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Spectrophotometric Reaction Rate Method for the Determination of Ultra Trace Amounts of Rhodium by its Catalytic Effect on the Oxidation of Thionine by Metaperiodate in Micellar Media

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A simple kinetic spectrophotometric method was developed for the determination of ultra trace amounts of Rh(III). The method is based on the catalytic effect of rhodium(III) on the oxidation of thionine by periodate at pH 6.2 in micellar media. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of thionine at 599 nm with a fixed-time method. The decrease in the absorbance of thionine is proportional to the concentration of Rh(III) in concentration range 6.0×10^{-4} - 0.080 μg/mL and 0.080-0.50 μg/mL with a fixed time of 0.5-4.5 min from initiation of the reaction. The limit of detection is 0.29 ng/mL Rh(III). The relative standard deviation of 0.020 and 0.05 μg/mL Rh(III) was 2.29 and 1.42 %, respectively. The method was applied to the determination of rhodium in water.

Key Words: Rhodium, Catalytic, Thionine, Metaperiodate.

INTRODUCTION

Rhodium is found at trace levels in the earth. Rhodium is used in standard thermocouples of various ranges of temperature, in electrothermal industry[1] and as catalysts in chemical reactions such as the removal of nitrogen oxide (NO_x) from automobile exhaust[2], purification of gases produced from alcoholic combusion systems[3], *etc.* Several spectrophotometric methods have been reported in literature[4-7] for the determination of trace amounts of rhodium. However, their sensitivity and selectivity is generally unsatisfactory and none of these methods are able to measure Rh(III) at the level of ppb. Catalytic kinetic methods[5-14] have also been reported for the determination of rhodium. Many of these methods suffer from many interfering ions[8-10] and they are either time-consuming[8,14] and have a high detection limit[8,9,13] or they have a small linear dynamic range[12,13]. The microwave irradiation technique[15] used for the determination of Rh(III) has several disadvantages, including long analysis time, expensive instrumentation and high limit of detection. Another kinetic method is based on chemiluminescence detection of a luminal system in the presence of Rh(III)[16]. It has a high limit of detection (> 50 ng/mL), small range of detection (0.40-1.0 μg/mL Rh(III)) and low selectivity.

The proposed method is based on the catalytic effect of Rh(III) on the oxidation of thionine by periodate in the presence of cetyl trimethylammonium bromide (CTAB) as a micellar media. The reaction was monitored spectrophotometrically at 599 nm, the method is highly sensitive and rapid for Rh(III) determination.

EXPERIMENTAL

Double distilled water and analytical reagent grade chemicals were used during all of the experimental studies. 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 Shimadzu model UV-210 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 599 nm. A thermostat water batch was used to keep the reaction temperature at 30°C. A pH meter metrohm model 744 used to preparing of buffer solutions.

Thionin solution 1.0×10^{-3} M was prepared by dissolving 0.0287 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 250 mL volumetric flask. Cetyl trimethyl ammonium bromide (CTAB) stock solution 0.0130 M, was prepared by dissolving 1.197 g CTAB (BDH) in water and diluted to the mark with water in a 250 mL volumetric flask. The other surfactants tested, *e.g.*, sodium dodecyl sulfate (SDS), Triton-X-100 and cetyl pyridinium chloride were prepared in a similar way. Standard stock Rh(III) solution (1000 μg/mL) was prepared by dissolving 0.2630 g of $RhCl_3$ in water and diluted to 100 mL in a 100 mL volumetric flask. Buffer solutions in the range of pH 4.0-8.0 was prepared by the addition of suitable volume of 0.20 M sodium hydroxide solution to 100 mL of a solution 0.040 M in acetic acid, phosphoric acid and boric acid. Stock solution (1000 μg/mL) of interfering ions was prepared by dissolving suitable salts in water, hydrochloric acid or sodium hydroxide solution.

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 6.0×10^{-4} - 0.080 μg/mL Rh(III) was transferred into a 10 mL volumetric flask and then 1 mL of buffer solution (pH = 6.2), 2.6 mL of CTAB solution

(0.013 M) and 1.6 mL of thionine solution (1.0×10^{-4} M) were added to the flask. The solution was diluted to *ca.* 8 mL with water, then 0.3 mL of metaperiodate solution (0.010 M) 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 599 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 Rh(III) solutionand the signal (blank signal) was labeled as ΔA_b. Time was measured just after the addition of last drop of periodate.

