Spectrophotometric Determination of Complexation of Ruthenium (IV) with 2-[(5-Bromo-2-Pyridylazo)]-5-Diethylaminophenol and N-Hydroxy-N, N'-Diphenylbenzamidine

Pushpa Ratre[1]* and Devendra Kumar[2]

[1, 2]Department of Applied Chemistry and Polymer Technology
Delhi Technological University (Formerly Delhi College of Engineering)
Shahbad Daulatpur, Bawana Road, Delhi-110042, India

***Corres. Author: pushpa.ratre.delhi@gmail.com**

Abstract: A new, simple and selective spectrophotometric method has been developed for the determination of trace amount of Ru(IV) which is based on the formation of orange colored mixed complex of ruthenate ion (RuO_4^{2-}) with 2-[(5-bromo-2-pyridylazo)]-5-diethylamino-phenol (5-Br-PADAP). The orange color complex was extractable with seven derivative of N-hydroxy-N,N'-diphenylbenzamidine (HDPBA) in dichloromethane in the ratio of tri-sodium citrate dehydrate to sodium acetate at 1:3. The molar absorptivity of Ru(IV)-(5-Br-PADAP)-HDPBA complex in dichloromethane at absorption maxima of 560 nm was calculated to be 3.0×10^4 Lit mol^{-1} cm^{-1} with the mole ratio of metal to ligand in the complex being at 1:1:1. The stability constant of the complex was calculated to be 4.73 dm^3mol^{-1} at 28°C. The system obeyed Beer's law up to 1.0 to 14.0 μg Ru(IV) per 5 mL in organic phase with the detection limit of the method at 2σ being 12.0 ng mL^{-1}. Most of the foreign ions do not interfere with the proposed method except palladium. The method has been successfully applied for the determination of trace analysis of Ru(IV) in real sample, synthetic mixture and different sources of water with the RSD value ranging between ±0.71% and ±4.75%. The proposed method caused the recovery of metal ions to be in the range of 86.0% to 101.5%.
Keywords: Ru(IV), 5-Br-PADAP, HDPBA, Spectrophotometric, Orange color complex.

1. Introduction

Ruthenium, which is associated with platinum ores, is a rare transition element found in about 10^{-8} % of the earth's crust. It is a hard, white metal discovered by Karl Klaus in 1844. The larger amount of ruthenium is found in chondrite and iron meteorites $(10^{-6}-10^{-4})$%[1]. All ruthenium compounds are highly toxic and carcinogenic. Compounds of ruthenium stain the skin very strongly and the ingested ruthenium is seen to be retained strongly in bones[2]. Nowadays, compounds and complexes of ruthenium have come to be used as drugs for treatment of cancer and tumor[3]. Some other applications include a ruthenium NO donors,

cis-[Ru(NO)(bpy)$_2$L]X*n* being used for Chagas's disease[4], ruthenium octahedral metal complexes being used as inducer for structural analysis of DNA[5], a ruthenium based catalysts being used for synthesis of ammonia, pharmaceutical industry[6] and fabrication of dye-sensitized solar cells (DSSCs)[7], etc.

In the proposed method, the hydroxyamidine is used as extracting analytical reagent. These reagent forms orange colored complexes with ruthenium (IV)-2-[(5-bromo-2-pyridylazo)]-5-diethylaminophenol (5-Br-PADAP) in the presence of the halo-group attached to the carbon atom and carbon-nitrogen double bond [8-10]. These hydroxyamidine is widely used in quantitative determination of metal ions in environment, organic, inorganic and pharmaceutical analysis. Recently, it has found a way in biotechnology as prodrugs of amidines (amidoximes) to study the reduction and hydrolytical metabolism of ximelagatran via two mono-prodrugs (*N*-hydroxy-melagatran and ethyl-melagatran)[11, 12].

Nowadays, new analytical techniques have been developed for the determination of ruthenium in trace quantities in various complex matrices, e.g., ores, alloys, seawater, biological samples, etc and in synthetic samples, e.g., electrothermal atomic absorption spectrometry[13], atomic absorption spectrometry (AAS)[14], flow injection analysis (FIA)[15], x-ray photoelectron spectroscopy[16], high-performance liquid chromatography [17], voltametric method[18], flow injection chemiluminescent[19], etc. Although all these techniques are highly sensitive but required costly maintenance and skilled hands for operation and are quite expensive. Instead, the spectrophotometric method is more popular and cheaper technique.

A survey of literature reveals that a lot of reagents, compound and surfactant have been employed for the determination of ruthenium. Kuchekar et al.[20] used a reagent *o*-methylphenyl thiourea for the extraction of ruthenium but the method was less sensitive. Gopala Krishna et al.[21] developed a 4-Hydroxy 3,5-dimethoxy Benzaldehyde-4-hydroxy Benzoylhydrazone [HDBHB] for the extraction of ruthenium but the method suffered from interference of Cu^{+2} and Fe^{+3}. Mathew et al.[22] developed a method which suffered from interferences of foreign ions using schiff's base derived from a triazine. Lokhande et al.[23] developed a less sensitive method for the analysis of ruthenium using Pyrimidine-2-thiol as reagent along with *N*-octylaniline as an extractant. El-Shahawi et al.[24] developed a less sensitive method using benzyltributylammonium chloride for the determination of ruthenium. Alaa et al.[25] described the solid phase extraction method using quinoxaline dyes into microcrystalline *p*-dichlorobenzene for trace analysis of ruthenium but it is a tedious job to filter the derivative of reagent mixed with ruthenium. El-Shahawi et al.[26] used a sodium periodate as a reagent for developing a iodometry titration and spectrophotometric method for the determination of ruthenium but the drawback of these method is precipitation of iodine which decreases the molar absorptivity. Islam et al.[27] used a reagent 3-(2-Pyridyl)-5,6-diphenyl-*as*-triazine (PDT) and ferrozine together to reduce the extraction time of ruthenium but was not able to increase its molar absorptivity. Keyvanfard et al.[28] studied the kinetic reaction and oxidation of metaperiodate in micellar medium for the determination of ruthenium but the method had low sensitivity. Solovey-Vandersteen et al.[29] used a reagent "xylenol orange" for the determination of ruthenium but the method had low molar absorptivity. Balcerzak et al.[30] used a high molecular weight amines for analysis of ruthenium but method was based on tedious job of preparation of compound. Druskovic et al.[31] used a reagent 4-pyridone derivatives for determination of ruthenium but the method had low molar absorptivity. Rezaei et al.[32] developed a less sensitive method for estimation of ruthenium which was based on oxidation of safranin O by metaperiodate. Hong-fu et al.[33] using a reagent malachite green, Praveen Kumar et al.[34] using a reagent 1,10-phenanthroline and Zhi-rong et.al[35] using a reagent chrome blue K contributed to a less sensitive method for ruthenium.

