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Spectrophotometric Reaction Rate Method for the Determination of Trace Amounts of Ruthenium(III) by Its Catalytic Effect on the Oxidation of Spadns by Metaperiodate in Micellar Medium

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A new, simple and highly sensitive kinetic spectrophotometric method was developed for the determination of trace amounts of Ru(III). The method is based on the catalytic effect of ruthenium(III) on the oxidation of 1,8-dihydroxy-2-(4-sulfophenylazo)naphthalene-3,6-disulfonic acid trisodium (Spadns) by metaperiodate in micellar medium at pH = 5.6. The reaction was monitored spectrophotometrically by measuring the decreasing in absorbance of Spadns at 517 nm with a fixed-time method. The decrease in the absorbance of Spadns is proportional to the concentration of Ru(III) in concentration range 0.005-0.3 mg/mL after 4.5 min from initiation of the reaction. The limit of detection is 0.36 ng/mL Ru(III). The relative standard deviation of 40.0 and 100.0 ng/mL Ru(III) was 1.7 and 2.4 %, respectively. The method was applied to the determination of ruthenium in real water samples.

Key Words: Ruthenium, Catalytic, Spadns, Metaperiodate.

INTRODUCTION

Ruthenium is one of the noble metals and its content in the earth shell is very low. Recently, platinum group metals especially ruthenium and its chloro complexes have been widely used in the catalytic oxidation of some organic compounds[1,2]. There is a need for analytical methods for determination of metals in various matrices. Selective methods, which allow the determination of particular metals in the presence of each other, are of special interest. Many spectrophotometric methods have been used for determination of Ru(III) *via* its catalytic effect on the oxidation of dyes, such as benzylamine[3], indigocarmine[2], hematoxilyin[4], thymolblue[5], rhodamine B[6,7] and Ce(IV)-As(III) system[8] by some oxidants. All of these methods have higher limit of detection (> 5.0 ng/mL) or have many interfering ions (not selective).

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 Spadns [1,8-dihydroxy-2-(4-sulfophenylazo)naphthalene-3,6-disulfonic acid trisodium salt] by metaperiodate in micellar medium. The method permits the determination of a Ru(III) concentration down to 0.36 ng/mL with a good accuracy and reproducibility.

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EXPERIMENTAL

Doubly distilled water and analytical reagent grade chemicals were used throughout the experiments.

Spadns solution 7.36 × 10^{-1} M was prepared by dissolving 0.0419 g of the compound (Merck) in water and solution was diluted to the mark in a 100 mL volumetric flask. Metaperiodate stock solution 0.010 M, was prepared by dissolving 0.5750 g of potassium metaperiodate (M = 230) in water and diluting to 250 mL in a volumetric flask. Standard stock Ru(III) solution (100 mg/mL) was prepared by dissolving 0.0128 g of $RhCl_3$ (Loba Chem) in ethanol and diluted to 100 mL in a 100 mL volumetric flask.

Cetyl pyridinium chloride (CPC) stock solution 1.2 × 10^{-2} M was prepared by dissolving 1.470 g of CPC in a 250 mL volumetric flask.

Stock solution (1000 µg/mL) of interfering ions were prepared by dissalving suitable salts in water, hydrochloric acid or sodium hydroxide solution.

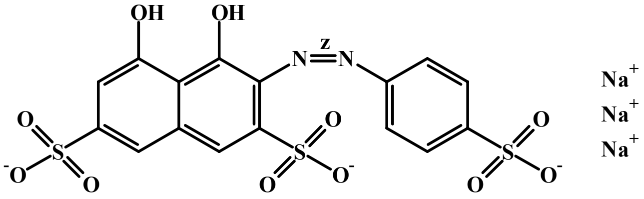
All glassware were cleaned with detergent solution, rinsed with tap water, soaked in dilute HNO_3 Solution (2 % v/v), rinsed with water and dried.

Absorption spectra were recorded with a model Carry 100, Varian 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 517 nm. A thermostate water batch was used to keep the reaction temperature at 30 °C. A pH meter metrohm model 744 used to prepare of buffer solutions.

Recommended procedure: All the solutions and distilled water were kept in a thermostated water batch at 30 °C for 20 min for equilibration before starting the experiment. An aliquot of the solution containing 5.0 × 10^{-2}-3.0 mg/mL Ru(III) was transferred into a 10 mL volumetric flask and then 1 mL of buffer solution (pH = 5.6, acetate), 0.6 mL cetyl pyridinium chloride 1.2 × 10^{-2} M and 1 mL 7.36 × 10^{-4} M Spadns solution were added to the flask. The solution was diluted to *ca.* 7 mL with water, then 2 mL 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 spectrophotometic cell. The reaction was followed by measuring the decrease in absorbance of the solution against water at 517 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

Spadns 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). Spadns has the following structure:



Influence of variables: In order to optimize the reaction to get the best sensitivity the variables affect the sensitivity such as pH, Spadns concentration, metaperiodate concentration, the effect of deferent kinds of surfactantants, surfactant concentration and temperature on the rate of catalyzed reaction [with Ru(III)] and uncatalyzed reaction [without Ru(III)] was studied.

