



Liquid-liquid Extraction of Ruthenium(III) from Malonate Media by Novel 4-Heptylaminopyridine: Analysis of Alloy and Water Samples

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Received 25th August 2017; Revised 29th August 2017; Accepted 04th September 2017

ABSTRACT

In this research paper, the liquid-liquid extraction of ruthenium(III) from malonate media has been examined by shaking aqueous phase having pH 2.5 with 10 ml of 0.07 mol L⁻¹ 4-heptylaminopyridine as a novel extractant diluted in xylene for 5 min. The extracted metal from organic phase was separated by stripping with 4:1 combination of 2% NaCl and 1.0 M HCl. The effect of various parameters such as pH, weak acid concentration, extractant concentration, stripping agents, equilibrium time, diluents, and aqueous to organic volume ratio on the extraction of ruthenium(III) was studied. The extracted species has been evaluated from log D versus log C, and species appears to be 1:2:1 (metal:acid:extractant). The selectivity of the method was checked by separating ruthenium(III) from binary and ternary mixtures of metal ions as well as platinum-group metals. The separation of ruthenium(III) from alloy and water samples was also investigated.

Key words: Ruthenium(III), 4-heptylaminopyridine, Liquid-liquid extraction, Water samples.

1. INTRODUCTION

Ruthenium is a scarce element that is found in about 10⁻⁸ % of the earth's crust. In larger amounts, it is present in such minerals as laurite, rutheniridosmine, and ruthenosmiridium, as well as in chondrites and iron meteorites (10⁻⁴ %) [1-3]. It usually occurs in association with other platinum-group metals (PGMs). As one of the most effective hardeners in high-density alloys, ruthenium is widely used in the electronic industry [4].

Alloyed with other PGMs, it serves to make electrical contacts for heavy wear resistance. Ruthenium and its alloys have also found a widespread application in jewelry. The chemical industry consumes significant volumes of ruthenium in process catalysts, used in the manufacture of acetic acid, ammonia, and special chemicals [5]. Recently, platinum and ruthenium have been applied as effective bimetallic catalysts in fuel cells and dye-sensitized solar cells [6-8]. The ruthenium complexes possessing chemiluminescent activities (e.g., tris (2, 2'-bipyridyl) ruthenium(III)) have been used for the development of sensitive and selective methods of the determination of number of

analytes [9-11]. In addition, ruthenium complexes (e.g., NAMI-A) have been investigated as anticancer drugs [12-14]. It acts as a versatile catalyst, used for removal of NO_x from air stream [15]. Ruthenium complexes are biologically important in detection of amino acids [16], iodine/iodide [17], Vitamin A [18], and chloropheniramine [19].

A variety of extractants has been examined and reported, including tertiary amines [20-22], phosphine oxides [23,24], alamines 300 and 336, and aliquat 336 [21], Cyanex 923 [23], bisacylated triethylenetetramine and dihexyl sulfoxide [25,26], 4-pyridone derivatives [27], tertiary amine, N235 [28], Cyanex 925 [29], and 2-dodecylaminopyridine [30]. There is no report on the development of analytical method for extraction and separation of ruthenium(III) from malonate media by novel 4-heptylaminopyridine (4-HAP).

Trace abundance, enhanced properties, and growing application in various fields demand the simple, affordable, and selective analytical method for separation and determination of ruthenium from water

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samples, and the liquid-liquid extraction is the best method.

2. EXPERIMENTAL

2.1. Apparatus

UV/VIS Spectrophotometer model-Optizen α (Mecasys Co., Ltd./made in South Korea) with 1 cm quartz cell was used for absorbance measurements, and pH measurements were carried out with an Elico Digital pH meter Model LI-120 with a combined glass electrode.

2.2. Reagents

2.2.1. Standard ruthenium(III) solution

A standard stock solution of ruthenium(III) was prepared by dissolving 1.0 g ruthenium trichloride, RuCl_3 (Jhonson Matthey, UK) in 2.0 M hydrochloric acid, and diluted up to mark with double-distilled water in a 250 mL standard volumetric flask and standardized [31]. A working solution of 200 $\mu\text{g/mL}$ was made by diluting the stock solution with water.

