Extraction and Estimation of Ruthenium (III) From Hydrochloric Acid Medium by Cyanex 302

Chemistry

KEYWORDS : Extraction, Ruthenium (III), Cyanex 302, Binary separation, Carbon Tetrachloride

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ABSTRACT

The paper embodies extraction behavior of Ru (III) from hydrochloric media in presence of SnCl2 in a carbon tetrachloride solution of Cyanex 302.Various parameters such as acid concentration, reagent concentration; SnCl2 concentration, shaking time, effect of diluents and effect of foreign ions were studied. Quantitative extraction of Ru (III) in 1.0 M HCl and 0.6 ml of 1M SnCl2 stannous chloride was possible with 0.06 M Cyanex 302 after 75 seconds of shaking .The light golden yellow coloured Ru- Cyanex 302complex exhibits maximum absorption 300 nm where extraction of reagent was found to be negligible. The complex is stable more than 48 hrs. The probable composition of the species has been deduced from the extraction data. Beer-Lambert law is obeyed in the concentration range 5µg - 45µg with Sandell's sensitivity of 1.240 x 10-3 µg/mL/cm2 and molar absorptivity of 91,904 x 104 mole-1cm-1dm3. A study of effect of diverse ions on the extraction showed that several metals ions like Ca+2, Ti+4,Mg+2, K+, Na+, Ce+4, Al+3, Mn+2 do not interfere during the extraction and estimation of ruthenium. The data has been successfully employed for the separation of binary mixtures containing the non interfering metal ions. The optimized conditions of extraction has been successfully utilized to recover metal from real samples.

1. Introduction

Ruthenium, atomic number (44), is a noble metal belonging to platinum group of elements in the periodic table. Ruthenium is inert to most chemicals. It is the 74th most abundant metal in earth's crust[1] . The oxidation state of ruthenium ranges from 0 to +8 and +2, +3, +4 states are common .Ruthenium trichloride which extists in the form of solid[2] was used during present study. Ruthenium dioxide and lead and bismuth ruthenates are used in thick film chip resistors [3, 4, 5] . Ruthenium is a versatile catalyst.[6] Many ruthenium based oxides show very unusual properties such as a quantum critical point[7] behavior, exotic superconductivity[8] and high temperature ferromagnetism.[9] .

Literature reveals that many studies have been done on ruthenium using various extractants. Ruthenium has been quantitatively extracted as a ruthenium thiocynate using pyridine [10] , polyurethane foam[11] and carbon tetrachloride [12] as a solvent . It has been also extracted in presence of capriblue [13] , hexamethyl phosphoramide [14] and rhodamine 66 [15, 16]. Ruthenium is extractable from nitrate solution usually as nitrosyl ruthenium complex into diethyl ether [17] , dibutyl cellosolve [18], melted napthol [19], alcohols and ketones [20-22] and various mixed solvents [23] .Extraction of Ru (III) was also done using o-methylphenyl thiourea as extractant and chloroform as diluent. [24] .Separation of ruthenium using tropolone as extractant which gives absorbance at 415nm is also reported [25] . Extraction of Ru using 4, 7-diphenyl-1,10phenanthroline at pH 4-6 required heating at 90oC for 60min[26]. The solvent extraction and separation performances of Ru from 1.0-4.5 M HCl acid solutions were investigated using thiobenzahydride diluted in chloroform [27]. Thiosalicylamide was also used as extractant for extraction of Ru and maximum absorbance was obtained at 390nm. [28] Separation of Ru (III) was also carried out using P-50 Oxime in nitrate medium [29] Ashok Mhaske, Purushottam Dhadke [30] used cyanex 921 for separation of Ru (III) by tin chloride using toluene as diluent. The extraction of Ru (III) was done by using Cyanex 923 in chloride media using kerosene.[31] Cyanex-302 [bis (2, 4, 4 trimethylpentyl) monothiophosphonic acid] marketed by Cytec Inc. Canada has been used as an extractant for some metal ions [32-46]. However there has been no detailed study on the use of this reagent for the direct extractive photometric determination of ruthenium. Hence, an attempt has been made to establish a method for the determination of Ruthenium using Cyanex 302 as an extractant.