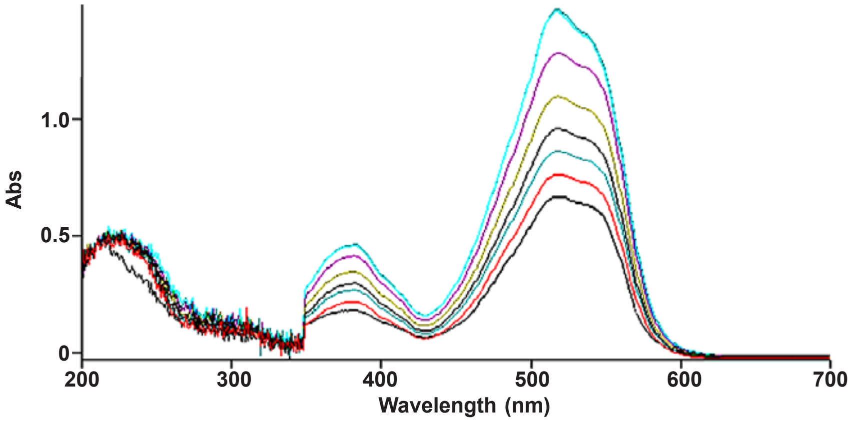


Fig. 1. Variation of the Spadns-IO_4^--Ru(III) system with time.condition: pH, 5.6; Spadns 7.36×10^{-5} M; IO_4^- 2.0×10^{-4} M; CPC 7.2×10^{-4}; Ru(III), 200.0 ng/mL; temperature, 30 ºC

The influence of pH on the sensitivity was studied in the range 3.5-7.0. Fig. 2 shows that the net reaction rate increases with pH up to 5.6 and decreases at higher pH values. This phenomenona is due to the fact that, in pH < 5.6, Spadns is protonated and thus the rate of reaction decreases. On the other hand at higher pH values (pH > 5.6), the ability of periodate to oxide Spadns increases with increasing hydroxide ions, thus, decreases the catalytic role of Ru(III).Therefore, a pH of 5.6 was selected as the optimum pH value.

Fig. 3 shows the effect of the Spadns concentration on the sensitivity for the range of 4.4×10^{-5}–1.03×10^{-4} M. This sensitivity (net reaction rate) increases with increasing Spadns concentration up to 7.36×10^{-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 7.36×10^{-5} M of Spadns was selected as the optimum concentration.

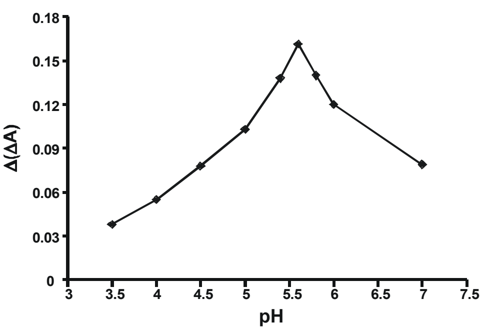


Fig. 2. Effect of pH on the sensitivity, conditions: 200 ng/mL Ru(III), 7.36 × 10^{-5} M Spadns 1.0 × 10^{-4} M metaperiodate and 1.2 × 10^{-3} CPC at 30 °C, in fixed time of 0.5-4.5 min from initiation of reaction

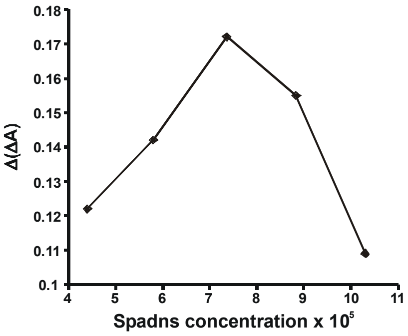
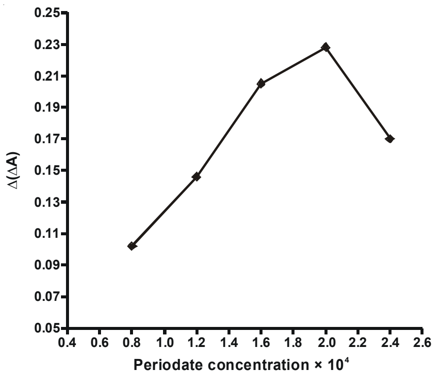


Fig. 3. Effect of Spadns concentration on the sensitivity, conditions: 200 ng/mL Ru(III), pH 5.6; 1.0 × 10^{-4} M metaperiodate; 1.2 × 10^{-3} CPC and at 30 °C, in fixed time of 0.5-4.5 min from initiation of reaction

The effect of the metaperiodate concentration on the rate of reaction was studied in the range of 8 × 10^{-5}–2.4 × 10^{-4} M (Fig. 4). The results show that the net reaction rate increases with increasing metaperiodate concentration up to 2 × 10^{-4} M and decreases at higher concentrations. Therefore, a metaperiodate concentration of 2 × 10^{-4} M was selected for further study.