The chief goal of the present work is to achieve a new, simple, more sensitive and reproducible method for the determination of Ru(IV) in the environmental samples. The trace amount of Ru(IV) has spectrophotometrically determined with 5-Br-PADAP in the presence of appropriate ratio of tri-sodium citrate and sodium acetate and its subsequent extraction with hydroxyamidines (HOA) in dichloromethane. By using the extraction method of Ru(IV) with HOA, most of the common ions do not interfere with the proposed method.

2. Experimental

2.1 Instrumentation

For characterization of ruthenium (IV) complex, double beam UV-Visible spectrophotometer 54440SS model equipped with 1cm quartz cell was used. A digital pH meter (DB-1011) was calibrated regularly with a standard buffer solution before use.

2.2 Reagents

All chemicals used were procured from Sigma Aldrich and E. Merck. Millipore double distilled water was used for the preparation of all solutions. The standard solution of ruthenium ($RuO_2.XH_2O$) was prepared by fusion of 75.0 mg of pure ruthenium powder in a 15 mL silver crucible with 1.0 g of sodium hydroxide and 0.20 g of sodium peroxide at dull-red heat for 10 min. The residue was dissolved with 2.0 mol L^{-1} sodium hydroxide in a 500 ml standard flask and made up to the mark[36]. The stock solution of 9.92×10^{-3} mol L^{-1} was standardized by thiourea method[37]. The lower concentration of solutions was prepared by diluting the stock solution.

A 3.47×10^{-3} mol L^{-1} (0.1%, w/v) solution of N-Hydroxy-N, N'-diphenylbenzamidine (HDPBA) (98.0% pure) was prepared in dichloromethane. A 2.89×10^{-4} mol L^{-1} (0.01%, w/v) 2-[2-(5-bromopyridyl) azo]-5-dimethylaminophenol (5-Br-PADAP) (97.0% pure) solution in methanol (95.0% pure) was employed for color development. A 3.40×10^{-2} mol L^{-1} (1.0%, w/v) of tri-sodium citrate dihydrate (TSC) and 2.0 mol L^{-1} (16.4%, w/v) solution of sodium acetate (SC) were prepared in distilled water. The above solutions were mixed in a volume ratio of 1:3, 1:2, 1:1, 2:3 (TSC: SC) in a final 12.0 mL volume is equivalent to pH 11.0±02. The solutions of diverse ions were prepared in mg/mL solutions of the ions as given in the literature[38].

2.3 General Procedure

Take an aliquot of the standard solution containing up to (1.0 to 14) µg/mL or (6.62×10^{-6} to 9.26×10^{-5}) mol L^{-1}Ru (IV) in a 125mL separatory funnel. To the above solution, add 0.6 mL of 5-Br-PADAP and then buffering the complex with mixture of (1:3) TSC-SC solutions up to total volume of 10.0 mL. The orange colored complex formed immediately within 2 min which was extracted with 3.0 mL of HDPBA solution prepared in dichloromethane. Wash the aqueous phase with 2x1 ml fresh dichloromethane. Then separate the orange colored dichloromethane extracts and dry over anhydrous sodium sulfate ($\approx$2 gm) in a 10.0 mL beaker. Transfer the combined extract into a 5.0 mL volumetric flask. Measure the absorbance of the complex against the solvent at λ_{max} 600 nm and 560 nm.

2.4 Sampling and Sample Preparation

2.4.1 Platinum Crucible

A different known amount of platinum crucible were weighed and dissolved in hot aquaregia to remove Osmium, if present in the solution. The resultant solution was evaporated three times with small amount of hydrochloric acid in order to remove nitric acid. The residues were diluted with 2 mol L^{-1} sulphuric acid and RuO_4 was separated by distillation after the oxidation of ruthenium by 0.02 mol L^{-1} $KMnO_4$. The volatile RuO_4 was absorbed in 2.0 mL of hydrochloric acid and the solutions were diluted to 10 mL in a volumetric flask with distilled water. The amount of ruthenium present in different sample solutions prepared as above was determined by the proposed method with the help of the pre-determined calibration plot.

2.4.2 Synthetic Mixtures and Water Samples

The synthetic mixtures were prepared according to the composition of ruthenium alloys which contain ruthenium and other platinum group metals and some transition series elements. Take a portion of synthetic mixture and follow the above procedure. The concentration of Ru (IV) present in mixture was determined with help of standard addition method.

The sample bottles were soaked in 10 percent HNO_3 for 24 h and rinsed several times with double distilled water prior to use. The water samples were filtered through 0.45 µm membranes filter and preserved with concentrated nitric acid to bring down the pH to < 2.0. The samples thus preserved were stored at 4ºC in

sampling kits and brought to the laboratory for metal analysis. The concentrations of Ru (IV) present in water samples were determined with the help of standard addition method.

3. Results and Discussion

The development of new analytical method for determination of Ru (IV) has been done by extracting Ru (IV)-(5-Br-PADAP)-HDPBA complex from dichloromethane in the presence of TSC-SC mixture. The optimum experimental conditions and some important spectral and statistical data obtained for the determination of Ru (IV) in the proposed method have been summarized in Table 1.

3.1 Spectral Studies

The complex Ru (IV)-(5-Br-PADAP) in aqueous and organic (HDPBA-dichloromethane), exhibits maximum absorbance at around 600 nm and 560 nm against the solvent (Figure 1). The reagent blank in both phase shows some absorbance (A=0.04) at this region and hence it was used in all experimental work.