2. Materials and Methods:

2.1 Stock Solutions

All the chemicals (E. Merck) and diluents used in the present experimental studies were of Analytical Reagent grade. The extractant Cyanex 302was supplied by Cytec Inc. Canada was used.

Stock solutions of various cations, anions were prepared from their respective salts. (Table .3) by taking proper precautions.

Ru (III) stock solution(1000 ppm) was prepared by dissolving 0.205 gm of ruthenium trichloride in a 100 mL std. measuring flask with distilled water containing about 5 mL conc. HCl.

2.2 Standardization of Ruthenium by spectrophotometric determination:

The standardization of ruthenium was done spectrophotometrically by di-thio oxamide (Rubeanic acid) method[47] at 650 nm.

2.2.1. Ruthenium solution:

The required strength of ruthenium (III) solution was prepared by further dilution of stock solution with distilled water.

2.2.2. 0.2% di-thio oxamide: 0.2 g of di-thio oxamide was dissolved in 100 mL distilled water.

2.2.3. 50% conc. Hydrochloric acid: 50 mL of 11.3 M HCl diluted to 100 mL with 95% ethanol.

Procedure: The sample solution containing ruthenium was first evaporated to dryness and to it 10 mL of 50% (V/V) concentrated hydrochloric acid in 95% ethanol solution and 5 mL of 0.2% di-thio oxamide solution was added. The solution was heated on water bath at 850C for 30 minutes, cooled and diluted to 25 mL with 50% V/V 6.0 M HCl in 95% ethanol. The absorbance was measured at λ max 650 nm using reagent blank.

All absorbance measurements were carried out on '**Spectronic Genesis 8**'UV- Visible spectrophotometer using 10mm path length quartz cuvettes.

2.3 General Extraction Procedure:

To an aliquot of the aqueous solution containing Ru (III) was added 0.6 mL of 1 mol dm^{-3} $SnCl_2$ to which was added hydrochloric acid to make it 1.0 mol dm^{-3} in a total volume of 15mL. The solution was transferred into a 125mL separating funnel and shaken for 75 sec. with 15 mL of 0.06 mol dm^{-3} Cyanex 302 solution in Carbon Tetrachloride. After allowing the two phases to separate, the organic phase was collected in a 25mL standard measuring flask and diluted up to the mark with carbon tetrachloride. A small quantity of anhydrous sodium sulphate was added to all the 25mL flasks to absorb the moisture. The absorbance of the extract was measured at 300 nm against the reagent blank prepared analogously.

3. Results and Discussion:

3.1.1 Absorption Spectrum:

The absorption of Ruthenium- Cyanex complex was studied over a wavelength range of 200-400 nm. The light golden yellow coloured complex exhibited absorption maxima at 300nm (Fig 1). At this wavelength the absorption of the reagent was negligible. Therefore, the wavelength of 300nm was chosen for all further measurements (fig.1)

