

## Liquid-liquid extraction studies of ruthenium(III) from malonate medium using *n*-octylaniline as an ion-pairing reagent: study of catalyst and alloys

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Herein we have developed a solvent extraction system for ruthenium(III) by using 0.1 M *n*-octylaniline in 0.05 M malonate medium at pH 3.5. Various operational parameters like pH, reagent concentration, weak organic acid, equilibrium time, and loading capacity of extractant were optimized for the quantitative recovery of ruthenium(III). Stoichiometry of the extracted species was resolved by the slope ratio analysis method. The extraction takes place by formation of an ion-pair complex between the  $[\text{CH}_3(\text{CH}_2)_7\text{C}_6\text{H}_4\text{NH}_3]^+_{(\text{org})}$  species and the  $[\text{Ru}(\text{C}_3\text{H}_2\text{O}_4)_2]^-_{(\text{aq})}$  species. The association of these two species yielded the uncharged neutral extractable species  $[\text{CH}_3(\text{CH}_2)_7\text{C}_6\text{H}_4\text{NH}_3^+\text{Ru}(\text{C}_3\text{H}_2\text{O}_4)_2]_{(\text{org})}$ . The stoichiometry of the extracted species was found to be 1: 2: 1 (metal: acid: extractant). The soundness of the proposed method was checked by extracting ruthenium(III) from binary and ternary mixtures and various catalysts were also investigated.

**Keywords:** Liquid-liquid extraction, *n*-Octylaniline, Ruthenium(III), Sodium malonate, Catalyst.

### INTRODUCTION

Ruthenium is a very rare element that is found about  $10^{-8}$  % on earth's crust. Chondrite and especially iron meteorites contain high amounts of ruthenium ( $1-6 \times 10^{-4}$  %). Ruthenium also occurs in alliance with other platinum group metals [1]. Ruthenium is a rare polyvalent hard white transition metal. Small amount of ruthenium can impart hardness to platinum and palladium. The resistivity to corrosion of titanium was noticeably increased by a small amount of ruthenium [2]. Ruthenium is a versatile catalyst. It is used to remove  $\text{H}_2\text{S}$  from oil in oil refineries [3]. The use of ruthenium is compatible with semiconductor processing techniques; therefore, it is used as a material for microelectronics [4]. Ruthenium is very hard and corrosion resistant, therefore it is used for coating of electrodes by the chloralkali process, the outcome of the process gives chlorine and caustic soda which are applicable for a wide range of industrial and domestic applications. The application of ruthenium in alloys of aircraft turbine blades will reduce the  $\text{CO}_2$  impact of air travel on the environment in the future. If present prototypes are doing well, its high temperature stability and high melting point will permit elevated temperatures and thus more efficient burning of aircraft fuel [5]. Recently, platinum group metals (PGMs), particularly ruthenium and its chlorocomplexes, have been largely used for the catalytic oxidation of organic compounds. Organometallic ruthenium carbene and allenylidene complexes are efficient catalysts for olefin

metathesis [6]. Generally, ruthenium complexes have better resistance to hydrolysis and have more choosy action on tumors. Ruthenium and its alloys have a well-known application in jewelry [1]. The increasing applications of ruthenium in various fields have made it compulsory to develop a simple, inexpensive and sensitive method for its separation and determination.

In current days a variety of reagents have been considered for liquid-liquid extraction of ruthenium(III). 2-Mercaptobenzimidazole is used as extractant for ruthenium(III) in *n*-butanol [7]; 3-hydroxy-2-methyl-1-phenyl-4-pyridone [8], Cyanex 921 [9], Cyanex 923, Cyanex 471, Cyanex 272, LIX 54, LIX860N-I [10] are reported for solvent extraction. Bis (2-ethylhexyl) phosphoric acid [11, 12] and tributylphosphate [13] extract the nitrosyl-ruthenium complex in dodecane. Solvent extractions using high molecular weight amines (HMWA) turn more and more popular in modern years. The HMWA are well-known as liquid anion exchangers, which combine several advantages of liquid-liquid extraction and ion exchange. High molecular weight amines (HMWA) reported for ruthenium(III) extraction are: Alamine 336 [14], Alamine 300, Aliquat 336 [10], *N*-octylamine [15]. Extraction of ruthenium from HCl media has been performed with *N,N'*-dimethyl-*N,N'*-dicyclo-hexylmalonamide (DMDCHMA) dissolved in 1,2-dichloroethane [16]. Alkylaniline hydrochloride [17] extracts ruthenium from chloride or sulfate medium into toluene. The oxygenated and hydrocarbon solvents like methyl isobutyl ketone

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**Table 1.** Evaluation of earlier reported extraction methods with the present method