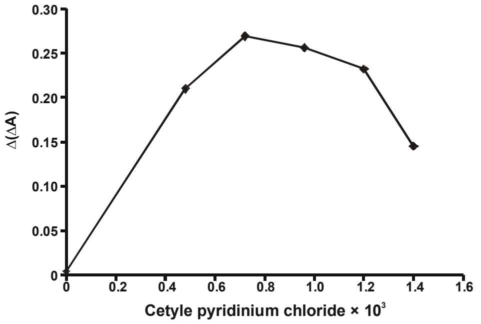


Fig. 4. Effect of metaperiodate concentration on the sensitivity, conditions: 200 ng/mL Ru(III), pH 5.6; Spadns 7.36 × 10^{-5} and 1.2 × 10^{-3} CPC at 30 ºC, in fixed time of 0.5-4.5 min from initiation of reaction

Fig. 5. Effect of CPC concentration on the sensitivity, conditions: 200 ng/mL Ru(III), pH 5.6; Spadns 7.36 × 10^{-5} and 2.0 × 10^{-4} M metaperiodate at 30 ºC, in fixed time of 0.5-4.5 min from initiation of reaction

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 the reactants, because the accelerating effect of micells arises essentially from electrotrostatic and hydrophobic ionteraction between the reactants and micellar surface[9].

Non-ionic micelles (such as Triton-X-100), anionic micelle (sodium dodecyl sulfate, SDS) and cationic micelle (cetyl trimethylammonium 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, CPC was selected for practical purposes.

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

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

The effect of the CPC concentration on the rate of reaction was studied in the range of 0-1.4×10^{-3} M (Fig. 5). This sensitivity increases with increasing CPC concentration up to 7.2×10^{-4} M and decreases at higher concentrations. This is due to the high aggregation of the surfactant and change in the molar absorptivity of the Spadns in the solution. Therefore a final concentration of 7.2×10^{-4} M was selected as the optimum concentration of CPC.

The effect of the temperature on the sensitivity was studied in the range 15-30 °C with the optimum pH and other reagent concentrations. The results showed that, as the temerature increases up to 30 °C, the net reaction rate increases, whereas higher temperature values decrease the sensitivity ($\Delta A = \Delta A_s – \Delta A_b$).This means that the rate of uncatalyzed reaction increases with temperature to a greater extent and the uncatalyzed reaction occurred at a sutable rate. 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 intiation of the reaction because it provided the best regression and sensitivity. Under the optimum conditions described above, a linear calibration range is obtained at 0.005-0.3 µg/mL Ru(III).

The equation of the calibration graph is $\Delta A = 1.745 \times 10^{-3} + 1.275 \times 10^{-3} C_{Ru(III)}$ (n = 7, r = 0.9998), 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 0.36 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 100 ng/mL Ru(III) was 1.7 and 2.4, respectively.

Interference study: In order to assess the application of the proposed method to synthetic samples, the efffect of various ions on the determination of 100 ng/mL Ru(III) was studied. The tolerance limit was defined as the concentration of added ions causing a relative error less than 3 % and 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.

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-2. Good recoveries with precise results show good reproducibility and accuracy of the method.

TABLE-2
EFFECT OF FOREIGN IONS ON THE DETERMINATION OF 100 ng/mL Ru(III)

Species	Tolerance limit ($w_{ion}/w_{Ru(III)}$)
Mg^{2+}, Ca^{2+}, Na^+, Li^+, K^+, NH_4^+, HSO_4^-, Br^-, Pd^{2+}, CH_3COO^-, $H_2PO_4^-$, SO_4^{2-}, $C_2O_4^{2-}$	1000
$S_2O_3^{2-}$, SO_3^{2-}, PO_4^{3-}, Cd^{2+}, Ce^{3+}	500
$S_2O_8^{2-}$, Mn^{2+}	300
Pb^{2+}, Zn^{2+}, Ba^{2+}, S^{2-}, Te^{6+}, Se^{6+}	200
Mo^{6+}, Fe^{3+}, Cr^{3+}	70
Al^{3+}, Ag^+, I^-	20

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

Sample	Ru(III) added (ng/mL)	Ru(III) found (ng/mL)	Recovery (%)	RSD (%) n = 3
River water	0	Less than detection limit	–	–
River water	10	10.4	2.3	104.0
River water	40	41.1	1.9	102.7
Drinking water	0	–	–	–
Drinking water	10	9.7	2.3	97.0
Drinking water	40	41.4	1.8	103.5

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

Method	DL (ng/mL)	LDR (ng/mL)	Reference no.
Spectrophotometry	30.00	100-2500	10
	0.33	1.12-300	11
	2.00	–	12
Voltammetry	1000	2000-60000	13
Fluorimetry	0.60	1.0-400	14
Atomic absorption	6.00	Up to 500	15
Present method	0.36	5-300	–

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. With this method, it is possible to determine ruthenium(III) at levels as low as 0.36 ng/mL without the need for any preconcentration step.

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