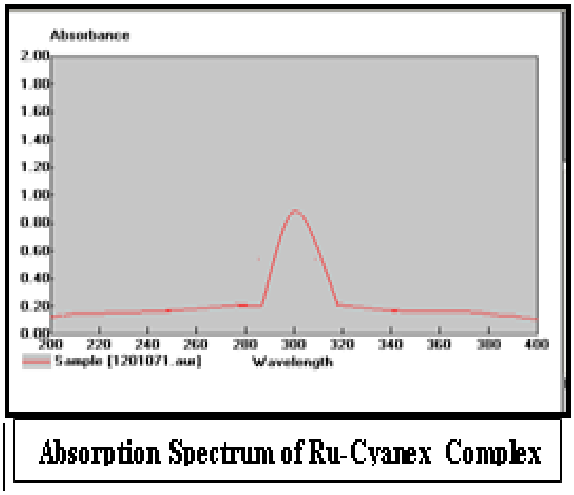

Fig.1. Absorption Spectra

3.1.2 Effect of reagent concentration:

The optimum concentration of Cyanex 302 for quantitative extraction of Ru (III) was ascertained by carrying out extractions with varying concentrations of Cyanex 302 from 0.01-0.10 mol dm^{-3} in carbon tetrachloride. The extraction was quantitative with 0.06 mol dm^{-3} Cyanex 302 (Fig 2). Hence 15mL of 0.06 mol dm^{-3} Cyanex 302 in carbon tetrachloride was used throughout the study.

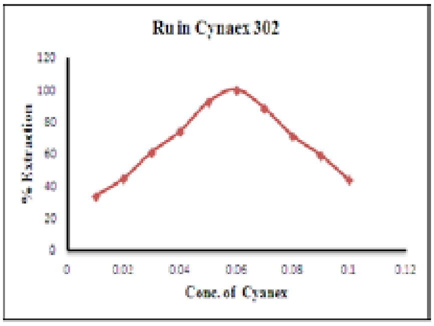

Fig.2. Cyanex Concentration

3.1.3 Effect of Hydrochloric acid concentration:

The effect of hydrochloric acid concentration on the absorbance of the extract was studied using the recommended procedure. By varying concentration of HCl between 0.5 to 4.0 $moldm^{-3}$. The absorbance of extract was found to be maximum for 1.0 mol dm^{-3}. Thus, 1.0 mol dm^{-3} HCl concentration was used for subsequent studies. (Fig.3)

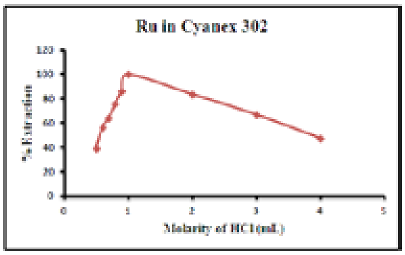

Fig.3. HCl Concentration

3.1.4 Effect of Stannous Chloride Concentration

Ruthenium was extracted in the presence of $SnCl_2$ which was used as a labializing agent. When tin is added to the solution, Ruthenium gets activated. This may be due to the reduction of Ru (III) to Ru (I) with $SnCl_2$ and thus making the complex very easily extractable into Cyanex 302. In the absence of $SnCl_2$, Ruthenium does not get extracted into Cyanex 302 using the recommended procedure. The effect of the molarity of $SnCl_2$ in the range of 0.006-0.066 mol dm^{-3} on the absorbance of the extract was studied using the recommended procedure at 300 nm with a sample containing 30µg of Ruthenium (III) and 1.0 mol dm^{-3} HCl. The extraction was done using 15mL of 0.06 mol dm^{-3} Cyanex 302 in Carbon Tetrachloride. The absorbance was maximum for 0.040 mol dm^{-3} of $SnCl_2$. Hence, all the extractions were carried out using 0.040 mol dm^{-3} of $SnCl_2$. (Fig.4)

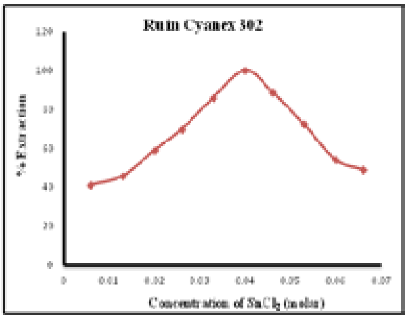

Fig.4. SnCl2 Concentration

3.1.5 Effect of various Diluents:

To find out the effect of diluents on extraction, the reagent 0.06 mol dm^{-3} of Cyanex 302 was prepared in different diluents and was used for extraction from aqueous phase containing 30 µg of Ruthenium in 1 mol dm^{-3} HCl, 0.040 mol dm^{-3} $SnCl_2$. For the diluents study, the absorbance and % extraction of Ruthenium decreased in the order: Carbon Tetrachloride (99.99%), Toluene (90.47%), Chloroform (97.32%), Benzene (85.21%), Xylene (76.20%), Cyclohexane (80.54%). (Fig.5). Carbon tetrachloride gave quantitative extraction and hence for all further studies carbon tetrachloride was chosen as diluent.