Sr. No	Extractant	Medium	Diluent	Strippant	Determination method	Equilibration time, min	Ref.
1	0.1M Cyanex 921	4 M HCl	Toluene	0.5M Na <sub>2</sub> SO <sub>4</sub>	Spectrophotometry	15	9
2	Alamine 336 (15% A336 + 5% decanol)	1 M HCl	Kerosene	Na <sub>2</sub> CO <sub>3</sub>	ICP-AES	20	14
3	<i>n</i> -Octylaniline 5%	1 M HCl	Xylene	2% NaCl	Spectrophotometry	1	15
4	N, N'-Dimethyl-N, N'-dicyclohexylmalonamide 0.3 M	7 M HCl	1,2 DCE	Water	Spectrophotometry	30	16
5	Aliquat 336 (15%) + LIX 54 (1%)	4 M HCl	Kerosene/dodecane	0.35M NaCl/2M NH <sub>3</sub> +3M NH <sub>4</sub> Cl	ICP-AES	20	44
6	N- <i>n</i> -octylaniline 4%	0.05 M HCl	Chloroform	1 M HCl	Spectrophotometry	--	45
7	25% Aliquat 336/ 25% Alamine 336	6 M HCl	Xylene	Na <sub>2</sub> CO <sub>3</sub>	Spectrophotometry	15	46
8	<i>n</i> -Octylaniline	Sodium malonate pH = 3.5	Xylene	2% NaCl: 1M HCl (4:1)	Spectrophotometry	5	PM

PM = Present method

(MIBK) [18], paraffin oil [19], mixture of isoamyl alcohol and isobutyl methyl ketone [20] have also been used as extractants for ruthenium. Ruthenium (III) from purex process is separated using paraffin oil in nitric acid medium but it is necessary to oxidize Ru to RuO<sub>4</sub> by addition of ceric nitrate before extraction [19]. Mixture of isoamyl alcohol and MIBK in 1:1 ratio extracts ruthenium in the presence of a large excess of platinum but iridium interferes with the extraction procedure [20]. Attempts have also been made to selectively separate ruthenium (III) from associated elements with P-50 oxime [21], di(2-ethylhexyl) sulfoxide [DHSO] [22]. The various investigated systems are presented in Table 1 to review the literature in terms of various extractants used and special characteristics regarding those systems. Previously we have reported liquid-liquid extraction techniques for the separation of various metals [23-31]. Development of a new extraction system for extraction of ruthenium(III) especially in weak organic acid solutions is a topic of great interest. The target of this effort is to investigate the extraction properties of *n*-octylaniline with respect to noble metals such as ruthenium(III) from weak organic acid media. In the present investigation, the *n*-octylaniline-malonate system was considered for the extraction of ruthenium(III) as a function of diverse physicochemical parameters. The proposed technique is applied for the rapid and selective separation of ruthenium(III) from associated metal ions in their binary mixtures. In addition to that, this technique was also tested for isolation and determination of ruthenium(III) from various real samples like catalysts and a synthetic mixture.

## EXPERIMENTAL

### Apparatus

Absorbance measurement was carried out with a digital UV-visible spectrophotometer model Optizen- $\alpha$  (Mecasys Co., Ltd Korea) with a 10 mm quartz cell. Elico digital pH meter model SL-127 with combined glass electrode was utilized for the pH measurement. Digital balance Mettler Toledo (Model ML 204/AOI, Switzerland) was used for the weighing purpose.

### Reagents

#### Standard ruthenium(III) solution

A solution of ruthenium(III) was prepared by dissolving 1.0 g of ruthenium chloride hydrate (Johnson Matthey, UK) in 1.0 M HCl, diluting with water to 250 mL in a standard volumetric flask and standardizing [32]. The required working solution (200  $\mu$ g/ mL) of ruthenium(III) was prepared by diluting the above solution in a standard volumetric flask with water.

#### 4'-Chloro-PTPT

1-(4'-Chlorophenyl)-4,4,6-trimethyl-(1*H*,4*H*)-pyrimidine-2-thiol (4'-chloro-PTPT) was synthesized by the reported method of Mathes [33-36] and was used for the spectrophotometric determination of ruthenium(III). The solutions of diverse ions were prepared in water or dilute HCl by dissolving their AR grade salts. Doubly distilled organic solvents were used for the extraction study and doubly distilled water was used throughout.

### *n*-Octylaniline

*n*-Octylaniline was synthesized by the reported method of Pohlandt's [37] and its working (0.1 M) solution was prepared by dissolving a weighed quantity of *n*-octylaniline with xylene in a 100 mL standard volumetric flask.