3.2 Effect of Extraction Solvent

Ruthenium(IV) complex is extractable into many polar and non-polar solvents, such as ethyl acetate ($\varepsilon= 1.10\times10^4$ L mol^{-1} cm^{-1}), isobutyl methyl ketone ($\varepsilon= 0.62\times10^4$ L mol^{-1} cm^{-1}), toluene ($\varepsilon= 2.81\times10^4$ L mol^{-1} cm^{-1}), benzene($\varepsilon= 1.73\times10^4$ L mol^{-1} cm^{-1}), chloroform ($\varepsilon= 2.99\times10^4$ L mol^{-1} cm^{-1}), dichloromethane ($\varepsilon= 2.99\times10^4$ L mol^{-1} cm^{-1}), *etc.* with value of $\lambda_{max,}$ 560 nm in all cases as shown in Table 2. The sensitivity of complex in terms of molar absorptivity in both dichloromethane and chloroform is maximum and similar. However, dichloromethane is preferred because of its less toxic nature than chloroform. Thus, due to its superiority, dichloromethane was therefore chosen as solvent for the extraction of Ru(IV)-(5-Br-PADAP)-HDPBA complex.

Figure 1 Absorption spectra of Ru(IV)-(5-Br-PADAP) complex in aqueous and organic phase against solvent. Ru(IV)[1.97×10^{-5} mol L^{-1}], aqueous phase; 5-Br-PADAP [5.72×10^{-5} mol L^{-1}]; TSC-SA[1:3] ; HDPBA[2.08×10^{-3} mol L^{-1}]
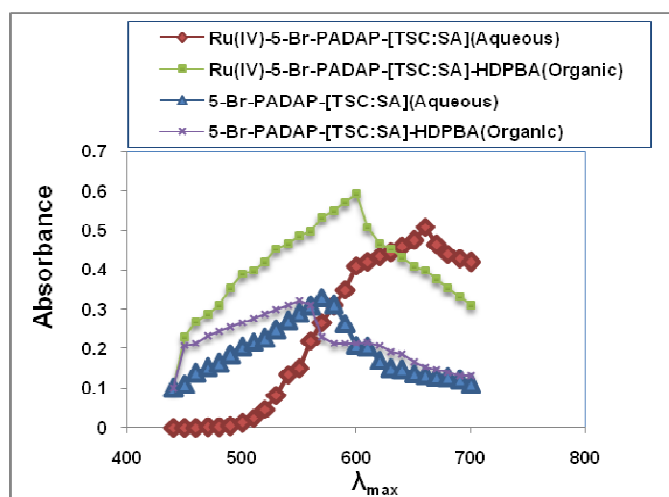
Table 1. Analytical Parameters of Ru(IV)-5-Br-PADAP-HDPBA in dichloromethane.

Colour of the complex	Orange
λ_{max}	600 nm[aqueous], 560 nm [organic phase]
TSC: Sodium Acetate	[1:3]
Concentration of 5-Br-PADAP	5.72×10^{-5} mol L^{-1}
Concentration of HDPBA	2.08×10^{-3} mol L^{-1}
Composition of complex (M: L:L)	1:1:1
Stability constant of the complex	4.731 $dm^3 mol^{-1}$ at 28°C
Beer's law	1.0 to 14 μg/5 mL
Molar absorptivity	3.0×10^4 L $mol^{-1} cm^{-1}$
Standard deviation (SD) N=10, Relative standard deviation(RSD) N=10	±0.0031, 0.52%
Stability of complex	24h
Sendell's Sensitivity, Detection limit (2σ) N=10	0.0033 μg cm^{-2}, 12 ng mL^{-1}
Intercept, slope, correlation coefficient	-0.00070, 0.060, 1.0

Table 2 Effect of solvent on the extraction of Ru(IV)-(5-Br-PADAP)-HDPBA complex

Solvent	Ru(IV), λ_{max}, nm	Molar absorptivity(ε) L $mol^{-1} cm^{-1} \times 10^4$	% Extraction
Ethyl acetate	500	1.113	53.5
Isobutyl methyl ketone	505	0.620	85.5
Xylene	560	0.235	75.0
Benzene	410	1.732	50.5
Toluene	400	2.810	50.0
Carbon tetrachloride	500	0.121	70.5
Chloroform	560	3.070	99.5
Dichloromethane	560	3.270	99.5

3.3 Effect of Derivatives of N-Hydroxy-N,N'-Diphenylbenzamidine (HDPBA)

The spectral characteristics of Ru(IV)-5-Br-PADAP complexes were examined using seven different derivatives of hydroxyamidines (HOAs) in dichloromethane. Compounds with chloro(Ph)- and methyl(Ph')-substitution in two phenyl rings of N'-atom in HOA were used. The complexes with various HOAs show different values of molar absorptivity, at their respective λ_{max}. Introduction of methyl (+I) or chloro (-I) group at *N'*-phenyl ring of HOAs slightly reduces the sensitivity in the following order $C_6H_5 > 4$-CH_3-C_6H_4 (Ph'-) > 3-CH_3-C_6H_4 (Ph'-) > 2-CH_3-C_6H_4 (Ph'-) > 4-Cl-C_6H_4(Ph-) > 3-Cl-C_6H_4(Ph-) > 2-Cl-C_6H_4(Ph-) as shown in Figure 2. The parent compound, HDPBA was chosen due to reasons, namely relatively easier synthesis, large yield of the compound and high reproducibility of the result.

3.4 Effect of Reagents

The result obtained indicated that at least $(4.00$-$6.29) \times 10^{-5}$ mol L^{-1} of the reagent in ethanol is required for maximum complexation. In subsequent studies, 5.72×10^{-5} mol L^{-1} of 5-Br-PADAP was used. The concentration of HDPBA in dichloromethane in the range of $(1.73$-$3.12) \times 10^{-3}$ mol L^{-1} was adequate for the complete extraction of the complex. Therefore, a 2.08×10^{-3} mol L^{-1} HDPBA was employed throughout the experiment. The concentration ranges of both the reagent were shown in the Figure 3.

