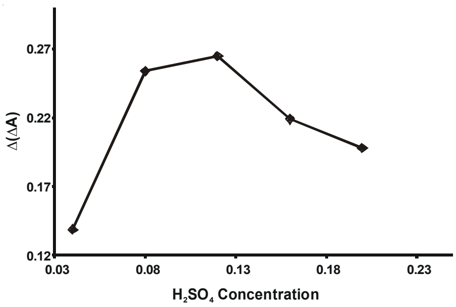


Fig. 2. Effect of sulfuric acid concentration on the sensitivity, conditions: neutral red concentration, 6.0×10^{-5} mol L^{-1}; Ru(III) concentration,100.0 ng/mL; metaperiodate concentration,2.0×10^{-4} mol L^{-1}; cetyltrimethyl amonium bromide concentration, 1.3×10^{-3} M; temperature, 30 ºC

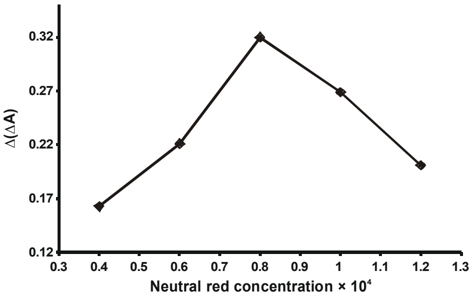


Fig. 3. Effect of neutral red concentration on the the sensitivity, conditions: sulfuric acid concentration, 0.12 M; Ru(III) concentration, 100 ng/mL; metaperiodate concentration, 2.0×10^{-4} mol L^{-1}; cetyltrimethyl amonium bromide concentration, 1.3×10^{-3} M, temperature, 30 ºC

The effect of the metaperiodate concentration on the rate of reaction was studied in the range of 0.8×10^{-4}–2.4×10^{-4} M (Fig. 4). The results show that the net reaction rate increases with increasing metaperiodate concentration up to 2.0×10^{-4} M and decreases at higher concentrations. Therefore, the metaperiodate concentration of 2.0×10^{-4} M was selected for further study.

A micelle usually can be formed by aggregation of charged organic molecules. These micelles have the same charge at the outer sphere. For those reactions which have charged species, these micelles can affect the rate of reaction by increasing the effective collisions. In order to choose an appropriate micelle system to enhance the sensitivity (rate of reaction rate), one must take into account the type of charge of the reactants, because the accelerating effect of micelles arises essentially from electrostatic and hydrophobic interaction between the reactants and micellar surface[31].

Non-ionic micelles (such as Triton-X-100), anionic micelle (sodium dodecyl sulfate, SDS) and cationic micelle (cetyltrimethyl amonium bromide, CTAB) and cetyl pyridinium chloride (CPC) were tested at concentration above their critical micelle concentration (CMC). The results are shown in Table-1. Therefore, from between these micelles, CTAB was selected for practical purposes.

The effect of the CTAB concentration on the rate of reaction was studied in the range of 0-9.1 × 10^{-3} M (Fig. 5). This sensitivity increases with increasing CTAB concentration up to 6.5 × 10^{-3} M and decreases at higher concentrations. This is due to the high aggregation of the surfactant and change in the molar absorptivity of the neutral red in the solution. Therefore a final concentration of 6.5 × 10^{-3} M was selected as the optimum concentration of CTAB.

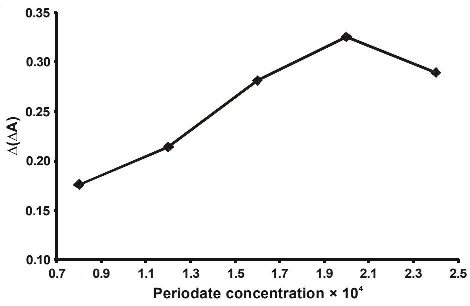


Fig. 4. Effect of metaperiodate concentration on the sensitivity. Conditions: sulfuric acid concentration, 0.12 M; Ru(III), 100 ng/mL; neutral red, 8.0 × 10^{-5} mol L^{-1} ; Cetyltrimethyl amonium bromide concentration, 1.3 × 10^{-3} M; temperature, 30 °C

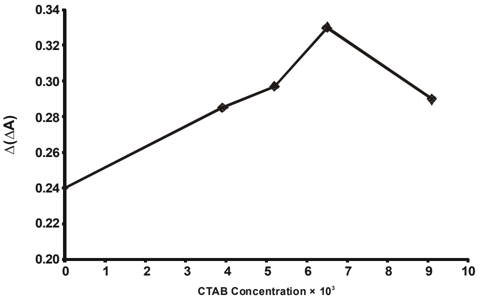


Fig. 5. Effect of cetyltrimethyl amonium bromide concentration on the sensitivity. Conditions: sulfuric acid concentration, 0.12 M; Ru(III) Ru(III) concentration,100 ng/mL; neutral red concentration, 8.0 × 10^{-5} mol L^{-1}; metaperiodate concentration, 2.0 × 10^{-4} mol L^{-1}; temperature, 30 ºC

The effect of the temperature on the sensitivity was studied in the range 20-45 °C with the optimum reagent concentrations. The results showed that with increasing of the temperature up to 30 °C, the net reaction rate increases, whereas in the higher temperature values sensitivity decrease ($\Delta A = \Delta A_s – \Delta A_b$).This means that the rate of uncatalyzed reaction increases with temperature greater extent than the rate of the catalyzed and uncatalyzed reaction diminished at high temperature. Therefore, 30 °C was selected for further study.