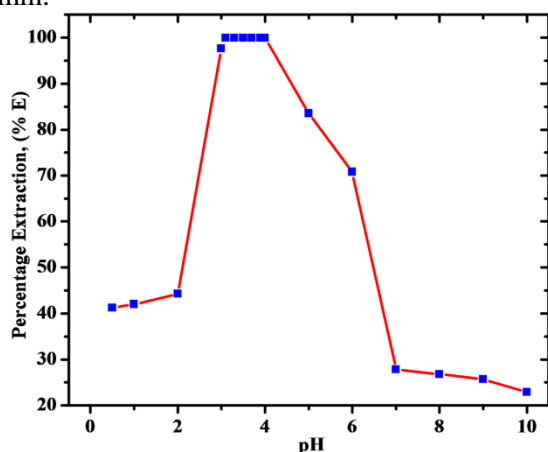
#### General procedure for extraction and determination of ruthenium(III)

To a solution containing 200 µg of ruthenium(III) in a 25-mL standard volumetric flask sodium malonate was added to obtain 0.05 M solution. The pH of the aqueous phase was adjusted to 3.5 with dilute HCl and NaOH solutions. The aqueous phase was shaken with 10 mL of 0.1 M *n*-octylaniline in xylene for 5 min. The phases were allowed to separate, the organic phase was used to back extract ruthenium(III) with a 4:1 combination of 2 % NaCl and 1.0 M HCl. The back extracted aqueous phase was evaporated to moist dryness, dissolved in a minimum amount of *aqua regia* and evaporated with two 2 mL portions of concentrated HCl to remove oxides of nitrogen. The resulting solution of ruthenium(III) was diluted with 0.1 M HCl and was determined spectrophotometrically by the 4'-chloro-PTPT method [38]. All experiments were repeated on an average five times.

## RESULTS AND DISCUSSION

### Influence of pH on the extraction of ruthenium(III)

The effect of pH on the quantitative extraction of ruthenium(III) was investigated in the pH range from 0.5 to 10. The extraction was carried out with 0.1 M *n*-octylaniline in xylene. The phase ratio (aq: org) was kept 2.5:1 and both phases were equilibrated for 5 min.

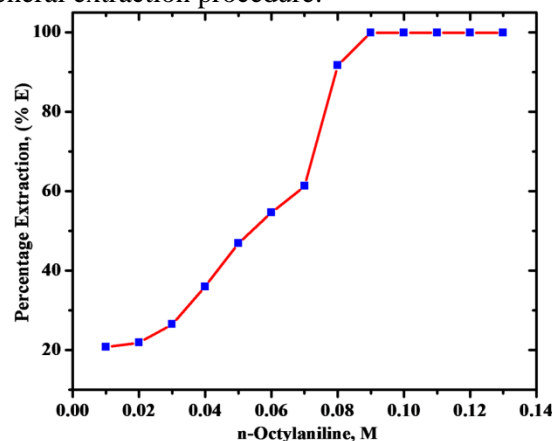


**Fig. 1.** Influence of pH on the extraction of ruthenium(III). Conditions: Ru(III) = 200 µg/ mL, sodium malonate = 0.05 M, extractant = *n*-octylaniline (0.1 M) in xylene, shaking time = 5 min, strippant = 2 % NaCl + 1 M HCl (4: 1)

Fig. 1 shows that quantitative extraction of ruthenium(III) takes place in the pH range from 3.1 to 4.0. As pH increases above 4.0, the extraction of ruthenium(III) decreases due to the lack of formation of ion-pair complex. Therefore, further extractions were carried out at pH 3.5.

### Influence of reagent concentration

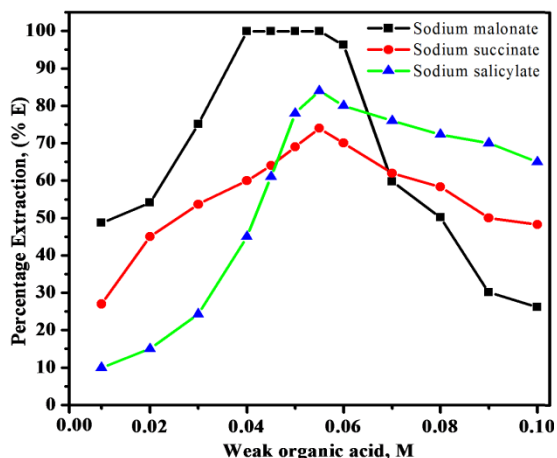
To find out the optimum concentration of reagent required for the quantitative extraction of ruthenium(III), *n*-octylaniline in the range of 0.01 - 0.15 M was investigated. Other physicochemical parameters like pH, period of equilibration and type of diluent were kept constant and extraction was carried out. As reagent concentration increased, there was an increase in ruthenium(III) extraction. The quantitative extraction of ruthenium(III) was observed in the range from 0.09 M to 0.13 M *n*-octylaniline in xylene (Fig. 2). Therefore, 10 mL of 0.1 M *n*-octylaniline in xylene was adopted for the general extraction procedure.



