

SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM UTILIZING ITS CATALYTIC ACTIVITY ON OXIDATION OF HEXACYANOFERRATE(II) BY PERIODATE ION IN WATER SAMPLES

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Abstract. The catalytic effect of ruthenium chloride on the outer sphere electron transfer of hexacyanoferrate(II) by periodate ion in aqueous alkaline medium has been effectively employed to determine ruthenium(III) at micro level. The optimum reaction condition has been established and fixed time procedure is adopted. A linear relationship between changes in absorbance and added Ru(III) concentration has been utilized for the trace level determination of Ru(III). The results reveal that the addition of interfering ions (up to 71 times higher concentration of Ru) does not have significant effect on the catalytic activity of Ru(III) on oxidation of hexacyanoferrate(II) by periodate ion. Polyaminocarboxylates (HEDTA, EDTA and IDA) suppress its catalytic power to maximum, if tolerance limit is more than 14.29 times. Due to the reproducibility, stability and selectivity, this method can also be quantitatively applied in different types of water samples for determination of ruthenium(III) at micro level.

Keywords: kinetics, mechanism, hexacyanoferrate(II), periodate, ruthenium(III).

1. Introduction

Ruthenium, a noble metal, is found in crustal materials at very low concentration (few ppb) [1], whereas meteorites and chondrite contain much higher percentage of ruthenium [2]. However, ruthenium compounds are highly toxic and carcinogenic, different studies have been reported for materials containing ruthenium complexes in electronic, electrochemical and electrical industries [1, 2]. The

complexes of ruthenium have found applications in pharmaceutical industries in the detection and determination of protein, antibiotic, chloramphenicol, and cefprozil [3-5]. Ruthenium along with its complexes exhibits excellent catalytic property in both alkaline and acidic medium for the reactions having environmental and commercial applications [6-18]. To fight against the deadly disease of cancer a number of ruthenium bearing complexes have been prepared and their antitumor properties are tested [19-21]. The life span of hosts bearing tumor increases by the intake of certain ruthenium compounds in spite of low cytotoxicity of ruthenium agents. Due to high catalytic activity of ruthenium, alloys of ruthenium are used as catalyst in fuel cells. Pt-Ru bimetallic alloy show the highest activity for the methanol oxidation reaction in methanol fuel cells [22]. Nanoparticles of Ru-Pt have also been used as an effective catalyst for carbon monoxide – tolerant fuel cell [23]. Thus, the potential application of ruthenium and its complexes in various areas, especially in pharmacology [24] and metallurgy [25] has made a challenge to develop a rapid, selective, simple and inexpensive method for the determination of ruthenium in different type of samples at trace level. The catalytic and inhibition properties have been extensively used for the growth and development of analytical methods for the trace level determination of different elements and compounds. The processes for the ruthenium determination viz. spectrophotometry, cyclic voltametry, atomic absorption spectrophotometry, mass spectrometry, HPLC, atomic absorption spectrometry, and X-ray fluorescence, have been used by investigators. Despite of good sensitivity and selectivity most of these methods are complicated, time consuming and require expensive chemicals. Therefore, the catalytic kinetic methods (CKMs) employing spectrophotometric monitoring (SPM) under pseudo condition still remain a popular method for achieving ruthenium(III) estimation at trace level [26-38]. A comparison of known CKMs along with reaction condition, types of sample and dynamic range of detection (DRD) are summarized in Table 1 [28, 29, 32-38].

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Table 1

A comparative study of determination of ruthenium(III) involving different reactions

Major reactants	D.R.D. (χ_d) $\text{ng}\cdot\text{ml}^{-1}$	Methods used and reaction conditions	Samples used	Ref. No.
Thymol blue and potassium bromate	1 to 25	CKM, SPM, λ_{max} 544 nm, temp. 308 K	Synthetic samples	32
Tren and hexacyanoferrate(III)	10.11 to 252.67	CKM, SPM, λ_{max} 420 nm, temp. 318 K, time 10 min	Water samples	28
Benzylamine and $[\text{Fe}(\text{CN})_6]^{3-}$	10 to 121 (6.90)	CKM, SPM, λ_{max} : 420 nm, temp. 308 K, time 5 min	Synthetic samples	34
Phenosafranin and NaIO_4	Nanogram range	CKM, SPM, λ_{max} 520 nm	Synthetic water samples	36
L-Phenylalanine and KMnO_4	0.101 to 2.526 (0.08)	CKM, SPM, λ_{max} 526 nm, temp. 318 K, time 5 min	Tap water, synthetic mixtures	29
Ce(IV) and As(III)	0.45 to 9.00 (0.08)	CKM, SPM, λ_{max} 625 nm, PC-ANN used	Synthetic samples	37
Hematoxylin and H_2O_2	5 to 120	CKM, SPM, λ_{max} 440 nm, temp. 308 K	Synthetic mixtures	35
Acridine orange and chlorite	1 to 10	CKM, SPM, λ_{max} 490 nm, temp. 298 K, time 5 min	Synthetic water samples	35
Safranin O and potassium metaperiodate	0.80 to 100.0 (0.25)	CKM, SPM, λ_{max} 521 nm, temp. 308 K, time 5 min	Synthetic water samples	33