3.4.1 Effect of Mixed Ratio of Tri-sodium Citrate (TSC)-Sodium Acetate (SC)

Tri-sodium citrate dihydrate and sodium acetate are widely used in foods, beverages and   various technical applications in industry, mainly as buffering, sequestering or emulsifying agent and stabilization of reactions. The TSC-SC mixture is used as stabilizer in our experiment.

The effect of concentration and volume ratio of TSC and SC on the absorbance and percentage of extraction of the complex were studied. The concentration range of $(2.72$-$4.76) \times 10^{-3}$ mol L^{-1} TSC and 0.4-1.2

mol L^{-1} SC was sufficient for maximum color development and stabilization of complex. Hence the author has chosen the mixture ratio of 3.40×10^{-3} mol L^{-1} TSC and 0.60 mol L^{-1} sodium acetate solution for further studies.

The effect of volume ratio of TSC: SC on the percentage of extraction of Ru (IV)-complex is as shown in Figure 4. The volume ratio of 1:2, 2:3, 1:1 and 1:3 were sufficient for the stability of the complex and show a maximum percentage of extraction of (89.4 to 89.8) of the complex at wavelength of 560 nm. There were no change in the *p*H of the complex up to (~ 11.0 ± 0.2), since RuO$_4$ was prepared in strong alkaline medium using NaOH fusion process.

3.5   Effect of Temperature, Electrolyte and Dilution

The variation in temperature of the aqueous phase from 10 to 50°C has no adverse effect on the extraction of the metal ions. Beyond this temperature range, the absorbance of the complex starts decreasing. Hence, all extraction work was carried out at room temperature.

Addition of 1 molL^{-1} KCl/NH$_4$Cl/K$_2$SO$_4$ solutions does not change the absorption characteristics and neither the shift in λ_{max} nor any change in absorbance of the complex was observed.

The effect of variation in the volume of the aqueous phase, keeping the other variables constant, on the extraction of the metal with HDPBA was studied. No change in the absorbance of the metal complex was observed on varying the volume ratio of the organic to aqueous phase from 1:4 to 1:1. For the sake of uniformity, all extraction was performed at a 1:1 volume ratio for both phases.

3.6   Stability Constant, Ionic Strength and Composition of the Ru(IV)-Complex

The stability constant(K') of the complex formed were calculated through Job's method[40] at the ratio of TSC: SC[1:3] and ionic strength (mμ) of 7.94×10^{-4} mol L^{-1} was calculated to be 4.731 dm^{3}mol^{-1} at 28°C for the complex Ru(IV)-(5-Br-PADAP)-HDPBA.

Figure 2 Absorption spectra of Ru(IV)- (HOA'S) Deivatives Complexes.
Ru(IV)[1.97×10^{-5} mol L^{-1}]; 5-Br-PADAP[5.72×10^{-5} mol L^{-1}]; TSC-SA(1:3) ;
HOA'S[2.08×10^{-3} mol L^{-1}]; [a] C$_6$H$_5$; [b] 4-CH$_3$-C$_6$H$_4$ (Ph'-) ;
[c] 2-CH$_3$-C$_6$H$_4$ (Ph'-) ; [d] 4-Cl-C$_6$H$_4$(Ph-); [e] 3-Cl-C$_6$H$_4$(Ph-)
[f] 2-Cl-C$_6$H$_4$(Ph-)
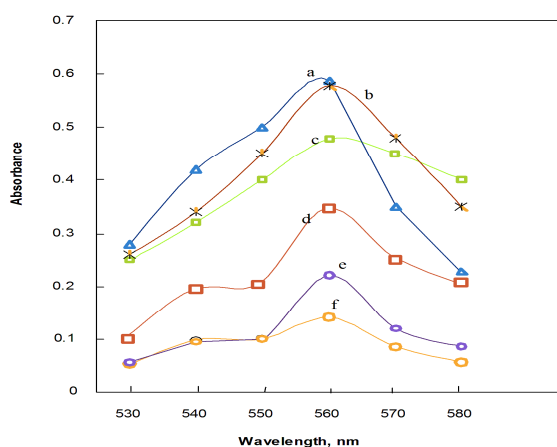
Figure 3 Effect of Reagent concentrations
on Ru(IV)- complex in dichloromethane.
Ru(IV)[1.97×10^{-5} mol L^{-1}]; TSC-SA(1:3)
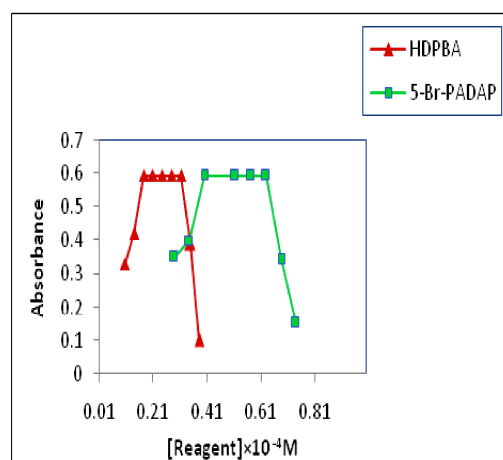
The composition of the ruthenium (IV) complex was determined by the curve fitting method[39] and Job's continuous variation method[40]. The molar ratio of metal to 5-Br-PADAP and HDPBA was determined by plotting logarithmic value of distribution ratio of metal versus logarithmic values of varied known concentrations of 5-Br-PADAP/ HDPBA in dichloromethane. The inclination of the curves for 5-Br-PADAP and HDPBA were found to be very close to integer 1 in all cases. Thus Figure 5 shows a 1:1:1 molar ratio complex of Ru(IV): 5-Br-PADAP: HDPBA in dichloromethane. The ruthanate ion, RuO_4^{2-}, forms a stable 1:1 mixed ligand complex by replacing H^+ available essentially in alkaline medium (pH > 9.0) from both OH-groups present in 5-Br-PADAP as well as in HOA. The probable reaction mechanism is as shown below.
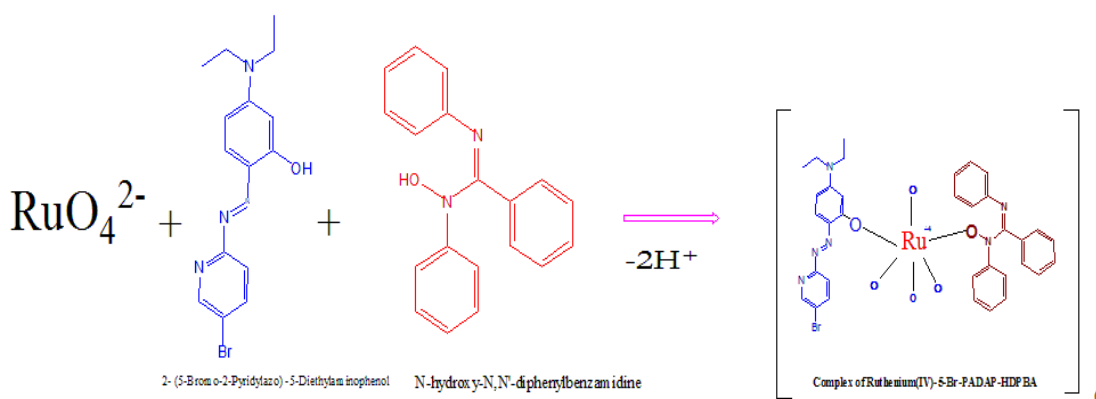
Subscript "o" here indicates organic phase *i.e.* dichloromethane and abbreviations HL and HOA have been used for representing 5-Br-PADAP and N-hydroxy-N,N'-diphenylbenzamidine, respectively.