RESULTS AND DISCUSSION

Thionine (TN) undergoes an oxidation reaction with metaperiodate to form a colorless product at slow rate. It is found that this reaction rate is sharply increased by addition of trace amount of Rh(III), especially in the presence of CTAB as a micellar medium. The rate equation of the catalyzed reaction is:

$$\begin{aligned} \text{Rate} &= -d[\text{TN}]/dt \\ &= K[\text{Rh(III)}][\text{TN}]^m[\text{IO}_4^-]^n \qquad (1) \end{aligned}$$

where k is the rate constant for the reaction. Because $[IO_4^-] >> [TN]$, IO_4^- could be considered to be constant. Integration of eqn. 1 and using Beer's law, the final expression is obtained as:

$$\Delta A = K'[\text{Rh(III)}]\,\Delta t \qquad (2)$$

where Δt is the reaction time and $K' = [IO_4^-]^n$

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

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

There are many methods, such as fixed-time, initial rate, rate constant and variable time methods for measuring the catalytic species. Among these, the fixed-time method is the most conventional and simplest, involving the measurement of ΔA at 599 nm. Fig. 1 shows the relationship between A and reaction time. It was found that the rate of reaction is proportional to the Rh(III) concentration. The reaction rate was monitored spectrophotometrically by measuring the decrease in absorbance of the characteristic band of thionine at 599 nm (Fig. 1). In many reactions, suitable micelles can affect the rate of reactions[17-20].

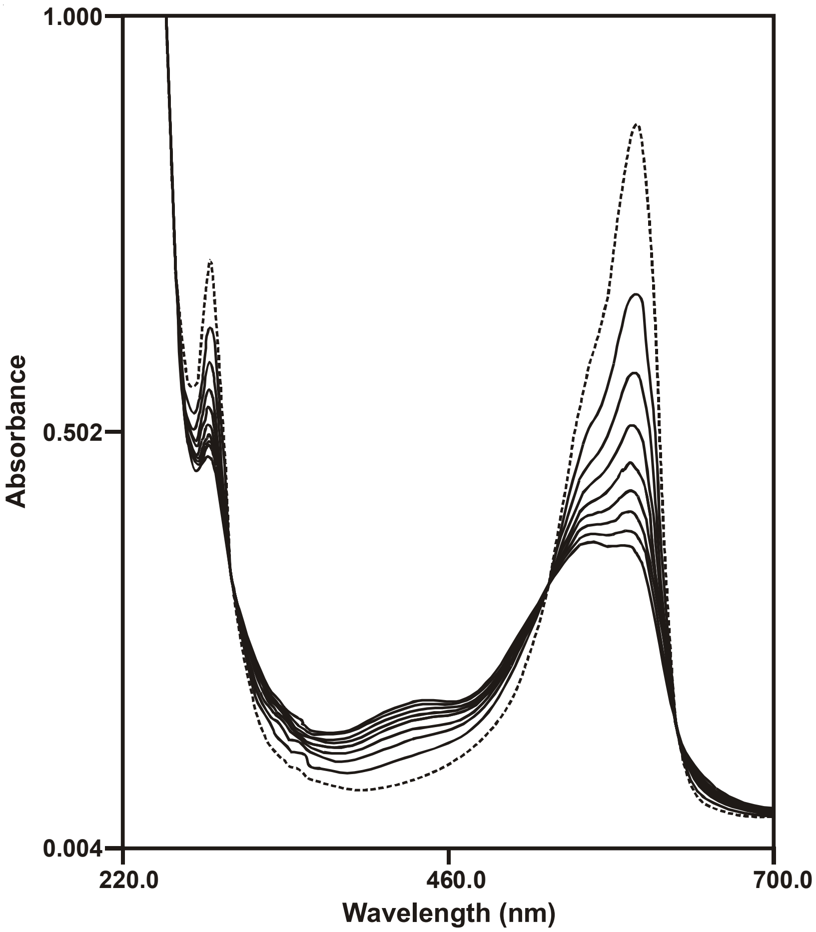

Fig. 1. Variation of the thionine-IO_4^--Rh(III) system with time condition: pH, 6.2; thionine 1.6×10^{-5} M; IO_4^-, 3.0×10^{-4} M; Rh(III), 0.080 μg/mL; CTAB, 3.4×10^{-3} M; temperature, 30°C

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[17].