In order to extend our efforts for development of CKMs for the determination of ruthenium(III) [28-29], the present study proposed a new, rapid, selective, sensitive, and less expensive method to determine Ru(III) by applying its catalytic property on oxidation of hexacyanoferrate(II) by periodate ion in highly basic condition. The proposed method permits to determine the $[\text{Ru(III)}]$ down to $10 \text{ ng}\cdot\text{ml}^{-1}$ with very good accuracy and reproducibility. The minute amount of ruthenium is also added in certain areas of rivers, lakes and oceans as industrial wastes. In the present study we have developed a selective CKM for Ru(III) determination in water samples.

2. Experimental

2.1. Reagents

Analytical grade chemicals and double distilled water were used throughout the investigation. Potassium hexacyanoferrate(II) (Sigma) was used as such for the preparation of stock solution and kept in dark colored container to prevent photo-degradation. The 1.0M solution of sodium metaperiodate (Merck) was prepared, to prevent decomposition it was always wrapped with aluminium foil. Calculated amount of ruthenium(III) chloride (Alfa) was used for the preparation of its stock solution ($100 \mu\text{g}\cdot\text{ml}^{-1}$) in 0.5M HCl. The potassium iodide (S. D. Fine) solution was used to check the possible oxidation of ruthenium(III) in hydrochloric acid. Sodium chloride (Merck) solution was used to fix ionic strength (0.1M) of reaction mixture. pH of the reactants were fixed

separately at 9.50 ± 0.02 using sodium hydroxide and perchloric acid. Standardization of pH meter was done by standard BDH buffers.

2.2. Apparatus

The progress of catalytic reaction was examined using Sisco single beam visible spectrophotometer, model GIGI-110 equipped with self designed thermostated cell chamber. The pH was maintained by Elico LI-120 digital pH meter. The glassware was cleaned thoroughly with detergent, rinsed with dilute EDTA, dipped in 10% HNO_3 for minimum 10 min and finally washed thoroughly with double distilled water. The spectrophotometer cuvettes were cleaned by soaking in 15% HNO_3 to discharge ruthenium traces adsorbed on cell walls.

2.3. Procedure

Except the Ru(III) concentration, the concentration of the reactants, pH and ionic strength were judiciously chosen from the kinetic examination of the catalytic electron transfer reaction [39]. The reaction conditions under which the catalytic activity of Ru(III) was optimum were selected for quantitative analysis. All the standard solutions were thermally equilibrated at $303.0 \pm 0.1 \text{ K}$. The pseudo-first-order conditions were applied to study the reaction by taking minimum 10 times excess of periodate over hexacyanoferrate(II). The progress of the electron transfer of hexacyanoferrate(II) by periodate was monitored using "fixed time procedure" in highly alkaline medium by computing the increase in absorbance at 420 nm. The change in absorbance at a definite time interval were computed to plot the calibration curve

between Ru(III) concentration and change in absorbance. To prevent the complications arising due to possible interference by the reagents and products present in the reaction system, the inceptive rate was followed to determine Ru(III).

3. Results and Discussion

The optimum reaction condition has been established and fixed time procedure was adopted to obtain regression equations. The graphs plotted between ΔA_t (change in absorbance at t , min) versus $[\text{Ru(III)}]$ (Fig.1) exhibited the linear dependency on $[\text{Ru(III)}]$ in the concentration range of $(1-20) \cdot 10^{-7} \text{ M}$ ($10-202 \text{ ng} \cdot \text{ml}^{-1}$), which is in good agreement with theoretical concept. The calibration equations relating ΔA_t ($t = 2, 5$ and 7 min) and $[\text{Ru(III)}]$, detection limit and correlation coefficients (r^2), are summarized in Table 2.

