

Inhibition Kinetic Determination of Trace Amounts of Ruthenium(III) by the Spectrophotometric method with Rhodamine B in Micellar Medium

Mohsen Keyvanfard

Abstract—A new, simple and highly sensitive kinetic spectrophotometric method was developed for the determination of trace amounts of Ru(III) in the range of 0.06-20 ng/ml. The method is based on the inhibitory effect of ruthenium(III) on the oxidation of Rhodamine B by bromate in acidic and micellar medium. The reaction was monitored spectrophotometrically by measuring the decreasing in absorbance of Rhodamine B at 554 nm with a fixed-time method. The limit of detection is 0.04 ng/ml Ru(III). The relative standard deviation of 5 and 10 ng/ml Ru(III) was 2.3 and 2.7 %, respectively. The method was applied to the determination of ruthenium in real water samples

Keywords—Ruthenium ;Inhibitory; Rhodamine B; bromate

I. INTRODUCTION

RUTHENIUM, Situated in the middle of the second row of the transition metal series and lies at the heart of the periodic table. This central location bestows upon ruthenium properties that are common to both its early and late transition metal cousins. 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 have shown 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 antitumor properties. Despite 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], metallurgy [6] and in high technology components [7], had made it necessary to develop simple, inexpensive and selective methods for the determination of traces of ruthenium in various samples.

. This work was supported by Islamic Azad University, Majlessi Branch. Mohsen Keyvanfard is with faculty of Science, Islamic Azad University – Majlessi Branch, Isfahan, Iran, E-mail:keyvan45638@yahoo.com

Different methods have been reported for detecting this metal such as voltammetry, atomic absorption spectrometry, fluorimetry and spectrophotometry [8,9]. The availability of spectrophotometric instruments and the simplicity of analytical procedure make the procedure very 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, rhodamine B [10,11] and Ce(IV) –As(III) system [12] by some oxidants. All of these methods have interferences effect or high limit of detection (>5.0 ng/ml). The availability Spectrophotometry apparatus and the simplicity of analytical procedures make the technique very 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 inhibitory effect on the oxidation of Rhodamine B by Bromate in acidic and micellar medium. The method permits the determination of a ruthenium (III) concentration down to 0.04 ng/ml with a good accuracy and reproducibility.

II. EXPERIMENTAL

A. Reagents

Doubly distilled water and analytical reagent grade chemicals were used during all of the experimental studies.

Rhodamin B Solution 1×10^{-3} M was prepared by dissolving 0.0479 g of the compound (Merck, MW=479.02) in water and Solution was diluted to the mark in a 100–ml volumetric flask.

Bromate stock Solution 0.10M, was prepared by dissolving 1.67 g of potassium bromate (M=167) in water and diluting to 100 ml in a 100-ml volumetric flask.

Standard stock Ru(III) solution (100 μ g/ml) was prepared by dissolving 0.0128 g of RuCl₃ (lobachem) in ethanol and diluted to 100 ml in a 100–ml volumetric flask.

Cetyl trimethyl ammonium bromide(CTAB) stock solution 0.0130M was prepared by dissolving 1.197g 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.

Sulfuric acid solution 6.0M was prepared by mixing 33.3 ml of Sulfuric acid (C) in water and diluted to 100-ml volumetric flask.

Stock Solution (1000 μ g/ml) of interfering ions were prepared by dissolving suitable salts in water, hydrochloric acid, or sodium hydroxide solution.

All glassware were cleaned with detergent solution, rinsed with tap water, soaked in dilute HNO₃ Solution (2%V/V), rinsed with water and dried.

B. Apparatus

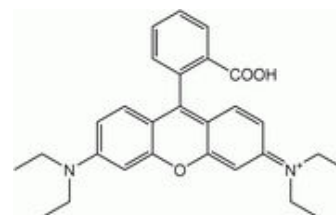
Absorption spectra were recorded with a CECIL model 7500 spectrophotometer with a 1.0cm quartz cell. A model 2501 CECIL Spectrophotometer with 1.0 cm glass cuvettes was used to measure the absorbance at a fixed wavelength of 554nm. A thermostat water bath was used to keep the reaction temperature at 27

III. RECOMMENDED PROCEDURE

All the Solutions and distilled water were kept in a thermostated water bath at 27°C for 20min for equilibration before starting the experiment. An aliquot of the solution containing 0.6–200 ng/ml Ru(III) was transferred into a 10-ml Volumetric flask, and then 0.2 ml of sulfuric acid 6M, 1ml 0.013 M CTAB Solution and 0.5 ml Rhodamin B Solution 1×10^{-3} M were added to the flask. The solution was diluted to ca.7ml with water, then 0.2ml 0.1M bromate 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 554 nm for 0.5–2 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 . Analytical signal was difference between sample signal and blank signal ($\Delta A_s - \Delta A_b$). Time was measured just after the addition of last drop of bromate..