Calibration graph, precision and limit of detection: Calibration graphs were obtained using the fixed-time method. This method was applied to the change in absorbance over an interval of 0.5-4.5 min from initiation of the reaction because it provided the best regression and sensitivity. Under the optimum conditions described above, a linear calibration range 0.001-0.14 mg/mL was Ru(III).

The equation of the calibration graph is ($\Delta A = 3.2044C_{Ru} + 0.001$ ($n = 7$, $r = 0.9999$), where ΔA is change in absorbance for the sample reaction for 0.5-4.5 min from initiation of the reaction (catalytic reaction) and C is Ru(III) concentration in µg/mL. The limit of detection from $Y_{LOD} = Y_b + 3S_b$ is 0.77 ng/mL, where, Y_{LOD} is signal for limit of detection, Y_b is average blank signal ($n = 10$) and S_b is standard deviation of blank signal ($n = 10$, uncatalyzed reaction). The relative standard deviation for six replicate determination of 40.0 and 80.0 ng/mL Ru(III) was 2.1 and 2.6, respectively.

Study of interference ions: In order to assess the application of the proposed method to synthetic samples, the effect of various ions on the determination of 40.0 ng/mL Ru(III) was studied. The tolerance limit was defined as the concentration of a added ions causing a relative error less than 3 % the results are summarized in Table-1. Many ions did not interfere, even when they were present in 100 fold excess over Ru(III). The results show that the method is relatively selective for ruthenium(III) determination.

TABLE-1
SURFACTANTS TESTED AS POTENTIAL MICELLAR CATALYSTS TO ENHANCE THE RATE OF NEUTRAL RED-IO_4^--Ru(III) REACTION

Surfactant	Type	CMC (M)	Micellar catalysis
Triton-X-100	Nonionic	3.0×10^{-4}	Negative
SDS	Anionic	8.1×10^{-3}	Negative
CTAB	Cationic	1.3×10^{-3}	Positive
CPC	Cationic	1.2×10^{-4}	Inert

TABLE-2
INTERFERENCES EFFECT ON THE DETERMINATION OF 40.0 ng/mL, Ru(III)

Species	Tolerance limit ($W_{ion}/W_{Ru(III)}$)
Na^+, K^+, Ca^{2+}, Mg^{2+}, Rb^+, Pb^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Br^-, Cl^-, $C_2O_4^{2-}$, $S_2O_8^{2-}$, HSO_4^-, ClO_3^-, CO_3^{2-}, NO_3^-, BO_3^{3-}, Tatarate	1000
Co^{2+}, Mn^{2+}, Hg^{2+}, Pd^{2+}	800
Rh^{3+}	400
SCN^-, Os^{8+}	200
Fe^{2+}, Ag^+	50

Sample analysis: In order to evaluate the applicability of the proposed method, water samples and synthetic water samples were analyzed to determine Ru(III) contents. The results are presented in Table-3. Good recoveries with precise results show good reproducibility and accuracy of the method.

TABLE-3
DETERMINATION OF Ru(III) IN REAL SAMPLES

Sample	Ru(III) added (ng/mL)	Ru(III) found (ng/mL)	Recovery (%)	RSD (%) n = 5
River water	0	Less than detection limit	–	–
River water	10.0	10.40	104	2.1
River water	40.0	37.50	94	1.7
Drinking water	0	–	–	–
Drinking water	10.0	9.60	96	1.7
Drinking water	40.0	42.00	105	2.3

Conclusion

The kinetic-spectrophotometric method developed for the determination of Ru(III) is inexpensive, uses readily available reagents, allows rapid determination at low operating costs and shows simplicity, adequate selectivity, low limit of detection and good precision and accuracy compared to other kinetic procedures (Table-4). With this method, it is possible to determine ruthenium(III) at levels as low as 0.77 ng/m without the need for any preconcentration step.

TABLE-4
COMPARISON OF SOME METHODS FOR DETERMINATION OF RUTHENIUM(III) WITH PROPOSED METHOD

Method	DL (ng/mL)	LDR (ng/mL)	Reference no.
Spectrophotometry	30.00	100-2500	32
	0.33	1.12-300	33
	2.00	–	34
Voltammetry	1000	2000-60000	35
Fluorimetry	0.60	1.0-400	36
Atomic absorption	6.00	Up to 500	37
Present method	0.77	1-140	–

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