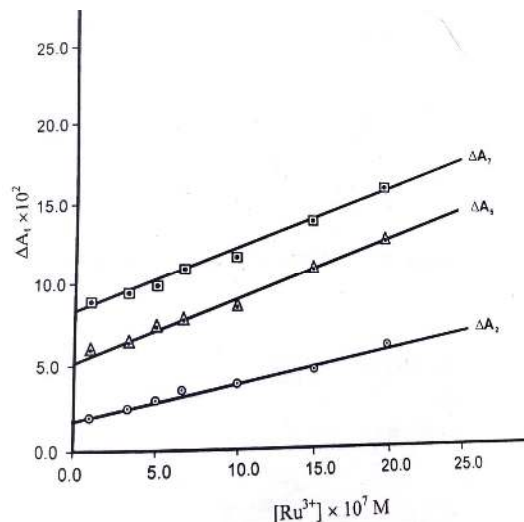


Fig. 1. Plot between ΔA_t (change in absorbance at t , min) vs. $[\text{Ru(III)}]$

Table 2

Determination of ruthenium(III)

at $[\text{Fe(CN)}_6]^{4-} = 2.25 \cdot 10^{-4}$, $[\text{NaIO}_4] = 7.5 \cdot 10^{-3}$, $\text{pH} = 9.5 \pm 0.02$, $T = 303 \pm 0.1 \text{ K}$, $I = 0.1 \text{ M (NaCl)}$

Calibration equations	Linear range, M	Detection limit, $\mu\text{g} \cdot \text{ml}^{-1}$	Correlation coefficient r^2
$\Delta A_2 = 2.25 \cdot 10^4 [\text{Ru}^{3+}] + 0.018$	$(1-20) \cdot 10^{-7}$	0.0081	0.9972
$\Delta A_5 = 3.28 \cdot 10^4 [\text{Ru}^{3+}] + 0.053$	$(1-20) \cdot 10^{-7}$	0.0053	0.9921
$\Delta A_7 = 4.31 \cdot 10^4 [\text{Ru}^{3+}] + 0.078$	$(1-20) \cdot 10^{-7}$	0.0038	0.9892

Table 3

Computation of recovered ruthenium(III) in spiked water with % error

at $[\text{Fe(CN)}_6]^{4-} = 2.25 \cdot 10^{-4}$, $[\text{NaIO}_4] = 7.5 \cdot 10^{-3}$, $\text{pH} = 9.5 \pm 0.02$, $T = 303 \pm 0.1 \text{ K}$, $I = 0.1 \text{ M (NaCl)}$

Ru(III) taken, $\text{ng} \cdot \text{ml}^{-1}$	ΔA_2		ΔA_5		ΔA_7	
	Ru(III) found, $\text{ng} \cdot \text{ml}^{-1} \pm \text{S.D. ng} \cdot \text{ml}^{-1}$	Error, %	Ru(III) found, $\text{ng} \cdot \text{ml}^{-1} \pm \text{S.D. ng} \cdot \text{ml}^{-1}$	Error, %	Ru(III) found, $\text{ng} \cdot \text{ml}^{-1} \pm \text{S.D. ng} \cdot \text{ml}^{-1}$	Error, %
10.11	10.08 ± 0.09	-0.30	9.96 ± 0.08	-1.51	9.91 ± 0.10	-2.02
33.35	33.66 ± 0.13	0.93	33.98 ± 0.21	1.85	33.82 ± 0.18	1.39
50.54	51.02 ± 0.28	0.95	51.09 ± 0.33	1.08	51.11 ± 0.62	1.12
67.72	66.98 ± 0.46	-1.09	67.02 ± 0.51	-1.04	66.82 ± 0.88	-1.35
101.07	102.13 ± 0.39	1.05	102.45 ± 0.56	1.35	102.82 ± 0.76	1.70
121.28	119.96 ± 0.53	-1.09	117.08 ± 0.25	-3.59	118.06 ± 0.44	-2.73
151.601	153.24 ± 0.76	1.08	152.41 ± 0.26	0.53	154.21 ± 0.32	1.69
181.93	181.06 ± 0.65	-0.48	180.26 ± 0.61	-0.93	180.06 ± 0.68	-1.04
202.14	200.86 ± 0.23	-0.63	198.25 ± 0.38	-1.96	199.61 ± 0.21	-1.27

The precision, accuracy and reproducibility of the present method for Ru(III) determination was tested by adding calculated amount of Ru(III) in double distilled water and conducting experiments for recovery. The percentage errors and standard deviation for the recovered ruthenium(III) concentration are given in Table 3. The error corresponding to regression equation ΔA_2 is less than that of ΔA_5 and ΔA_7 (Table 3) because

ΔA_2 is a close study of the initial rate than ΔA_5 or ΔA_7 . Therefore, a fixed time interval of 2 min was preferred for further measurement, which shows a good agreement between short time of analysis and reproducibility. The results in Table 3 show excellent reproducibility of the proposed method. The regression equation ΔA_2 is therefore advocated for trace level determination of Ru(III).