Figure 4 Effect of volume ratio of TSC and SA on extraction of Ru(IV)-(5-Br-PADAP)-HDPBA complex. Ru(IV)[1.97×10⁻⁵ mol L⁻¹] ; 5-Br-PADAP[5.72×10⁻⁵ mol L⁻¹]; HDPBA[2.08×10⁻³ mol L⁻¹].
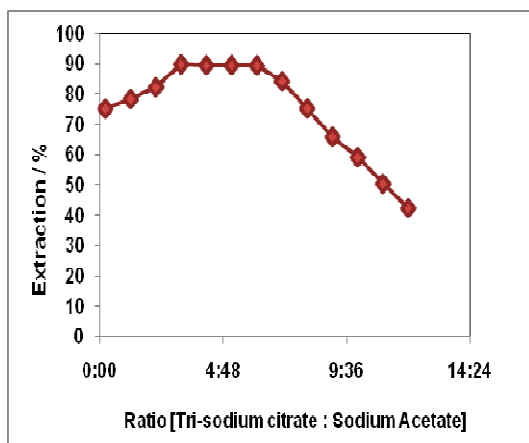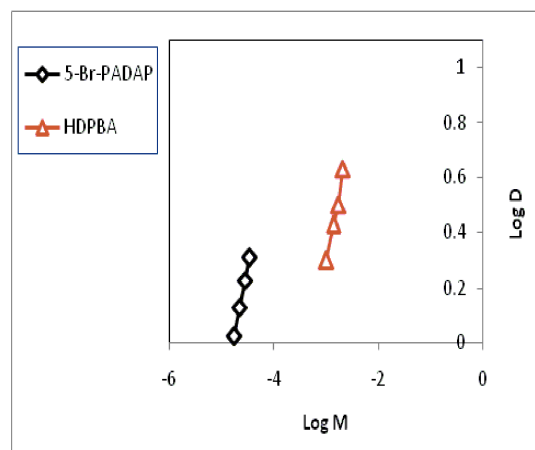
Figure 5. Plot of curve-fitting method for determination of molar ratio of Ru(IV) to 5-Br-PADAP and HDPBA in Ru(IV)- complex.

3.7 Beer's law, correlation Coefficient, Molar Absorptivity, Sensitivity, Detection Limit and Precision

The orange coloured Ru(IV)-5-Br-PADAP-HDPBA complex obeyed Beer's law up to 1.0-14.0μg Ru(IV)/5mL in both aqueous and organic phase at λ_{max} 600 nm and 560 nm respectively, as shown in Figure 6. Intercept, slope, correlation coefficient, (2σ) detection limit, Sandell's sensitivity [41] are as given in Table 1. The molar absorptivity value of the complex with various hydroxyamidines (HOA) tested to lie in the range is (2.8-3.0)×10⁴ L mol⁻¹ cm⁻¹. The molar absorptivity value of orange colored Ru(IV)- 5-Br-PADAP complex in aqueous and organic phase were 2.57×10⁴ L mol⁻¹cm⁻¹ at 600 nm and 3.0×10⁴ L mol⁻¹cm⁻¹ at 560 nm respectively. The precision of the method was checked by taking 10 replicate measurements each containing 6.62×10⁻⁵ mol L⁻¹ Ru(IV) per 5 mL organic phase. The mean absorbance value and the standard deviation value

were calculated to be 0.593 and ±0.003, respectively which gave a relative standard deviation of 0.52%. The range within which the value of molar absorptivity of the system may fall with the measured precision at 95% confidence level was calculated and the value of confidence limit [41] in terms of molar absorptivity was found to be $(3.0\pm0.03)\times10^4$ L mol^{-1}cm^{-1}.

3.8 Effect of Diverse Ions

To study the effect of diverse ions [42], variable amounts of foreign ions were introduced to a fixed amount of ruthenium (IV). PGEs, namely Pd (II) interferes at concentrations > 2-fold excess. However, interference due to Pd (II) may be minimized by masking it with 3 ml of 4% sodium thiosulphate. Mn(II) and Pb(II) are tolerated not more than 10-fold excess concentration. The tolerance limit of various diverse ions, in mg, in the determination of 1.0 µg Ru(IV)/mL is summarized in Table 4.