2.2.2. 4-HAP solution (0.07 M)

4-HAP was synthesized using the method of Singh *et al.* [32], and its 0.07 M solution was prepared in xylene.

2.2.3. Thiourea solution (10% w/v)

Thiourea was prepared by dissolving 10 g thiourea (SD Fine-Chem) in 100 mL water. Standard solutions of diverse ion were prepared by dissolving AR grade reagents in double-distilled water or diluted HCl. All the organic solvents were used after double distillation. All chemicals used were of AR grade. Double-distilled water was used throughout the experiment.

2.2.4. General procedure for extraction and determination of ruthenium(III)

An aliquot of solution containing 200 μg ruthenium(III) in 25 mL volumetric flask, a sodium malonate was added to get the concentration of solution 0.04 M. The pH was adjusted to 2.5 with diluted NaOH and diluted HCl solution. The aqueous solution was equilibrated with 10 mL 0.07 M 4-HAP dissolved in xylene for 5 min. The two phases were allowed to separate, and ruthenium(III) from organic phase was back stripped with the 4:1 combination of 2% NaCl and 1.0 M HCl. The back extracts were evaporated to moist dryness and dissolved in minimum amount of aqua regia and evaporated with two 2 mL portions of concentrated HCl to remove oxides of nitrogen, and ruthenium(III) was determined spectrophotometrically using thiourea [33].

3. RESULTS AND DISCUSSION

3.1. Effect of pH on Extraction of Ruthenium(III)

The effect of pH on the percentage extraction of ruthenium(III) was examined in the pH range of 0.5-9 with 0.07 M 4-HAP in xylene. Figure 1 shows that the extraction of ruthenium(III) was found to be

quantitative in the pH range of 2.0-3.0. To ensure the complete extraction of ruthenium(III), pH 2.5 was chosen for recommended procedure.

3.2. Effect of 4-HAP Concentration on Extraction of Ruthenium(III)

A set of experiment was arranged to determine the suitable range of 4-HAP concentration for the quantitative extraction of ruthenium(III). Therefore, the experiments were carried out by varying the concentration of 4-HAP in the range of 0.01-0.13 M, at a pH 2.5 and 0.04 M sodium malonate concentration. Figure 2 showed that extraction efficiency of ruthenium(III) increases sharply from 16.1% to 100% when the concentration of 4-HAP increased from 0.01 M to 0.06 M. Further increase in 4-HAP concentration up to 0.13 M does not affect the extraction of ruthenium(III). Therefore, 10 mL of

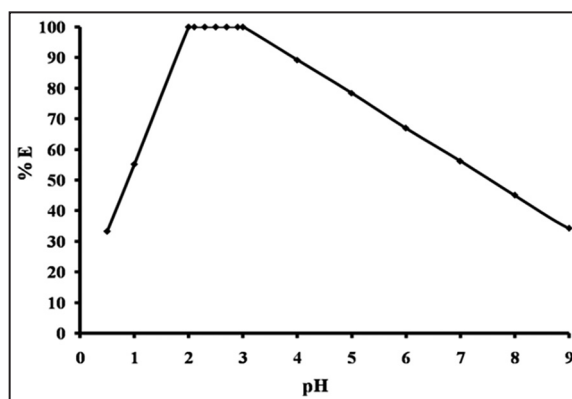


Figure 1: Effect of pH on extraction of ruthenium(III). Conditions: Ruthenium(III)=200 μg , sodium malonate=0.04 M, organic=0.07 M 4-heptylaminopyridine in xylene, aqueous organic=2.5:1.0, equilibrium time=5.0 min, strippant=2% + 1 M HCl (4:1).

