

Kinetic-Catalytic-Spectrophotometric Determination of Ultra Trace Amounts of Rhodium(III) by Its Catalytic Effect on The Oxidation of SPADNS by Metaperiodate in Micellar Media

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A new, sensitive and 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 Rh(III) on the oxidation of sodium 2-(*p*-sulfophenyl-azo)-1,8-dihydroxy-naphthalene-3,6-disulfonate (SPADNS) by metaperiodate at pH 7.5 in micellar media. The reaction was monitored spectrophotometrically by measuring the decrease 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 Rh(III) in concentration range 1.0-250.0 ng/mL, with a fixed time of 0.5-4.5 min from initiation of the reaction. The limit of detection is 0.77 ng/mL Rh(III). The relative standard deviation of 0.020 and 0.040 $\mu\text{g/mL}$ Rh(III) was 1.9 and 2.3 %, respectively. The method was applied to the determination of rhodium in water sample and synthetic water sample.

Key Words: Kinetic, Catalytic, Rhodium, Metaperiodate, SPADNS.

INTRODUCTION

Rhodium is found at trace levels in the earth. Rhodium is used in standard thermocouples of various ranges of temperature, in electrothermal industry¹ and as catalysts in chemical reactions such as the removal of nitrogen oxide (NO_x) from automobile exhaust², purification of gases produced from alcoholic combustion systems³, etc. Several spectrophotometric methods have been reported⁴⁻⁷ 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 ultra trace levels. Yagi *et al.*⁸ used the catalytic effect of Rh(III) for the oxidation of α -naphtholphthalein dye with KIO_4 . However, the method is linear over a range 0.02-0.40 $\mu\text{g/mL}$ Rh(III). The microwave irradiation technique⁹ 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)¹⁰. It has a high limit of detection (> 50 ng/mL), small range of detection (0.40-1.0 µg/mL Rh³⁺) and low selectivity.

The proposed method is based on the catalytic effect of Rh(III) on the oxidation of SPADNS by metaperiodate in the presence of cetyl trimethyl-ammonium bromide (CTAB) as a micellar media. The reaction was monitored spectrophotometrically at 517 nm and the method is highly sensitive and rapid for Rh(III) determination.

EXPERIMENTAL

Doubly 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 HNO₃ solution (2 % v/v), rinsed with water and dried. Absorption spectra were recorded with a Cary model 100 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 bath was used to keep the reaction temperature at 30°C. A pH meter metrohm model 744 used to preparing of buffer Solutions.

SPADNS solution 7.36×10^{-4} 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 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, namely, sodium dodecyl sulfate (SDS), Triton-X-100 and cetyl pyridinium chloride (serva), were prepared in a similar way.

Standard stock Rh(III) solution (1000 µg/mL) was prepared by dissolving 0.2630 g of RhCl₃ in water and diluted to 100 mL in a 100 mL volumetric flask.

Buffer solutions in the range of 4.0-8.5 was prepared by addition of suitable volume of NaOH solution 0.20 M to 100 mL of solution 0.040 M respect to acetic acid, phosphoric acid and boric acid.

Stock Solution (1000 µg/mL) of interfering ions were prepared by dissolving suitable salts in water, HCl or NaOH solution.

Recommended procedure: All the solutions and distilled water were kept in a thermostated water bath at 30°C for 20 min for equilibration before starting the experiment. An aliquot of the solution containing 0.010-

2.50 $\mu\text{g/mL}$ Rh(III) was transferred into a 10 mL volumetric flask and then 1.0 mL of buffer solution (pH = 7.5), 1.2 mL 0.013 M CTAB solution and 1.0 mL 7.36×10^{-4} M SPADNS solution were added to the flask. The solution was diluted to *ca.* 7 mL with water, then 2.4 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 spectrophotometric 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 Rh(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 in the presence of CTAB as a micellar medium, this reaction rate is sharply increased by addition of trace amount of Rh(III). The rate equation of the catalyzed reaction is:

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

where k is the rate constant because $[\text{IO}_4^-]$, $[\text{SPADNS}]$, IO_4^- can be considered to be constant and m was found to be 1. By integration of eqn. 1 and by incorporating Beer's law, the final expression obtained is,

$$\Delta A = K[\text{Rh(III)}]t \quad (2)$$

where t is the reaction time.

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 517 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 SPADNS at 517 nm. In many reactions, suitable micelles can affect the rate of reactions¹¹⁻¹⁴.

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 charge species, this 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 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 surface¹⁵.