IV. RESULTS AND DISCUSSION

Rhodamin B undergoes a oxidation reaction with bromate in acidic and micellar medium at very fast rate. We found that ultra trace amounts of ruthenium(III) have a inhibitory effect on the this reaction. Therefore, by measuring the decrease in absorbance of Rhodamin B for a fixed time of 0.5-2.0 min initiation of the reaction, the ruthenium (III) contents in the sample can be measured. The reaction rate was monitored spectrophotometrically by measuring the decrease in absorbance of the characteristic band of Rhodamin B at 554nm .In many reactions, Suitable micelles can affect the rate of reactions [14-16].



V. INFLUENCE OF VARIABLES

In order to optimize the reaction to get the best sensitivity the variables affect the sensitivity such as sulfuric acid concentration, Rhodamin B concentration, bromate concentration, the effect of different kinds of surfactants, surfactant concentration and temperature on the rate of inhibited reaction (with Ru(III)) and uninhibited reaction (without Ru(III)) was studied.

The influence of sulfuric acid concentration on the sensitivity was studied in the range 0.06–0.36 M. Figure 1 shows that the analytical signal increases with sulfuric acid concentration up to 0.12 M and decreases at higher sulfuric acid concentration. Therefore, a sulfuric acid concentration of 0.12 M was selected as the optimum sulfuric acid concentration.

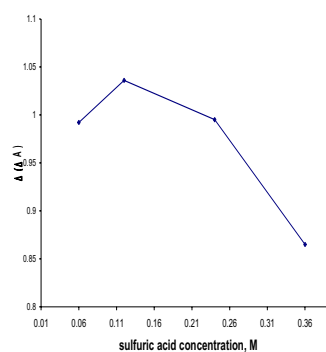


Fig.1. Effect of H₂SO₄ concentration on the sensitivity, conditions: 5 ng/ml Ru(III), 4.0×10^{-5} M Rhodamin B 6.0×10^{-3} M bromate and 1.2×10^{-3} CTAB at 27 °C, in fixed time of 0.5–2min from initiation of reaction

Figure 2 shows the effect of the Rhodamin B concentration on the sensitivity for the range of 4.0×10^{-5} – 8.0×10^{-5} M. This sensitivity increases with increasing Rhodamin B concentration up to 5.0×10^{-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 5.0×10^{-5} M of Rhodamin B was selected as the optimum concentration

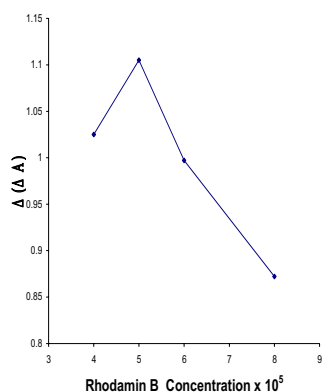


Fig. 2 Effect of Rhodamin B concentration on the sensitivity, conditions: H₂SO₄, 0.12M; 5 ng/ml Ru(III); 6.0×10⁻³ M bromate and 1.2 × 10⁻³ CTAB at 27 °C, in fixed time of 0.5–2min from initiation of reaction

The effect of the bromate concentration on the rate of reaction was studied in the range of 1 × 10⁻³– 1×10⁻² M(Fig 3). The results show that analytical signal increases with increasing bromate concentration up to 2.×10⁻³ M and decreases at higher concentrations. Therefore, a bromate concentration of 2.×10⁻³ M was selected for further study.

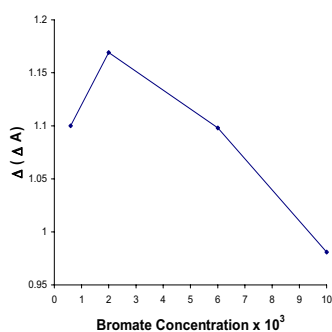


Fig. 3. Effect of bromate concentration on the sensitivity. Conditions: H₂SO₄, 0.12M; 5 ng/ml Ru(III); Rhodamin B 5 × 10⁻⁵ M ; 1.2 × 10⁻³ M CTAB at 27 °C, in fixed time of 0.5–2min from initiation of reaction

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 electrostatic and hydrophobic interaction between the reactants and micellar surface[13].