**Fig. 2.** Influence of *n*-octylaniline concentration. Conditions: Ru(III) = 200 µg/ mL, pH = 3.5, sodium malonate = 0.05 M, shaking time = 5 min, strippant = 2 % NaCl + 1 M HCl (4: 1)

### Effect of weak organic acid concentration

The extraction of ruthenium(III) was carried out in the presence of varying concentrations of sodium malonate, sodium succinate and sodium salicylate as weak acid media (Fig. 3) at pH 3.5 with 0.1 M *n*-octylaniline in xylene. It was observed that the extraction of ruthenium(III) starts at 0.01 M and becomes quantitative in the range of 0.04 M - 0.055 M for sodium malonate, beyond that the extraction decreased. Other weak organic acids such as salicylate and succinate showed incomplete extraction of ruthenium(III). Thus, for further experimental work 0.05 M malonate was adopted.



**Fig. 3.** Influence of weak organic acid concentration. Conditions: Ru(III) = 200 µg/ mL, pH = 3.5, extractant = *n*-octylaniline (0.1 M) in xylene, shaking time = 5 min, strippant = 2 % NaCl + 1 M HCl (4: 1)

*Effect of diluents*

In this study, the extraction of ruthenium(III) was carried out by applying various aromatic and aliphatic organic diluents. It was found that xylene, toluene and benzene showed quantitative extraction of ruthenium(III); there was incomplete extraction in methyl *isobutyl* ketone (93.04 %), *n*-butyl alcohol (42.2 %) and no extraction in chloroform, amyl alcohol, amyl acetate, 1, 2-dichloroethane and carbon tetrachloride (Table 2). Therefore, xylene was used as solvent throughout the experiment.

**Table 2.** Extraction of ruthenium(III) with various diluents

Solvent	Dielectric constant, (ε)	Percent extraction, (% E)	Distribution ratio, (D)
Xylene*	2.30	99.9	2497.5
Toluene	2.38	99.9	2497.5
Benzene	2.27	99.9	2497.5
Methyl <i>isobutyl</i> ketone (MIBK)	13.10	93.1	33.73
<i>n</i> -Butyl alcohol	17.80	42.2	1.82
Chloroform	4.80	No extraction	-
Amyl alcohol	13.90	No extraction	-
Amyl acetate	4.80	No extraction	-
1,2- Dichloro ethane	10.50	No extraction	-
Carbon tetrachloride	2.24	No extraction	-

Conditions: Ruthenium(III) = 200 µg/ mL, pH = 3.5, aq: org ratio = 2.5: 1, sodium malonate = 0.05 M, strippant = 2 % NaCl + 1 M HCl (4:1).

\* Recommended for the general extraction procedure,

*Influence of stripping reagents*

Ruthenium(III) laden organic phase was back extracted with various stripping agents (Table 3). Ruthenium(III) was quantitatively stripped with a mixture of 2 % NaCl and 10 mL 1.0 M HCl (3 ×

**Table 3.** Effect of stripping agents on ruthenium(III) recovery

Strippant	Concentration	% Recovery	Distribution ratio, (D)
HCl	Concentrated (2 × 10 mL)	99.9	2497.5
HBr	Concentrated (2 × 10 mL)	99.9	2497.5
2% NaCl+ 1 M HCl*	40 mL + 10 mL	99.9	2497.5
Ammonia	7 M (3 × 10 mL)	34.5	1.31
Ammonia + NH <sub>4</sub> Cl	2 M + 3 M (2 × 10 mL)	43.0	2.74
NaOH	1 M (2 × 10 mL)	60.8	3.87
KOH	1 M (2 × 10 mL)	55.8	3.15
H <sub>2</sub> O	2 × 10 mL	-	-
NH <sub>4</sub> Cl	2 % (3 × 10 mL)	26.3	0.89

**Conditions:** Ruthenium(III) = 200 µg/ml, pH = 3.5, aq: org ratio = 2.5: 1, extractant = 0.1 M *n*-octylaniline in xylene, sodium malonate = 0.05 M.

\* Recommended for the general extraction procedure,

10 mL). However, the back extraction of ruthenium(III) from the extract was incomplete with other reagents like acetate buffer, sodium hydroxide, ammonia and potassium hydroxide. In the recommended procedure, a mixture of 2 % NaCl and 10 mL 1.0 M HCl was applied for the quantitative recovery of ruthenium(III) from the loaded organic phase.