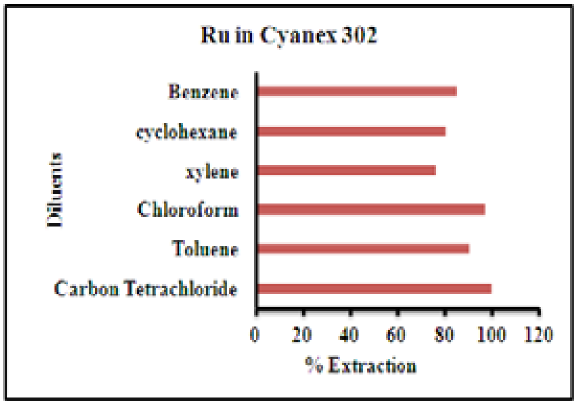

Fig.5. Effect of Diluents

3.1.6 Effect of Shaking period:

The absorbance of the extract ,by shaking the aqueous phase containing 30µg ruthenium (III) + 0.6 mL of 1M $SnCl_2$ diluted to 15mL with 1.0 M Hydrochloric acid, with an organic phase containing 0.06 M Cyanex 302 in carbon tetrachloride was measured for varying time periods from 15 sec to 120 sec. It was observed that the extraction was quantitative after 75 sec. of equilibration. Hence, optimum period chosen for shaking was 75 sec. (Fig.6)

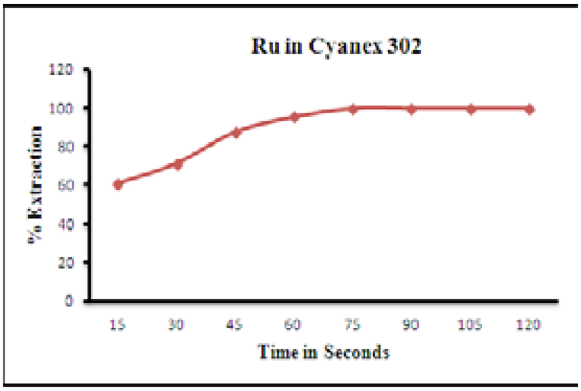

Fig. 6 Shaking Period

4. Optimum Conditions for Extraction of Ruthenium (Table.1)

Parameter	Optimum Condition
Ruthenium(III)	30 µg/mL
Hydrochloric acid concentration	1.0 mol dm^{-3}
$SnCl_2$ concentration	0.040 mol dm^{-3}
Cyanex 302concentration	0.06 mol dm^{-3}
Shaking Time	75 seconds
Diluent	Carbon tetrachloride

5.1 Validity of Beer-Lambert law:

A calibration curve for absorbance measurements of ruthenium complex at varying concentrations of ruthenium was plotted under optimum experimental conditions (0.040 mol dm^{-3} $SnCl_2$, 1 mol dm^{-3} HCl, and 0.06 mol dm^{-3} Cyanex in Carbon Tetrachloride). Beer's law was found to be obeyed in the range of 5µg to 45µg of ruthenium at 300nm. (Fig.7)