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(C.M.C).The results are shown in table I .Therefore, from between these micelles, CTAB was selected for practical purposes.

TABLE I THE EFFECT OF SURFACTANTS ON THE ANALYTICAL SIGNAL

Surfactant	Type	c.m.c (M)	Micellar effect
Triton-x-100	Nanionic	3.0 × 10 ⁻⁴	Inert
SDS	Anionic	8.1 × 10 ⁻³	Positive
CTAB	Cationic	1.3 × 10 ⁻³	Inert
CPC	Cationic	1.2 × 10 ⁻⁴	Positive

The effect of the CTAB concentration on the rate of reaction was studied in the range of 0-3.12×10⁻³ M(Fig.4). This sensitivity increases with increasing CTAB Concentration up to 1.3×10⁻³M and decreases at higher concentrations.. Therefore a final concentration of 1.3×10⁻³M was selected as the optimum concentration of CTAB.

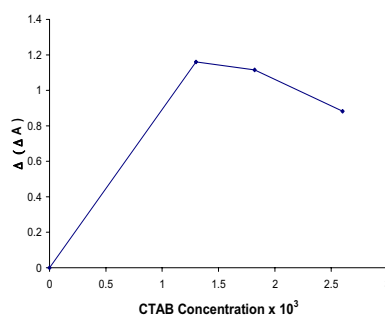


Fig. 4. Effect of CTAB concentration on the sensitivity. Conditions: H₂SO₄, 0.12M; 5 ng/ml Ru(III); Rhodamin B 5 × 10⁻⁵ M; 2.0×10⁻³ M bromate at 27 °C, in fixed time of 0.5–2min from initiation of reaction

The effect of the temperature on the sensitivity was studied in the range 15–30°C with the optimum reagent concentrations. The results showed that, as the temperature increases up to 27°C,the analytical signal increases, whereas higher temperature values decrease the analytical signal (ΔA=ΔA_s-ΔA_b).. Therefore, 27 °C was selected for further study.

A. 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 0.5–2 min from initiation of the reaction because it provided the best regression and sensitivity. Under the optimum conditions described above, a linear calibration range 0.06-20 ng/ml Ru(III).

The equation of the calibration graph is ΔA=1.058+0.0213 C_{Ru(III)} (n=6,r =0.9997), where ΔA is change in absorbance

for the sample reaction for 0.5–2 min from initiation of the reaction and C is Ru(III) concentration in ng/ml. The limit of detection from $Y_{LOD} = Y_b + 3 S_b$ is 0.04 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 ($n=10$, uninhibited reaction). The relative standard deviation for six replicate determination of 5 and 10 ng/ml Ru(III) was 2.3 and 2.7 respectively.

B. Interference Study

In order to assess the application of the proposed method to synthetic samples, the effect of various ions on the determination of 5 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 2. Many ions did not interfere, even when they were present in 500 fold excess over Ru(III). The results show that method is relatively selective for rhtenium determination.

TABLE II EFFECT OF FOREIGN IONS ON THE DETERMINATION OF 5 ng/ml Ru(III)

Species	Tolerance Limit ($W_{ion}/W_{Ru(III)}$)
Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺ , Rb ⁺ , Pb(II), Zn(II), Ba ²⁺ , Al ³⁺ , Ag ⁺ , Cu(II), Fe(II), Te(IV), Se(IV), C ₂ O ₄ ²⁻ , S ₂ O ₈ ²⁻ , HSO ₄ ⁻ , ClO ₃ ⁻ , S ₂ O ₃ ²⁻ , SO ₃ ²⁻ , PO ₄ ³⁻ , Cd(II), CO ₃ ²⁻ , NO ₃ ⁻ , Tatarate, Borate, Cl ⁻ ,	1000
Ni(II), Rh(III),	500
I ⁻	100

C. 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 III 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	5	5.4	108	3.1
DRINKING WATER	0	Less than detection limit -	-	-
DRINKING WATER	10.0	9.7	97	2.6

TABLE IV COMPARISON OF SOME METHODS FOR DETERMINATION OF RUTHENIUM WITH PROPOSED METHOD

Method	DL. (ng/mL)	LDR (ng/mL)	reference no.
Spectrophotometry	30	100-2500	17
	0.33	1.12-300	18
	2	19
Voltammetry	1000	2000-60000	20
Fluorimetry	0.6	1.0-400	21
Atomic absorption	6	Up to 500	22
Proposed Method	0.04	0.06-20	-

VI. 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 0.04 ng/ml without the need for any preconcentration step.

ACKNOWLEDGMENTS

The author is Thankful to the Islamic Azad University – Majlessi Branch for the support of this work.