*Influence of equilibration time*

The equilibration time required for the complete extraction of ruthenium(III) was studied by equilibrating the aqueous and the organic phase from 1 to 18 min. The extraction of ruthenium(III) increased with time, and became quantitative over a period of 3 min equilibration of the solutions, but with prolonged equilibration (over 12 min, Fig. 4) the percent extraction of ruthenium(III) decreased due to the dissociation of the ion-pair complex. Thus, 5 min of equilibration time was kept throughout the study of ruthenium(III) extraction.

*Metal loading capacity of n-octylaniline*

Varying concentrations of ruthenium(III) (50 – 2000 µg) were extracted with 0.1 M *n*-octylaniline in xylene (10 mL) from 0.05 M sodium malonate medium at pH 3.5. It was observed that 10 mL of 0.1 M *n*-octylaniline can quantitatively extract 500 µg of ruthenium(III) from the aqueous phase. Beyond the amount of 500 µg the extraction decreased. Therefore, 200 µg of ruthenium(III) was chosen for the extraction study.

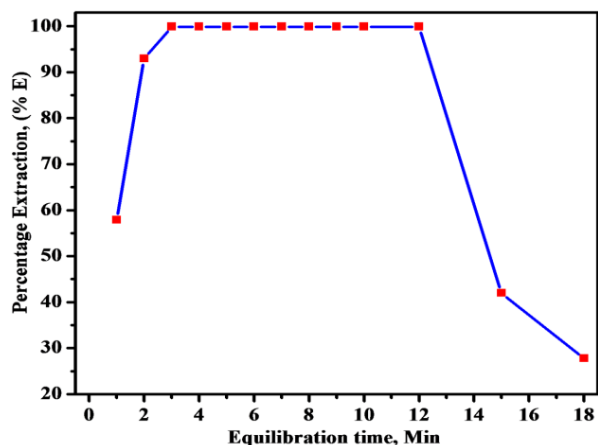


Fig. 4. Function of equilibration period

Conditions: Ru(III) = 200 µg/ mL, sodium malonate = 0.05 M, pH = 3.5, extractant = *n*-octylaniline (0.1 M) in xylene, strippant = 2 % NaCl + 1 M HCl (4:1)

#### Effect of aqueous to organic volume ratio

The influence of various ratios of aqueous to organic phase was investigated. The various phase ratios were studied to optimize the ratio for quantitative extraction of ruthenium(III). The results show a quantitative aqueous/organic (A/O) phase ratio between 1:1 and 4:1. Above the 4:1 ratio there was a decrease in extraction due to the worse availability of reagent. Therefore, in the recommended extraction procedure, the phase ratio was maintained at 2.5:1.

#### Stoichiometry of extracted species

The nature of the extracted complex species was determined by using log D - log C plots. The graph of log D<sub>[Ru(III)]</sub> vs log C<sub>[*n*-octylaniline]</sub> at a fixed sodium malonate concentration (0.05 M) was found to be linear having slopes of 1.01 and 0.99 at pH 5.0 and 6.0, respectively (Fig. 5).

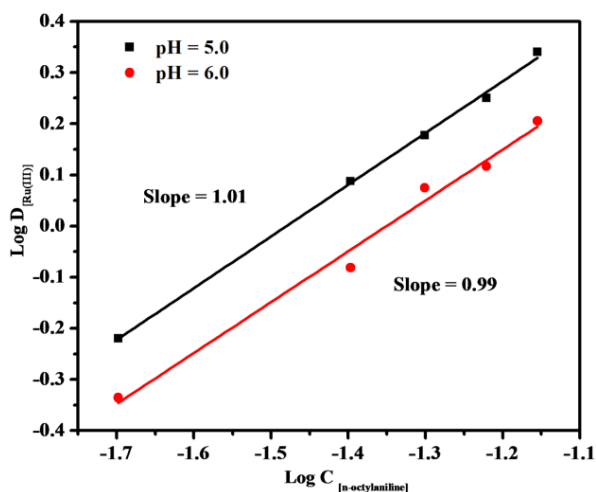


Fig. 5. Log-log plot of log D<sub>[Ru(III)]</sub> versus log C<sub>[*n*-octylaniline]</sub> at a fixed malonate concentration.

Also the graph of log D<sub>[Ru(III)]</sub> vs log C<sub>[malonate]</sub> at a fixed *n*-octylaniline concentration (0.1 M) was

linear and the slope values were 1.98 and 1.83 at pH 5.0 and 6.0, respectively (Fig. 6).