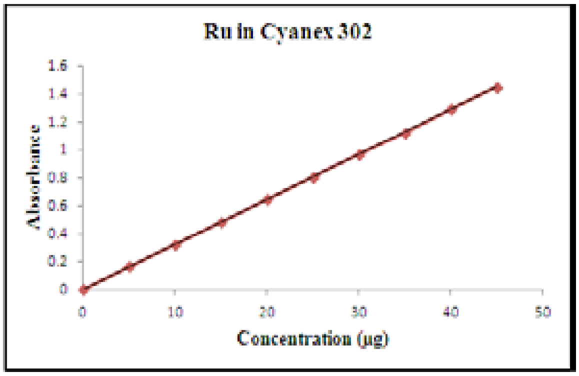

Fig.7. Beer's law plot

6. Spectrophotometric data for the determination of ruthenium after extraction with Cyanex 302(Table.2)

The molar absorptivity of complex was found to be 91,904 x 10^4 $mole^{-1}.cm^{-1}.dm^3$. The Sandell's sensitivity was found to be 1.240 x10^{-3} µg cm^{-2}. The spectral characteristics are given in Table.2.

Molar absorptivity	91,904 x $10^4 mole^{-1}.cm^{-1}.dm^3$
Sandell's sensitivity	1.240 x10^{-3} µg cm^{-2}
Mean absorbance of 6 determinations (30µg ruthenium)	0.967
Beer's law range	5-45µg/mL
Standard deviation	3.7010 x 10^{-3}
Coefficient of variation	0.38 %

6.1 Nature of extracted species

An attempt was made to find out the probable composition of the extracted species from a plot of log D vs. log C (Cyanex 302) at fixed acid and $SnCl_2$ concentration. The slope of this plot was found to be 0.97 ≈ 1 indicating the complex to be 1:1 with respect to Cyanex 302, thus confirming the oxidation state of Ruthenium as +1 in the extracted species. (Fig. 8)

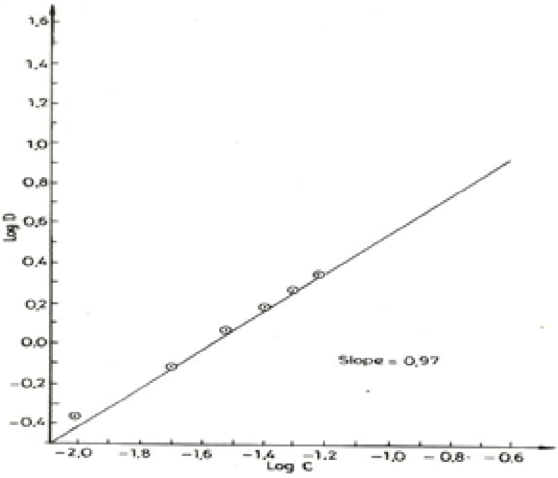

Fig.8. Log D vs Log C

7. Effect of diverse ions & binary separation:

7.1 Effect of diverse ions

The extraction of Ru (III) was carried out according t the recommended procedure to examine the effect of interference from various foreign ions. The tolerance limit was set at an amount to cause an error of + 2% in the recovery of the metal ion. It was observed that, a large number of cations and anions were tolerated (Table .3)

Table.3: Effect of foreign ions

Tolerance Ratio Ru (III): Diverse ions	Diverse Ions	
	Cation	Anions
1:10	Mo^{+6}, Zr^{+4}, Co^{+2}, Ni^{+2} ,Zn^{+2} ,Th^{+4}	---------
1:15	Co^{+2} ,La^{+3}, Sr^{+2}, Ba^{+2} ,Sb^{+3}	
1:20	Be^{+2}, K^{+}	SCN^{-} ,Oxalate
1:25	Al^{+3} ,Na^{+} , Fe^{+2} ,Fe^{+3}	F^{-} ,I ,CO_2^{-3} ,Br
1:30	Ca^{+2}, Ti^{+4}, Te^{+2} ,Mg^{+2}, Mn^{+2} ,Ce^{+4}	SO_3^{2-} ,SO_4^{2-} ,NO_3^{-}
Strongly Interferes	Cu^{+2}, Pb^{+2}, Cd^{+2}, Pd^{+2}, Rh^{+3}, Ru^{+3}, Hg^{+2}, Bi^{+3} ,Cd^{+2}	-----