Table 4

Impact of various cations and anions on determination of $1.4 \cdot 10^{-7}$ M $[\text{Ru}^{3+}]$ using ΔA_2 calibration curve
 $[\text{Fe}(\text{CN})_6]^{4-} = 2.25 \cdot 10^{-4}$, $[\text{NaIO}_4] = 7.5 \cdot 10^{-3}$, $\text{pH} = 9.5 \pm 0.02$, $T = 303 \pm 0.1$ K, $I = 0.1$ M (NaCl)

Foreign ions	Concentration taken, $\text{M} \cdot 10^5$	Tolerance level ($[\text{interfering ion}] / [\text{Ru}^{3+}]$)
Ca^{2+}	1.45	103.57
Co^{3+}	1.75	125.00
Ba^{2+}	1.25	89.29
SCN^-	1.25	89.29
$\text{S}_2\text{O}_3^{2-}$	1.6	114.29
CH_3COO^-	1	71.43
Cl^-	1.75	125.00
Br^-	1.3	92.86
NO_3^-	1.4	100.00
EDTA	0.20	14.29
HEDTA	0.20	14.29
IDA	0.20	14.29

Table 5

Application of developed method in tap water samples using ΔA_2 calibration curve
 $[\text{Fe}(\text{CN})_6]^{4-} = 2.25 \cdot 10^{-4}$, $[\text{NaIO}_4] = 7.5 \cdot 10^{-3}$, $\text{pH} = 9.5 \pm 0.02$, $T = 303 \pm 0.1$ K, $I = 0.1$ M (NaCl)

Samples of tap water	$[\text{Ru}^{3+}]$ added, $\text{ng} \cdot \text{ml}^{-1}$	$[\text{Ru}^{3+}]$ found, $\text{ng} \cdot \text{ml}^{-1}$	Recovery, %
Sample 1	10.33	10.51	101.74
Sample 2	12.84	13.28	103.43
Sample 3	16.54	17.02	102.90

3.1. Study of Interferences (Sensitivity)

The sensitivity of the proposed method was studied under optimum reaction condition by addition of various cations, anions and poly-aminocarboxylates to fixed ruthenium(III) concentration ($1.5 \cdot 10^{-7}$ M). The tolerance limit of the added ions was considered not more than ± 5 % relative error. The results (Table 4) reveals that the catalytic activity of Ru(III) was not significantly affected by most common ions up to 71 times higher concentration. Polyaminocarboxylates (HEDTA, EDTA and IDA) containing free amino and carboxylic groups form strong co-ordinate complexes with Ru(III), which suppress its catalytic power to maximum, if tolerance limit is more than 14.29 times.

3.2. Analytical Application of Developed Method

To test the applicability and reliability, the proposed method was applied to determine the $[\text{Ru}(\text{III})]$ in three different samples of tap water having Ru(III) concentration in increasing order.

Because of very low content of Ru(III) in tap water it was added to the water samples so that the concentration of Ru(III) will be in detection range of proposed method (Table 3). The recovery results in Table 5 indicates the

quantitative and higher recovery of Ru(III) in every case, which may be due to the synergistic effect of other cations present in tap water. Thus, the developed method can be effectively used for the quantitative determination of ruthenium(III) in mixtures of several metal ions in comparatively higher concentration (Table 3).

4. Conclusions

The experimental data confirms the reproducibility, stability and selectivity of the developed method to determine Ru(III) quantitatively in different types of water samples using readily available and inexpensive reagents. The proposed catalytic spectrophotometric method has good sensitivity with low detection limit as compared to other developed CKM-SPM. In most of other methods, substrates used are expensive and rarely available while other few used quencher and activator for analysis. Over all, the developed method can be effectively applied for the trace level ruthenium(III) analysis in tap water.

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СПЕКТРОФОТОМЕТРИЧНЕ ВИЗНАЧЕННЯ РУТЕНІЮ З ВИКОРИСТАННЯМ ЙОГО КАТАЛІТИЧНОЇ АКТИВНОСТІ НА ОКИСНЕННЯ ГЕКСАЦІАНОФЕРРАТА(II) ПЕРІОДАТНИМ ЙОНОМ В ВІЗКАХ ВОДИ

Анотація. Для визначення рутенію(III) на мікрорівні застосовано каталітичний ефект хлориду рутенію на зовнішнє перенесення електронів гексаціаноферрату(II) періодатним йоном у водному лужному середовищі. Встановлено оптимальні умови реакції та необхідний час. Лінійна залежність між поглинальною здатністю та концентрацією Ru(III) використана для визначення слідів Ru(III). Показано, що додавання інтерферентних іонів (в концентраціях, до 71 разів вищих за концентрацію Ru) істотно не впливає на каталітичну активність Ru(III) при окисненні гексаціаноферрату(II) періодатним йоном. Поліамінокарбоксилати пригнічують його каталітичну здатність до максимального значення, якщо допустима межа є більшою за 14,29. Враховуючи відтворюваність, стабільність та селективність цього методу, запропоновано використовувати його для різних типів зразків води для визначення рутенію(III) на мікрорівні.

Ключові слова: кінетика, механізм, гексаціаноферрат(II), періодат, рутеній(III).