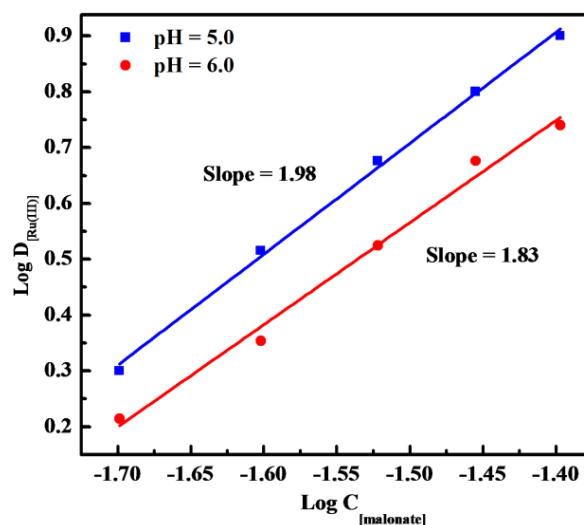
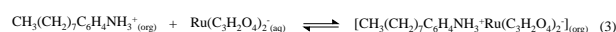
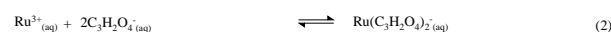
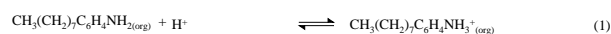


Fig. 6. Log-log plot of log D<sub>[Ru(III)]</sub> versus log C<sub>[malonate]</sub> at a fixed *n*-octylaniline concentration.

The probable composition of the extracted species was calculated to be 1: 2: 1 (metal: acid: extractant). The possible mechanism of extraction appears to be as follows: protonated *n*-octylaniline forms the cationic species [CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>]<sup>+</sup><sub>(org)</sub> while malonate (bidentate ligand) combines with ruthenium(III) to form the anionic species [Ru(C<sub>3</sub>H<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]<sup>-</sup><sub>(aq)</sub> and both of them associate to form an ion-pair of the type [CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>3</sub><sup>+</sup>Ru(C<sub>3</sub>H<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]<sub>(org)</sub> which, being neutral, constitutes an extractable species.

The possible extraction mechanism of the ion-pair complex is as follows:



## APPLICATIONS

### Effect of diverse ions

The influence of a large number of cations and anions on the extraction of 200 µg/mL of ruthenium(III) with *n*-octylaniline was investigated by the recommended procedure. The tolerance limit of individual diverse ions was set so that the error in percent recovery was not more than ± 2 %. The proposed method shows a high tolerance limit over various cations and anions. Some interfering cations are masked to increase the tolerance limit. Rhodium(III) and Pd(II) are masked with 25 mg of tartrate and Ir(III) with 25 mg of oxalate. Gold(III) is masked with 10 mg of bromide (Table 4). Ascorbate, thiourea, citrate and thiocyanate interfere with the extraction procedure.



**Table 4.** Effect of foreign ions on the extraction of ruthenium(III).

Tolerance limit, mg	Foreign ion added
50	Tartrate, oxalate, fluoride, acetate
25	Bromide, EDTA, Mg(II)
15	Fe(III), Zn(II), Mo(VI), Se(IV), Ba(II), Ce(IV)
10	Iodide, Ni(II), Co(II), U(VI), Hg(II)
5	Cu(II), Pb(II), Cr(VI), Bi(III), Te(IV), Cd(II)
2	Phosphate, Tl(I), Ca(II), Al(III), Cr(III), Cd(II),
1	Ag(I), Pt(IV), Os(VIII)
0.5	Rh(III) <sup>a</sup> , Pd(II) <sup>a</sup> , Ir(III) <sup>b</sup> , Au(III) <sup>c</sup>

Conditions: Ruthenium(III) = 200 µg/mL, pH = 3.5, extractant = 0.1 M *n*-octylaniline, aq: org ratio = 2.5: 1, sodium malonate = 0.05 M in xylene, stripping = 2 % NaCl + 1 M HCl (4:1)

<sup>a</sup> Masked by 25 mg of tartrate,

<sup>b</sup> Masked by 25 mg of oxalate,

<sup>c</sup> Masked by 10 mg of bromide

**Table 5.** Separation of ruthenium(III) from binary mixtures

Metal ions	Amount taken, µg	Average recovery*, %	Chromogenic ligand	Ref
Ru(III)	200	99.8	-	
Pd(II) <sup>a</sup>	200	99.7	4'-Chloro PTPT	[38]
Ru(III)	200	99.8	-	
Pt(IV)	300	99.2	SnCl <sub>2</sub>	[39]
Ru(III)	200	99.8	-	
Ir(III) <sup>b</sup>	100	98.6	SnCl <sub>2</sub> - HBr	[39]
Ru(III)	200	99.8	-	
Rh(III) <sup>a</sup>	200	99.7	SnCl <sub>2</sub> + KI	[39]
Ru(III)	200	98.0	-	
Os(VIII)	200	99.3	Thiourea	[39]
Ru(III)	200	99.8	-	
Au(III) <sup>c</sup>	200	98.8	SnCl <sub>2</sub>	[39]
Ru(III)	200	99.7	-	
Fe(III)	1000	98.8	Thiocyanate	[39]
Ru(III)	200	99.8	-	
Cu(II)	2000	98.8	4'-Chloro-PTPT	[40]
Ru(III)	200	99.7	-	
Co(II)	1000	98.8	Thiocyanate	[41]
Ru(III)	200	99.8	-	
Ni(II)	5000	98.8	DMG	[41]
Ru(III)	200	99.8	-	
Se(IV)	300	98.8	4'-Bromo-PTPT	[42]
Ru(III)	200	99.8	-	
Te(IV)	200	98.8	4'-Bromo-PTPT	[43]