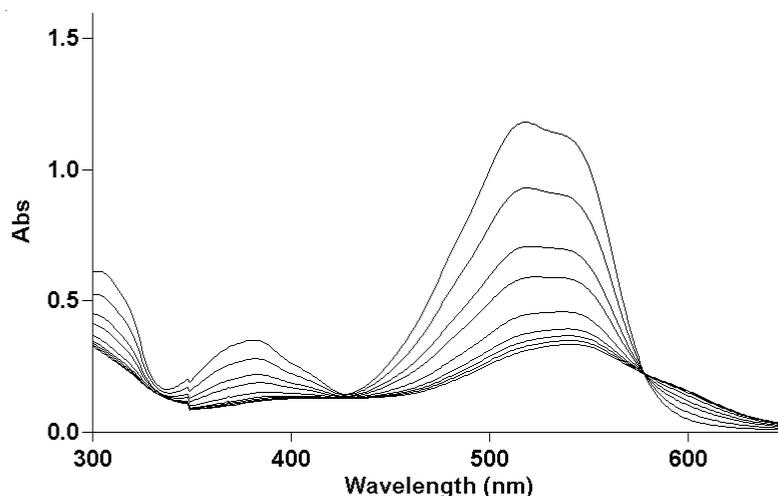


Fig. 1. Variation of the SPADNS- IO_4^- -Rh(III) system with time condition: pH, 7.5; SPADNS, 7.36×10^{-5} M; IO_4^- , 2.4×10^{-4} M; Rh(III), 0.040 $\mu\text{g/mL}$; CTAB, 1.56×10^{-3} M; temperature, 30°C

TABLE-1
SURFACTANT TESTED US A POTENTIAL MICELLAR CATALYST
FOR THE ENHANCED RATE OF SPADNS- IO_4^- -Rh(III) REACTION

Surfactant	Type	C.M.C. (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}	Inert

Rhodium as rhodium tetrachloride and metaperiodate is negatively charged and SPADNS positively charged. Therefore, it seems logical to consider that the cationic micelles can enhance the rate of SPADNS- IO_4^- -Rh(III) reaction. Nonionic micelles (such as Triton-X-100), anionic micelle (sodium dodecyl sulfate, 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, among all micelles, CTAB was selected for practical purposes.

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, type of surfactants and their concentration and temperature on the rate of catalyzed reaction (with Rh^{3+}) and uncatalyzed reaction (without Rh^{3+}) was studied.

The influence of pH on the sensitivity was studied in the range 4.0-8.5. Fig. 2 shows that the net reaction rate increases with pH up to 7.5 and decreases at higher pH values. This means that the rate of uncatalyzed reaction increases with pH value (> 7.5) to a greater extent than the catalyzed reaction and the difference between the rates of catalyzed and uncatalyzed reactions ($\Delta A_s - \Delta A_b$) diminishes at higher pH value concentrations. Therefore, pH value of 7.5 was selected for further study.

The effect of the metaperiodate concentration on the rate of reaction was studied in the range of 1.2×10^{-4} – 4.0×10^{-4} M (Fig. 3). The results show that the net reaction rate increases with increasing metaperiodate concentration up to 2.4×10^{-4} M and decreases at higher concentrations. This means that the rate of uncatalyzed reaction increases with metaperiodate concentration ($> 2.4 \times 10^{-4}$ M) to a greater extent than the catalyzed reaction and the difference between the rates of catalyzed and uncatalyzed reaction ($\Delta A_s - \Delta A_b$) diminishes at higher metaperiodate concentrations. Therefore, a metaperiodate concentration of 2.4×10^{-4} M was selected for further study.

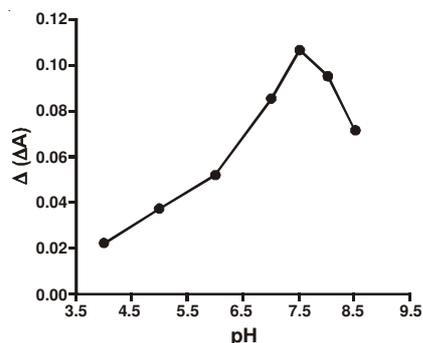


Fig. 2. Influence of pH on the sensitivity, conditions: 0.040 $\mu\text{g/mL}$ Rh(III), CTAB, 1.3×10^{-3} M, SPADNS, 7.36×10^{-5} M and metaperiodate 2.0×10^{-4} M at 30°C

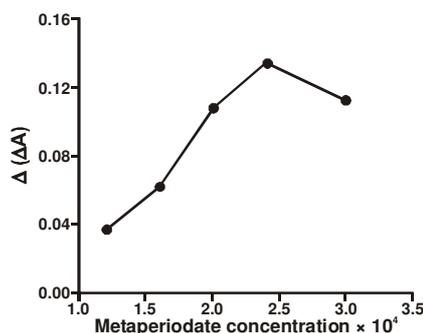


Fig. 3. Effect of metaperiodate concentration on the sensitivity. Conditions: 0.040 $\mu\text{g/mL}$ Rh(III), CTAB, 1.3×10^{-3} M, pH 7.5 and SPADNS, 7.36×10^{-5} M at 30°C

Fig. 4 shows the effect of the SPADNS concentration on the sensitivity for the range of 4.42×10^{-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.