3.9 Applications

The proposed method was successfully applied for the determination of Ruthenium (IV) in real samples (Platinum crucible), synthetic mixture and different sources of water samples. The trace amount of Ruthenium (IV) present was determined by standard addition method and actual concentration is calculated from a pre-determined calibration plot. The result presented in Table 5 shows a concentration of Ru(IV) present in real samples was found to lie between 2.87-3.0 µg / mL with RSD value ranging from ±1.50 % to ± 2.85 % and percentage recovery of metal ions was determined between 96.0 % and 98.50 %. The RSD value obtained for Ru(IV) content in the synthetic mixture and in different sources of water samples ranged between ±1.0 % and ±4.75% . The result obtained from the proposed method was highly satisfactory and it was also verified from the reported method [29] as shown in Table 5,6 and 7.

Table 4 Tolerance limit (TL) of diverse ions in the determination of 10 µg Ru(IV) / 5 mL aqueous phase.

Foreign Ions Added	TL*mg/mL	Foreign Ions Added	TL*mg/mL
Rh(III), Pd(II), Pt(IV),Os(VIII)	2.0, 0. 014[a], 1.0	Bi(III), Mo(VI)	2000, 1000
V(V)	0.9	Co(II), Mg(II), Fe(III)	15, 18, 25
Cu(II),Mn(II),Sb(III),Se(IV),	1.0	Ca(II), Ni(II), Cr(III), Ti(IV), Zr(IV), W(VI)	50
Pb(II), La(III)	2.0, 3.0	Zn(II)	40
Nb(V), U(VI)	4.0, 3.5	Fluoride, Phosphate, Nitrate, Citrate	2.0, 4.0, 10.0, 100
Th(IV), Sr(II)	5.0, 6.0	EDTA, Tartrate, Bromide	140, 300, 200
Hg(II), Be(II)	1.0	Thiosulphate, Oxalate	500, 1000

*Ions were considered to be interfere when they caused a change in the absorbance of the Ru(IV)-(5-Br-PADAP)-HDPBA complex (A=0.593) by ≥ ±≤ 2%. a- Masked by 3 ml of 4% sodium thiosulphate.

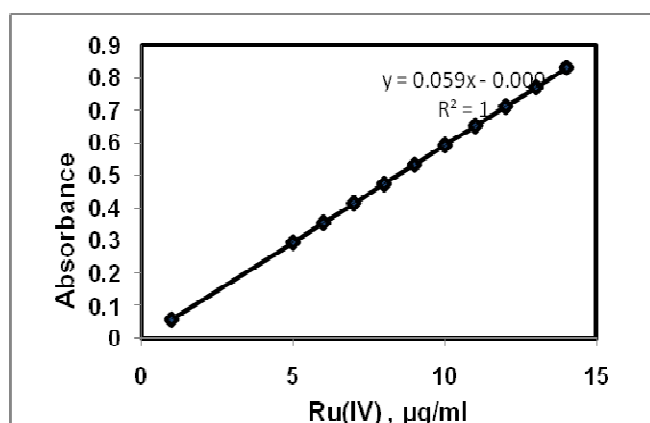**Figure 6 Applicability of Beer's law on Ru(IV)-complex in dichloromethane.**

Table 5 Determination of Ru(IV) in Platinum crucible

Weight of the sample (g)	Ru(IV) added, (µg)/mL	Ru(IV) found, (µg) / mL	RSD* ±, %, N=4	(Recovery ± RSD) %, N=4
1.0	----------------	2.87	2.00	----
2.0	----------------	3.75	2.50	----
2.5	---------------	4.00	2.85	------
2.0	5.0	8.25	1.50	96.02 ± 1.7
2.5	5.0	9.50	2.45	97.06 ± 1.5
3.0	5.0	10.55	1.50	98.50 1.7

LEGENDS- N: Number of analysis, RSD: Relative Standard Deviation

Table 6 Determination of Ru (IV) in the Synthetic Mixture.

Sample No.	Synthetic Mixture	Ru found in µg/ 5 mL			
		Proposed method*		Reported method[29]	
		Concentration of Ru(IV), µg/mL	RSD*±, %, N=4	Concentration of Ru(IV), µg/mL	RSD*±, %, N=4
[S-1]	$Ru^{IV}(10)$; $Pd^{II}(5)$;$Os^{VIII}(30)$; $Fe^{III}(30)$; $Pt^{IV}(20)$; $Mn^{II}(10)$.	9.96	1.17	9.90	1.01
[S-2]	$Ru^{IV}(20)$; $Co^{II}(10)$; $Ni^{II}(20)$; $Mo^{VI}(10)$; $Fe^{III}(30)$; $Rh^{III}(10)$.	19.96	1.19	20.1	1.31
[S-3]	$Ru^{IV}(10)$; $Rh^{III}(10)$;$Os^{VIII}(15)$; $Pd^{II}(5)$; $Co^{II}(10)$; $Pt^{IV}(20)$.	10.10	1.58	9.90	1.01

LEGENDS-S-1, S-2, S-3 are the synthetic mixture, N: Number of analysis, RSD: Relative Standard Deviation

Table 7 Determination of ruthenium in different sources of water samples by standard addition method.

Water Samples	Ru(IV) Added, µg / mL	Proposed method, Ru(IV) found, µg/ mL	RSD ±, %, N=4	(Recovery±RSD)%, N=4	Reported method[29] Ru(IV) found, µg/ mL	RSD ±, %, N=4	(Recovery ± RSD)%, N=4
River water	10.0	9.5, 10.0, 10.0, 9.9	2.50	98.5 ± 0.1	9.9, 10.1, 10.0, 9.9	0.71	99.75 ± 0.2
Bore well	10.0	8.5, 9.0, 9.2, 8.7	3.50	88.5 ± 0.1	8.2, 9.0, 9.1, 8.7	4.75	87.5 ± 0.50
Sea water	10.0	10.1, 10.2, 10.0, 10.2	1.70	101.0 ± 0.1	10.1, 10.1, 10.0,10.2	1.80	101.5 ± 0.2
Dam	10.0	8.5, 8.5, 8.9, 8.7	2.20	86.5 ± 0.2	8.5, 8.5, 8.7, 8.7	1.34	86.0 ± 0.30

LEGENDS- N: Number of analysis, RSD: Relative Standard Deviation

4. Conclusion

The spectrophotometric method are more selective, sensitive and rapid for the determination of trace amount of Ru(IV) using reagent 2-[(5-bromo-2-pyridylazo)]-5-diethylaminophenol (5-Br-PADAP) along with *N*-hydroxy-*N,N'*-diphenylbenzamidine. The selected reagent advantageously increases the sensitivity and selectivity of the method. The accuracy of the method is comparable with other reported methods in the literature. Most of the foreign ions, even at high concentration, do not interfere with determination of Ru(IV). Only palladium interferes in this method which could effectively be masked by the addition of sodium thiosulfate. The proposed method has been successfully applied for the determination of Ru(IV) in real samples, synthetic mixture and different sources of water samples. The proposed method overcomes with many drawbacks of classical photometric methods.