\*Average of six determinations

<sup>a</sup> Masked by 25 mg of tartrate,

<sup>b</sup> Masked by 25 mg of oxalate,

<sup>c</sup> Masked by 10 mg of bromide

#### Separation of ruthenium(III) from binary mixtures

The method allows the separation of ruthenium(III) from binary mixtures with some associated metal ions such as Os(VIII), Pt(IV), Cu(II), Fe(III), Co(II), Ni(II), Se(IV) and Te(IV).

The proposed method was successfully used for the separation of ruthenium(III) from these associated metal ions, under the optimum extraction conditions while all other added metal ions remained quantitatively in the aqueous phase where they were determined spectrophotometrically by standard methods [38-43]. Ruthenium(III) was back extracted from the organic phase and determined by spectrophotometry with the 4'-chloro- PTPT method (Table 5). At the same conditions of extraction of ruthenium(III), some metals like Rh(III), Pd(II), Ir(III) and Au(III) were co-extracted. Therefore, prior to the extraction of ruthenium(III), rhodium(III) and Pd(II) were masked with 25 mg of tartrate, Ir(III) was masked with 25 mg of oxalate and Au(III) was masked with 10 mg of bromide. The masked metal ions remained in the aqueous phase; they were demasked with perchloric acid followed by hydrochloric acid. Then the residue was dissolved in 10 mL of water and the aqueous phase was evaporated to almost dryness to completely remove traces of acid. The residue containing Rh(III), Pd(II), Ir(III) and Au(III) was analyzed spectrophotometrically by standard methods.

#### Separation of ruthenium(III) from ternary mixtures

The selectivity of the proposed extraction method was increased by using an appropriate masking agent for added metal ions. A ternary mixture of ruthenium(III), palladium(II) and rhodium(III) was extracted from 0.05 M malonic acid at pH 3.5 with 10 mL of 0.1 M *n*-octylaniline in xylene by masking Pd(II) and Rh(III) with tartrate (25 mg). It was found that ruthenium(III) was extracted while palladium(II) and rhodium(III) remained unextracted. Ruthenium(III) was stripped with 2% of NaCl and 1.0 M HCl (4:1) and determined by the recommended procedure [38].

The aqueous phase containing palladium(II), rhodium (III) and excess of malonic acid was decomposed by the addition of concentrated hydrochloric acid, and sodium malonate was added up to 0.03 M. Rhodium(III) was extracted quantitatively with 10 mL of 0.1 M *n*-octylaniline in xylene at pH 9.0. Rhodium(III) was stripped from the organic phase with 1.0 M hydrochloric acid (2×10 mL) and determined spectrophotometrically using the stannous chloride–potassium iodide method [39]. The malonate from the aqueous phase was decomposed with concentrated hydrochloric acid and the residue was extracted with 0.1 M hydrochloric acid. The aqueous phase was made 0.085 M with respect to sodium salicylate and

**Table 6.** Sequential separation of ruthenium(III) from a ternary mixture

Metal ion	Amount taken, $\mu\text{g}$	Aqueous phase (25 mL)	Stripping agent	Determination method	Recovery* %	Ref
Ru(III)	200	0.05 M Malonate pH = 3.5	2 % NaCl + 1 M HCl (4: 1)	4'-Chloro PTPT	99.8	[39]
Rh(III) <sup>e</sup>	200	0.03 M Malonate pH = 9.0	1 M HCl (2 $\times$ 10 mL)	SnCl <sub>2</sub> + KI	99.7	[40]
Pd(II) <sup>a</sup>	200	0.085 M Salicylate pH = 1.5	5 M Ammonia (3 $\times$ 10 mL)	4'-Chloro PTPT	99.7	[39]

\*Average of six determinations

<sup>a</sup> Masked by 25 mg of tartrate

extraction of palladium(II) was carried out with 10 mL of 0.07 M *n*-octylaniline at pH 1.5. Palladium(II) extracted from the organic phase was stripped with 5.0 M ammonia (2 $\times$ 10 mL) and determined spectrophotometrically with 4'-chloro- PTPT [38] (Table 6).