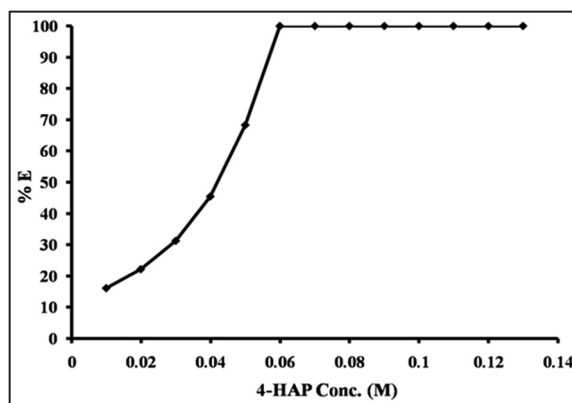


Figure 2: Effect of 4-heptylaminopyridine concentration on the extraction of ruthenium(III). Conditions: Ruthenium(III)=200 μg , sodium malonate=0.04 M, pH=2.5, aqueous organic=2.5:1.0, equilibrium time=5.0 min, strippant=2% NaCl + 1 M HCl (4:1).

0.07 M 4-HAP concentration was adopted for further extraction.

3.3. Effect of Weak Organic Acid Concentration on Extraction of Ruthenium(III)

The extraction of ruthenium(III) was carried out at pH 2.5 with 0.07 M 4-HAP in xylene in the presence of varying concentrations of sodium malonate, sodium succinate, sodium ascorbate, and sodium salicylate as weak acid media. The extraction of ruthenium(III) was found to be quantitative in the range of 0.03-0.05 M for sodium malonate, and further increase in malonate concentration, there was a decrease in percentage extraction. The extraction of ruthenium(III) was found to be incomplete in the succinate, salicylate, and ascorbate media. Hence, quantitative extraction was carried out with 0.04 M sodium malonate (Figure 3).

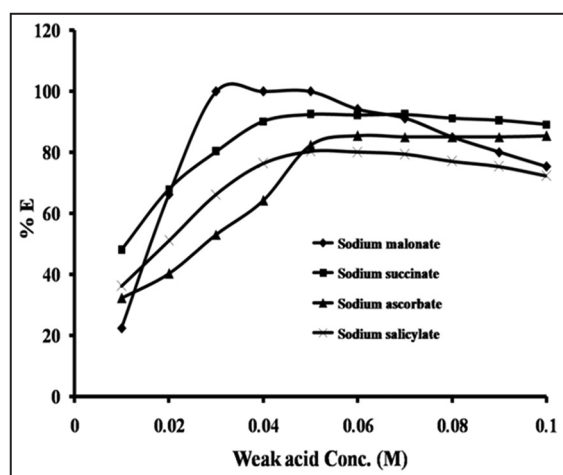


Figure 3: Effect of weak organic acid concentration on the extraction of ruthenium(III). Conditions: Ruthenium(III)=200 μ g, pH=2.5, aqueous organic=2.5:1.0, organic=0.07 M 4-heptylaminopyridine in xylene, equilibrium time=5.0 min, strippant=2% NaCl + 1 M HCl (4:1).

3.4. Effect of Diluents on Extraction of Ruthenium(III)

A number of different aromatic and aliphatic organic diluents were tested for the extraction of ruthenium(III). To detect the effect of nature of various aromatic and aliphatic diluents on the extraction of ruthenium(III), the organic diluents, namely, xylene, toluene, amyl acetate, amyl alcohol, chloroform, methyl isobutyl ketone (MIBK), *n*-butyl alcohol, 1, 2-dichloroethane, and carbon tetrachloride were used (Table 1). It was found that the extraction of ruthenium(III) was quantitative with xylene and toluene while there was incomplete extraction in MIBK (85.1%), *n*-butyl alcohol (32.3%), and chloroform (20.5%) and no extraction in amyl acetate, amyl alcohol, 1,2-dichloroethane, and carbon tetrachloride. Throughout the experiment, xylene was used as diluent.