Non-ionic micelles (such as Triton-X-100), anionic micelle (SDS) and cationic micelle (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.

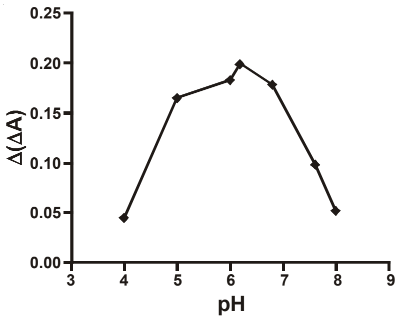

Fig. 2. Influence of pH on the sensitivity, conditions: 0.080 μg/mL Rh(III), 0.0026 M CTAB, 1.0 × 10^{-5} M; thionine and 2.0 × 10^{-4} metaperiodate at 25°C

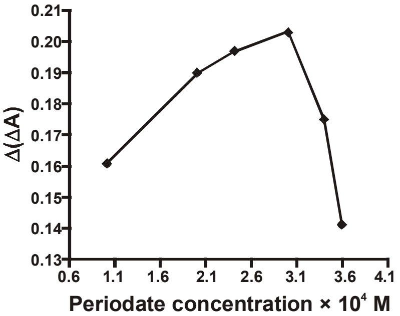

Fig. 3. Effect of metaperiodate concentration on the sensitivity. Conditions: 0.080 μg/mL Rh(III), 0.0026 M CTAB, pH 6.2 and 1.0 × 10^{-5} M thionine at 25°C

Influence of variables: In order to optimize the reaction to get the best sensitivity the variables affect the sensitivity such as pH, thionine concentration, metaperiodate concentration, type of surfactants and their concentration and temperature on the rate of catalyzed reaction (with Rh(III)) and uncatalyzed reaction (without Rh(III)) was studied.

The influence of pH on the sensitivity was studied in the range 4.0-8.0. Fig. 2 shows that the net reaction rate increases with pH up to 6.2 and decreases at higher pH values. This phenomenon is due to the fact that, in pH < 6.2, thionine is protonated and thus the rate of reaction decreases. At higher pH values (pH > 6.2), the uncatalyzed reaction accelerated and thus, the change in absorbance for the net reaction decreases. Thus, pH 6.2 was selected for the study.

The effect of the metaperiodate concentration on the rate of reaction was studied in the range of 1.0 × 10^{-4} - 3.6 × 10^{-4} M (Fig. 3). The results show that the net reaction rate increases with increasing metaperiodate concentration up to 3.0 × 10^{-4} M and decreases at higher concentrations. This means that the rate of uncatalyzed reaction increases with metaperiodate concentration (> 3.0 × 10^{-4} M) to a greater extent than the catalyzed reaction and the difference between the rates of catalyzed and uncatalyzed reaction (ΔA_s-ΔA_b) diminishes at higher metaperiodate concentrations. Therefore, a metaperiodate concentration of 3.0 × 10^{-4} M was selected for further study.

Fig. 4 shows the effect of the thionine concentration on the sensitivity for the range of 4.0×10^{-6} - 2.4×10^{-5} M. This sensitivity (net reaction rate) increases with increasing thionine concentration up to 1.6×10^{-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 1.6×10^{-5} M of thionine was selected as the optimum concentration.

The effect of the CTAB concentration on the rate of reaction was studied in the range of 1.3×10^{-3} - 4.4×10^{-3} M (Fig. 5). This sensitivity increases with increasing CTAB Concentration up to 3.4×10^{-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 thionine in the solution. Therefore, a final concentration of 3.4×10^{-3} M was selected as the optimum concentration of CTAB .