5. Acknowledgment

References

1. R. Hamond, The elements, in Lide, D. R., ed., CRC Handbook of Chemistry and Physics, 86th ed., CRC Press: Boca Raton (FL), 2005.

2. W. P. Griffith, "Ruthenium Oxidation Complexes: Their Uses as Homogenous Organic Catalysts," *Platinum Metals Rev.*, vol. 55 (3), July 2011, pp.193-195.

3. S. Atak and M. S. Celik, Innovations in Mineral and Coal Processing, 1st ed., Taylor and Francis, 1998.

4. L. Staurengo-Ferrari, S.S. Mizokami, J. J. Silva, F.O. da Silva, E. H. Sousa, L. G. da Franca, M.L. Matuoka, S.R. Georgetti, M.M. Baracat, R. Casagrande, W. R. Pavanelli and Jr. W. A. Verri, "The ruthenium NO donor, [Ru(bpy)2(NO)SO3](PF6), inhibits inflammatory pain: involvement of TRPV1 and cGMP/PKG/ATP-sensitive potassium channel signaling pathway," *Pharmacol Biochem Behav.*, vol.105, Apr 2013, pp.157-165.

5. A. D. Richards and A. Rodger, "Synthetic Metallomolecules as Agents for the control of DNA structure," *Chem. Soc. Rev.*, vol. 36, 2007, pp. 471-475.

6. D. Kuang, S. Ito, B. Wenger, K. Cedric, J-E. Moser, B. Humphry, Z. Robin, M. Shaik and M. Gratzel, "High Molar Extinction Coefficient Heteroleptic Ruthenium Complexes for Thin Film Dye-Sensitized Solar Cells," *J. American Chem. Soc.*, vol. 128, 2006, pp. 4146-4154.

7. C-L Lee, W-H Lee and C-H Yang, "The effects of co-sensitization in dye-sensitized solar cells," *J. Mat. Sci.*, vol. 48 (9), May 2013, pp. 3448-3453.

8. P. Ratre and D. Kumar, "Spectrophotometric Determination of Trace Amounts of Samarium in Environmental Samples," *American Inter. J. Res. Formal, Appl. Nat. Sci.* vol. 3 (1), June-Aug 2013, pp. 110-118.

9. P. Ratre and D. Kumar, "Spectrophotometric Determination of Pt (II) and Pd (II) in Environmental Samples Collected from Highly Polluted Areas of Delhi Region of India," *Inter. J. Emerging Techno. Computational. Appl. Sci.*, vol. 5 (4), June-Aug 2013, pp. 421- 429.

10. S. Biswas, P. N. Pathak and S. B. Roy, "Development of an extractive spectrophotometric method for estimation of uranium in ore leach solutions using 2-ethylhexyl phosphonic acid-mono-2-ethylhexyl ester (PC88A) and tri-n-octyl phosphine oxide (TOPO) mixture as extractant and 2-(5-bromo-2-pyridylozo)-5-diethyl aminophenol (Br-PADAP) as chromophore," *Spectrochim Acta A Mol Biomol Spectrosc.* vol. 91, Jun 2012, pp. 222-227.

11. M. P. Gulseth, , "Ximelagatran: an orally active direct thrombin inhibitor," *American Journal of Health System Pharmacy*, vol. 62 (14), Jul 2005, pp.1451-1467.

12. C. Colwell and P. Mouret, "Ximelagatran for the prevention of venous thromboembolism following elective hip or knee replacement surgery," *Semin Vasc Med.*, vol. 5 (3), Aug 2005, pp. 266-275.

13. M. Taddia, C. Lucano and A. Juris, "Analytical characterization of supramolecular species determination of ruthenium and osmium in dendrimers by electrothermal atomic absorption spectrometry," *Analytica Chimica Acta*, vol. 375 (3), Nov. 1998, pp. 285–292.

14. W. Heinig and K. Mauersberger, "Ruthenium determination in synthetic purex waste solutions by AAS," *Talanta*, vol. 32(2), Feb. 1985, pp. 145-147.

15. A. A. Ensafi, M. Arab Chamjangali and H. R. Mansour, "Catalytic spectrophotometric determination of ruthenium by flow injection method," *Talanta*, vol. 55 (4), 2001, pp. 715-720.

16. E. Giuseppe De Benedetto, R. Maria Guascito, R. Ciriello and R. I. Tommaso Cataldi, "Analysis by X-ray photoelectron spectroscopy of ruthenium stabilised polynuclear hexacyanometallate film electrodes," *Analytica Chimica Acta*, vol. 410 (1-2), Apr. 2000, pp. 143-152.

17. H. Yoshida, K. Hidaka, J. Ishida, K. Yoshikuni, H. Nohta and M. Yamaguchi, "Highly selective and sensitive determination of tricyclic antidepressants in human plasma using high-performance liquid

chromatography with post-column tris(2,2′-bipyridyl) ruthenium(III) chemiluminescence detection, ” *Analytica Chimica Acta*, vol. 413 (1-2), May 2000, pp. 137-145.

18. B. Nalini and S. Sriman Narayanan, "Amperometric determination of ascorbic acid based on electrocatalytic oxidation using a ruthenium(III) diphenyldithiocarbamate-modified carbon paste electrode," *Anal. Chim. Acta*, vol. 405 (1-2), Jan 2000, pp. 93-97.