#### Determination of ruthenium(III) in synthetic mixtures

The proposed method was used for the extraction and determination of ruthenium(III) from malonate media at pH 3.5 in various ternary mixtures (Table 7).

**Table 7.** Determination of ruthenium(III) in synthetic mixtures

Synthetic mixture Ions	Metal ion taken, $\mu\text{g}$	Ruthenium(III) found, $\mu\text{g}$	Amount of ruthenium(III) extracted, %	RSD, %
Ru(III)	200			
Pd(II) <sup>a</sup>	100	197.0	98.5	1.5
Pt(IV)	100			
Ru(III)	200			
Ir(III) <sup>b</sup>	100	198.7	99.3	0.7
Rh(III) <sup>a</sup>	100			
Ru(III)	200			
Ni(II)	100	197.0	98.5	1.5
Au(III) <sup>c</sup>	100			
Ru(III)	200			
Co(III)	200	198.7	99.3	0.7
Fe(III)	200			
Ru(III)	200			
U(VI)	100	197.5	98.7	1.3
Te(IV)	100			

<sup>a</sup> Masked by 25 mg of tartrate, <sup>b</sup> Masked by 25 mg of oxalate, <sup>c</sup> Masked by 10 mg of bromide

RSD = Relative standard deviation

Ruthenium(III) was quantitatively extracted with 0.1 M *n*- octylaniline in xylene while Pt(IV), Ni(II), Te(IV), Fe(III), Co(II), U(VI) remained unextracted in the aqueous phase. Rh(III) and Pd(II) were masked with 25 mg of tartrate and Ir(III), and Au(III) with 25 mg of oxalate and 10 mg of bromide, respectively. The extracted ruthenium(III) was

stripped and determined spectrophotometrically by the 4'-chloro-PTPT method.

#### Analysis of ruthenium(III) in catalysts samples

Ruthenium(III), activated carbon and 0.1 g of alumina were added to 20 mL of *aqua regia*. The solution was heated to evaporate till moist dryness. The nitric acid was removed by evaporating with two 5 mL portions of hydrochloric acid. The solution was then filtered and diluted to 100 mL in a volumetric flask. An aliquot of the diluted solution was used for the analysis of ruthenium(III) content by the developed method. The results obtained were found in good agreement with the certified value (Table 8).

## CONCLUSIONS

- I. The extraction equilibria of ruthenium(III) and sodium malonate were investigated systematically using *n*-octylaniline in xylene.
- II. The results demonstrated that *n*-octylaniline is an excellent reagent for the extraction of ruthenium(III) from malonate media at pH 3.5 compared with some other high-molecular-weight amines and organophosphorus compounds. Further, *n*-octylaniline has good regeneration and loading capacities.
- III. The extractability of ruthenium(III) in presence of other associated elements was investigated. The proposed method was applied for the separation of ruthenium(III) from binary mixtures of associated transition metal ions and other rare earths.

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ТЕЧНО-ТЕЧНА ЕКСТРАКЦИЯ НА РУТЕНИЙ (III) В СРЕДА НА МАЛОНАТ ПРИ  
ИЗПОЛЗВАНЕТО НА N-ОКТИЛАНИЛИН КАТО ЙОН-СВЪРЗВАЩ АГЕНТ:  
ИЗСЛЕДВАНЕ НА КАТАЛИЗАТОРА И СПЛАВИ

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(Резюме)

Ние разработихме система за течна екстракция на рутений (III), използвайки 0.1 М *n*-октиланилин в среда на 0.05 М малонат при рН 3.5. Оптимизирани са различни работни параметри като рН, концентрации на реагентите, време за установяване на равновесието и капацитет на екстрагента за количественото определяне. Стехиометрията на екстрахираните вещества бе определена от наклона на правата линия. Екстракцията се извършва при формирането на йонни двойки комплекси между  $[\text{CH}_3(\text{CH}_2)_7\text{C}_6\text{H}_4\text{NH}_3]^+_{(\text{org})}$  и  $[\text{Ru}(\text{C}_3\text{H}_2\text{O}_4)_2]^-_{(\text{aq})}$ . Асоциирането на тези два йона води до неутрален незареден компонент  $[\text{CH}_3(\text{CH}_2)_7\text{C}_6\text{H}_4\text{NH}_3^+ \text{Ru}(\text{C}_3\text{H}_2\text{O}_4)^-_2]_{(\text{org})}$ . Стехиометрията на екстрахираните компоненти е 1: 2: 1 (метал: киселина: екстрагент). Валидността на предложения метод е проверена чрез екстракцията на рутений (III) от бинарни и тройни смеси и са изследван и различни катализатори.