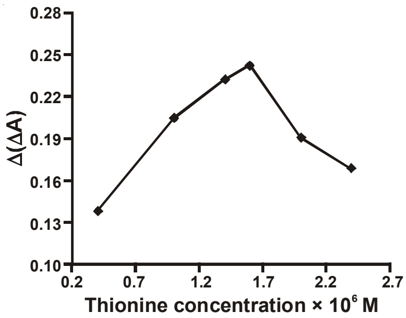

Fig. 4. Effect of thionine concentration on the reaction rate. Conditions: 0.080 µg/mL Rh(III), 0.0026 M CTAB, pH 6.2 and 3.0×10^{-4} M, metaperiodate at 25°C

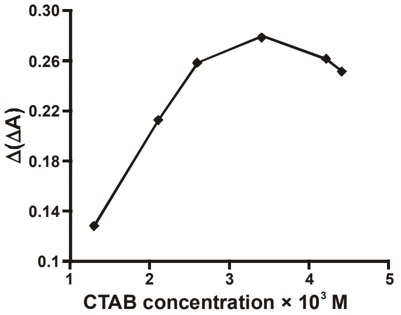

Fig. 5. Effect of CTAB concentration on on the reaction rate. Conditions: 0.080 µg/mL Rh(III), pH 6.2, 1.6×10^{-5} M, thionine and 3.0×10^{-4} M, metaperiodate at 25°C

The effect of the temperature on the sensitivity was studied in the range 15-55°C with the optimum pH and other reagent concentrations. The results showed that as the temperature 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.

Analytical parameters

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 6.0×10^{-4} - 0.080 µg/mL Rh(III).

The equation of the calibration graph is $\Delta A = 9.4 \times 10^{-3} + 4.801\ C_{Rh(III)}$ and in the range 0.080-0.50 μg/mL with regression equation of $\Delta A = 0.1761 + 1.314\ C_{Rh(III)}$ (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 Rh(III) concentration in μg/mL. The limit of detection from $Y_{LOD} = Yb + 3\ S_b$ is 0.29 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 0.02 and 0.050 μg/mL Rh(III) was 2.29 and 1.42, 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 0.080 μg/mL Rh(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-2. Many ions did not interfere, even when they were present in 100-fold excess over Rh(III). The results show that method is relatively selective for rhodium determination.

TABLE-2
EFFECT OF FOREIGN IONS ON THE DETERMINATION
OF 0.080 μg/mL Rh(III)

Species	Tolerance limit ($w_{ion}/w_{Rh(III)}$)
Mg^{2+}, Na^+, Rb^+, Li^+, K^+, Br^-, Ca^{2+} NH_4^+, $H_2PO_4^-$, SO_4^{2-}, $C_2O_4^{2-}$	1000
Ce(III), Cd(II), $S_2O_3^{2-}$, SO_3^{2-}, PO_4^{3-}	400
Mn(II), $S_2O_8^{2-}$	200
Ni(II), Zn^{2+-} , Pb^{2+}	100
Ti(III),Co(II),Cu(II)	50
Fe(III),Cr(III),Mo(VI)	20
Al^{3+}, Ag^+, Te(IV), Se(IV), I^-	10

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

Conclusion

The kinetic-spectrophotometric method developed for the determination of Rh(III) is inexpensive, uses readily available reagents, allows rapid determination at low operating costs. Using the proposed method, it is possible to determination rhodium(III) at trace levels as low as 0.6 ng/mL without the need for any preconcentration step.

TABLE-3
DETERMINATION OF Rh(III) ADDED TO WATER SAMPLES

Sample	Rh(III) added (ng/mL)	Rh(III) found (ng/mL)	Recovery %	RSD % n = 5
Well water	-	Less than detection limit	-	-
Well water	20.0	19.2	96	1.7
Well water	40.0	40.8	102	2.2
Zayandeh Roud water	-	Less than limit detection	-	-
Zayandeh Roud water	20.0	21.0	105	1.9
Zayandeh Roud water	50.0	49.1	98.2	2.6
Tap water	-	Less than detection limit	-	-
Tap water	20.0	18.8	94	1.9
Tap water	40.0	38.0	95	2.1

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