7.2 Binary Separations of Ruthenium (III)

Ions such as Ca^{+2}, Ti^{+4},Mg^{+2}, K^{+}, Na^{+}, Ce^{+4}, Al^{+3}, Mn^{+2} do not get extracted into Cyanex 302 under optimum extraction conditions for Ruthenium(III) up to a certain concentration. Hence, it was possible to separate them from their binary mixtures. The unextracted Ti^{+4}, Mg^{+2}, Mn^{+2} , Ce^{+4}, Al^{+3} was determined spectrophotometrically by known methods (Table. 4)

Table.4 Binary Separation of Ruthenium

Composition µg	Recovery of Ru (III)* %	Coefficient of Variation	Recovery of the added ion* %	Coefficient of Variation	Estimation procedure for the added ion and its reference
Ru (III) :Ti(IV) 100 : 100	99.99	0.39%	95.61	0.48%	Hydrogen peroxide Method [48]
Ru (III):Mg (II) 100 : 100	99.99	0.67 %	97.25	0.72%	Murexide Method [49]
Ru(III): Mn(II) 100 : 100	99.99	0.76 %	98.71	0.65%	Potassium Periodate Method[50]
Ru(III) : Al(III) 100 : 100	99.99	44%	96.76	0.40%	Spectrophotometric Determination Eriochrome CyanineR method[51]

* Mean of five determinations

8. Analysis of Ruthenium (III) in real samples:

8.1.Recovery of Ruthenium from catalysts:

8.1.1Dichloro [(S)-(-) 2, 2'-bis (diphenylphosphino)-1, 1'-binaphthyl] ruthenium (III) is a catalyst used in the reduction reaction of nitro to amine and aromatic cyclic to saturated cyclic compound. It contains 4.5% of ruthenium. To prepare stock solution , 1 gm of catalyst was weighed and diluted to 20ml with diluents (2 ml conc. HCl +18 ml Water). It was shaken vigorously and filtered through Whatman filter paper No. 41 to get clear transparent solution. From this working stock, 0.1 ml of solution was taken for extraction. Ruthenium in the extracted solution was determined by the proposed method and the results obtained were found to be in close agreement with certified values. (Table 5)

Analysis of Ruthenium in real samples (Table. 5)

Samples	Amount of Ru (III) certified	Amount of Ru (III) Found with ICP spectroscopic method	Amount of Ru (III) Found with Proposed method	% Found with Standard method (with ICP spectroscopic method)	% Found with Proposed method	R.S.D. (%)
Dichloro [(S)-(-) 2, 2'-bis (diphenylphosphino)-1,1'-binaphthyl] ruthenium (III)	4.5%	4.44%	4.42 %	99.99%	99.97%	0.64 %

*Average of six determinations

8.1.2. 0.1 g Ru – CaCO3 catalyst (S.D. fine chemicals Ltd, India) was taken in a beaker with aquaregia and evaporated to dryness. The residue was leached with dilute hydrochloric acid and diluted to 100mL with distilled water. 2 mL of the sample Solution was taken and Ru (III) was extracted and estimated using the proposed method. The results obtained were in close agreement with theoretical values. (Table 6)

Analysis of Ruthenium in real samples (Table 6)

Samples	Amount of Ru (III) certified	Amount of Ru (III) Found with ICP spectroscopic method	Amount of Ru (III) Found with Proposed method	% Found with Standard method (with ICP spectroscopic method)	% Found with Proposed method	R.S.D. (%)
Ru- $CaCO_3$	5%	4.99 %	4.96 %	99.99%	99.95%	0.76 %

*Average of six determinations

9. Conclusion:

The proposed method for the extraction of ruthenium using cyanex 302 is superior to existing methods due to the following reasons:

i) It is a direct extractive spectrophotometric method.
ii) It is sensitive indicated by low value of Sandell's sensitivity and high value of molar absorptivity .
iii) Many binary separations of ruthenium was possible .
iv) The method finds application in the determination of ruthenium in real samples.

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