19. P-R. Tomas, M-L. Carmen, T. Virginia and M. Jesus, "Flow injection chemiluminescent determination of N-nitrosodimethylamine using photogenerated tris(2,2′-bipyridyl) ruthenium (III), *Analytica Chimica Acta*, vol. 541 (1-2), June 2005, pp. 67-72.

20. R. S. Kuchekar, S. Y. Shelar, R. H. Aher, H. S. Han, "Development of a reliable analytical method for extraction spectrophotometric determination of ruthenium(III) from catalyst and fissium alloy using o-methylphenyl thiourea as a chromogenic chelating ligand," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,* vol. 106, 2013, pp. 1-11.

21. D. Gopala Krishna, N. Devanna, K. B. Chandrasekhar, "Direct And Derivative Spectrophotometric Determination Of Ruthenium (III) In Presence Of Micellar Medium In Water And In Alloy Samples Using 4-Hydroxy 3,5dimethoxy Benzaldehyde-4-hydroxy Benzoylhydra-zone (Hdmbhbh)," *International Journal of Inorganic and Bioinorganic Chemistry*, vol.1(1), 2011, pp. 8-12.

22. B. Mathew,V. Mini, A.Vinnifred, "Microquantitative determination of ruthenium(III) spectrophoto metrically using a schiff's base derived from a triazine," *Der Chemica Sinica*, vol. 1(3), 2010, pp. 7-14.

23. N. Lokhande, G. B. Kolekar, M. A. Anuse and M. B. Chavan, "Extraction of Ruthenium(IV) from Hydrochloric Acid Medium with N-Octylaniline and Its Determination Spectrophotometrically with Pyrimidine-2-thiol," *Separation Science and Technology*, vol. 35 (1), 2000, pp. 153-157.

24. M. S. El-Shahawi, A. Z. Abu Zuhri, and S.M. Al-Daheri, "Spectrophotometric determination of ruthenium after extraction of perruth-enate with benzyltributylammonium chloride," *Fresenius' J. Anal. Chem.*, vol. 350 (12), 1994, pp. 674-677.

25. S. A. Alaa, "Simple and Selective Spectrophotometric Determination of ruthenium after Solid Phase Extraction with some Quinoxaline Dyes into Microcrystalline P-Dichlorobenzene," *Spectrochim. Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 58 (9), July 2002, pp. 1831-1837.

26. B. Rezaei and N. Majidi, "A Simple and High Sensitive Spectrophotometric Method for Ultra Trace Determination of Ruthenium With Its Catalytic Effect On The Oxidation Of Pyronin B By Periodate," *Spectrochim. Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 66 (4-5), April 2007, pp. 869–873.

27. M. A. Islam and W. I. Stephen, "Evaluation of some as-triazines and re-evaluation of PDT and ferrozine as reagents for spectrophotometric determination of ruthenium," *Talanta* , vol. 39 (11), Nov. 1992, pp. 1429–1435.

28. M. Keyvanfard and M. Karamian, "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," *Asian Journal of Chemistry*, vol. 21 (2), 2009, pp. 942-948.

29. A. Solovey-Vandersteen, "T. Vrublevska and H. Lang, UV-Visible and IR Spectroscopic Studies of Ruthenium(II)-Xylenol Orange Complex," *Acta Chimica Slovnica.*, vol. 51, 2004, pp. 95-106.

30. M. Balcerzak and E. Wyrzykowska, "Extraction Preconcentration of Platinum and Ruthenium using High Molecular Weight Amines Prior to Simultaneous Determination by Derivative Spectrophotometry," *Analusis*, vol. 27(10), 1999, pp. 829-834.

31. V. Druskovic, V.Vojkovic and T. Antonic, "Extraction of Ruthenium and Its Separation from Rhodium and Palladium with 4-Pyridone Derivatives," *Croatica Chemica Acta*, vol. 78, 2005, pp. 617-626.

32. B. Rezaei and M. Keyvanfard, "Spectrophotometric Reaction Rate Method for the Determinationof 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*, vol. 50 (6), 2005, pp. 311-316.

33. W. Hong-fu, Z. Su-lan, SU Zhi-xian, HE Li-ming and Y. Qin, "Determination of trace Ruthenium(III) by Catalytic Kinetic spectrophotometry with malachite green, *Chinese Journal of Analysis Laboratory*, vol. 8, 2009, pp. 90-93.

34. A. Praveen Kumar, P. Raveendra Reddy, and V. Krishna Reddy, "Direct and Derivative Spectrophoto metric Determination of Ruthenium(III)," *International Journal of ChemTech Research CODEN(USA)*, vol. 5 (4), April-June 2013, pp 1442-1447.

35. Z. Zhi-rong, W. Qun and Z. Shu-yuan, "Kinetic spectrophotometric determination of trace ruthenium(III) based on catalytic effect of ruthenium(III) on oxidation of acid chrome blue K by potassium bromate," M*etallurgical Analysis*, vol. 7, 2007, pp. 13-19.

36. M. Balcerzak, "Sample Digestion Methods for the Determination of Traces of Precious Metals by Spectrometric Techniques," *Analytical sciences*, vol.18, 2002, pp. 737-750.

37. G. H. Ayres and Y. Frederick, "Spectrophotometric Study of Ruthenium-Thiourea Complex,". *Analytical Chemistry*, vol. *22* (10), October 1950, pp. 1277-1280.

38. E. B. Sandell and O. Hiroshi, Photometric determination of traces of metals, John Wiley & Sons: New York, 1978.

39. L.G. Sillen, "Some graphical methods for determing equilibrium constant II on Curve-fitting method for two-variables data", *Acta Chemica Scandinavica*, vol. 10, 1956, pp.186-202.

40. P. Job, "Job plot", *Annali di Chimica Applicata*, vol. 9, 1928, pp. 113-203.

41. B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. Tatchell, Vogel's textbook of Practical organic chemistry, Pearson Education: London, 2005.

42. D.D. Perin, Chemical Analysis-Masking and Demasking, vol. 33, 4th. ed. John Wiley & Sons: New York, 1999.

*****