The effect of the CTAB concentration on the rate of reaction was studied in the range of 0– 1.82×10^{-3} M. This sensitivity increases with increasing CTAB Concentration up to 1.56×10^{-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 SPADNS in the solution. Therefore, a final concentration of 1.56×10^{-3} M was selected as the optimum concentration of CTAB (Fig. 5).

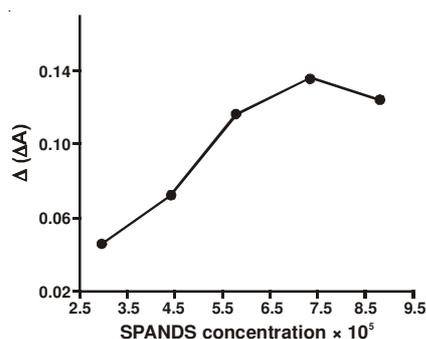


Fig. 4. Effect of SPADNS concentration on the reaction rate. Conditions: 0.040 $\mu\text{g/mL}$ Rh(III), CTAB, 1.3×10^{-4} M, pH 7.5 and metaperiodate, 2.4×10^{-4} M, at 30°C

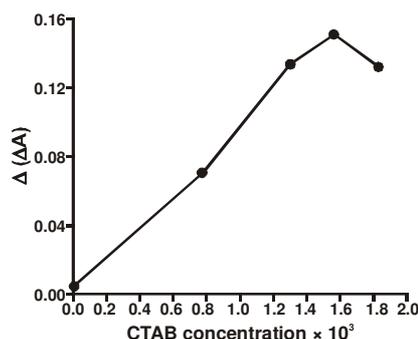


Fig. 5. Effect of CTAB concentration on the reaction rate. Conditions: 0.040 $\mu\text{g/mL}$ Rh(III), pH, 7.5 and metaperiodate, 2.4×10^{-4} M; SPADNS, 7.36×10^{-5} M, at 30°C

The effect of the temperature on the sensitivity was studied in the range 20-55°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 suitable 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 is 0.001-0.250 $\mu\text{g/mL}$ for Rh(III).

The equation of the calibration graph is $\Delta A = 2.83 \times 10^{-3} + 3.49 C_{\text{Rh(III)}}$ ($n = 8$, $r = 0.9998$), 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 $\mu\text{g/mL}$. The limit of detection from $Y_{\text{LOD}} = Y_b + 3 S_b$ 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 0.020 and 0.040 $\mu\text{g/mL}$ Rh(III) was 1.9 and 2.3, respectively.

Interference study

In order to assess the application of the proposed method to synthetic water samples, the effect of various ions on the determination of 0.040 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 % and 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 0.040 µg/mL Rh(III)

Species	Tolerance limit ($W_{ion}/W_{Rh(III)}$)
Na ⁺ , Rb ⁺ , Li ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺ , NH ₄ ⁺ , H ₂ PO ₄ ⁻ , SO ₄ ²⁻ , C ₂ O ₄ ²⁻ , ClO ₃ ⁻ , CH ₃ OO ⁻ , NO ₃ ⁻ , CO ₃ ²⁻ , Br ⁻	1000
V(V), S ₂ O ₈ ²⁻	500
Mn ²⁺ , Ag ⁺ , SCN ⁻ , SO ₃ ²⁻	200
Zn ²⁺ , Hg ²⁺	100
Ti ³⁺ , Cu ²⁺ , Fe ³⁺ , Te ⁴⁺ , Se ⁴⁺	50
Mo ⁶⁺ , Co ²⁺ , Pb ²⁺	20
Ru ³⁺ , Ni ²⁺	5

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. The results are presented in Table-3. Satisfactory recoveries with precise results show good reproducibility and accuracy of the method.

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

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

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 and shows simplicity and adequate selectivity, low limit of detection and good precision and accuracy compared to other kinetic procedures. With this method, it is possible to determine rhodium(III) at levels as low as 0.77 ng/mL without the need for any preconcentration step.

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