REFERENCES

- [1] M. Zahmakiran, S. Özkar, " Water dispersible ruthenium(0) nanoclusters as catalyst for the hydrolysis of sodium borohydride" . J.Molecular Catalysis A: Chemical , 258, 95-103, 2006.
- [2] M.G. Buonomenna, E.Gallo, F.Ragaini,S.Cenini,E. Drioli, "New ruthenium porphyrin polymeric membranes: preparation, characterization and catalytic activity in alkenes aziridination" Desalation 199,167,2006.
- [3] J. Garcia, H.T.Gomes,Ph, Serp, Ph, Kalck, J.L. Figueiredo, J.L. Faria, "Carbon nanotube supported ruthenium catalysts for the treatment of high strength wastewater with aniline using wet air oxidation" Carbon 44,2384,2006.

- [4] I. Paseka, Characterisation of ruthenium catalysts and determination of their surfaces by electrochemical oxidation and reduction", Applied Catalysis A: General 207,257,2001.
- [5] A.R. Timerbaev, A.V. Rundev, O. Semenova, C.G. Hartinger, B.K. Keppler.; Comparative binding of antitumor indazolium [*trans*-tetrachlorobis(1*H*-indazole)ruthenate(III)] to serum transport proteins assayed by capillary zone electrophoresis "Analytica Biochemistry, 341,326,2005.
- [6] O. Novokova, C. Hofr, V.Brabec, "Modification of natural, double-helical DNA by antitumor *cis*- and *trans*-[Cl₂(Me₂SO₄)₄Ru] in cell-free media " Biochemical Pharmacology ,60 ,1761(2000).
- [7] V. Brabec, O. Novakova, "DNA binding mode of ruthenium complexes and relationship to tumor cell toxicity" Drug Resistance Updates 9,111,2006.
- [8] M. Keyvanfard, B. Rezaei". Spectrophotometric Reaction Rate Method for the Determination of Ultra Trace Amounts of Ruthenium(III) by its Catalytic Effect on the Oxidation of Safranin O by Metaperiodate" Canadian journal of Analytical sciences and Spectroscopy 50, 311-316,2005.
- [9] A.A. Ensafi, M. Chamjangali, H. Rahimi Mansour, Catalytic spectrophotometric determination of ruthenium by flow injection method Talanta 55, 715,2001.
- [10] S.B. Yonnalagadda, C. Chinake, I. Love, Fresenius J. Anal. Chem., 349, 829(1949).
- [11] Z. Ziang, Huaxue Tongbao., 1, 38(1992).
- [12] J.B. Worthington, H. L. Pardue, Anal. Chem., 42, 1157, 1970.
- [13] Rubio, D. Perez-Bendito, Anal. Chim. Acta., 224, 85(1989).
- [14] A.A. Ensafi, M. Keyvanfard," Catalytic Kinetic Spectrophotometric Determination Palladium(II) by Spectrophotometric Method in Anionic Micellar Medium", Anal. Lett, 35, 423,, 2002.
- [15] A.A. Ensafi, M. Keyvanfard," Kinetic Spectrophotometric Determination of Palladium in Hydrogenation Catalytic Effect on the Oxidation of Pyrogallol Red by Hydrogen Peroxide", Spectrochim. Acta, Part a, 58, 1567,2002,.
- [16] A.A. Ensafi, M. Keyvanfard," Kinetic-Spectrophotometric Determination of Tellurium(IV) By Its Catalytic Effect On The Reduction of Thionin By Sodium Sulfide In Cationic Micellar Medium" Intern. J. Environ. Anal. Chem, 83, 397,2000.
- [17] A. Almuaibed, A. Townshend, Microchem. J. 48, 275,1993.
- [18] M. Toral, C. Papia, J. Narvaez, P. Richter, Microchem. J. 73, 317(2002).
- [19] L. Q. Qwabe B. Pare, S.B. Jonnalagadda" ruthenium determination by kinetic -Catalytic method using the Nile blue-acidic chlorite reaction" Bull. Chem. Soc. Ethiop., 21(2), 171-178(2007).
- [20] A.A. Ensafi, K. Zarei, T. Khayamian, "Determination of Ultratrace Amounts of Ruthenium by Differential Pulse Voltammetry Using Factorial Design for Optimization" Microchem. J. 63, 235,1999.
- [21] B. Pal, M. Rahman, Talanta 48, 1075,1999.
- [22] H. Minamisawa, H. Kuroki, N. Arai, T. Okutani, Anal. Chim. Acta 398, 289,1999.