3.5. Effect of Shaking Time on Extraction of Ruthenium(III)

The effect of shaking time on the extraction of ruthenium(III) from 0.04 M sodium malonate at pH=2.5 using 0.07 M 4-HAP in xylene has been studied. The shaking time was varied from 1 to 18 min. The extraction of ruthenium(III) was quantitative over 3 min shaking of the solution, but with prolonged shaking over 10 min, there was a decrease in the percentage extraction of ruthenium(III) due to the dissociation of ion-pair complex (Figure 4). Thus, shaking time for extraction of ruthenium(III) was kept about 5 min throughout the study.

3.6. Effect of Stripping Agents

Stripping of ruthenium(III) from organic phase was carried out with NH_3 , water, 2% NH_4Cl , $\text{NH}_3 + \text{NH}_4\text{Cl}$, HCl, HBr, 2% NaCl + 1 M HCl (4:1), NaOH, and KOH (Table 2). Ruthenium(III) was quantitatively stripped with 2% NaCl + 1 M HCl (4:1), HCl, and HBr. However, incomplete recovery of ruthenium(III) from organic phase with strippants include NH_3 , water, 2% NH_4Cl ,

Table 1: Effect of diluents on the extraction of ruthenium(III).

Solvent	Dielectric constant	Amount of ruthenium (III) extracted, %E	D
Xylene*	2.30	100	∞
Toluene	2.38	100	∞
Amyl acetate	4.80	0.0	-
Amyl alcohol	13.90	0.0	-
Chloroform	4.80	20.5	0.64
MIBK	13.10	85.1	14.2
<i>n</i> -butyl alcohol	17.80	32.3	1.19
1,2-dichloro-ethane	10.50	0.0	-
Carbon tetrachloride	2.24	0.0	-

Ruthenium (III)=200 μ g, pH=2.5, aqueous organic ratio=2.5:1, sodium malonate=0.04 M, strippant=2% NaCl+1 M HCl (4:1). *Recommended for general extraction procedure. %E=Percentage extraction, D=Distribution ratio, MIBK=Methyl isobutyl ketone

$\text{NH}_3 + \text{NH}_4\text{Cl}$, NaOH , and KOH . In recommended procedure, 2% $\text{NaCl} + 1 \text{ M HCl}$ (4:1) was used for the complete stripping of loaded organic phase.

3.7. Loading Capacity of 4-HAP

Varying concentrations of ruthenium(III) (100-2000 μg) were extracted with 10 mL portions of 0.07 M 4-HAP in xylene from 0.04 M sodium malonate media. It was observed that extraction of ruthenium(III) was quantitative up to 800 μg .

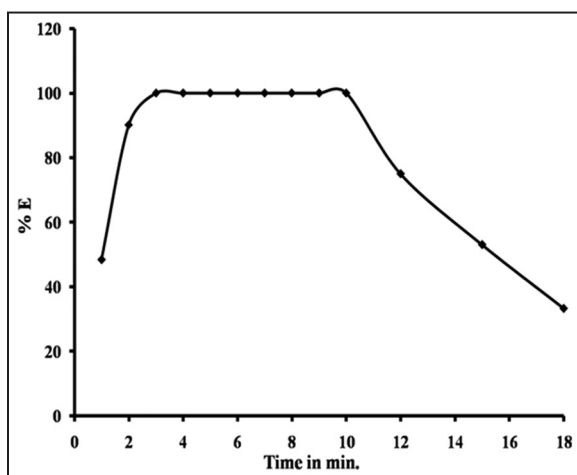


Figure 4: Effect of shaking time on the extraction of ruthenium(III). Conditions: Ruthenium(III)=200 μg , $\text{pH}=2.5$, aqueous organic=2.5:1.0, organic=0.07 M 4-heptylaminopyridine in xylene, strippant=2% $\text{NaCl}+1 \text{ M HCl}$ (4:1).

3.8. Effect of Phase Ratio on Extraction of Ruthenium(III)

To find whether large aqueous, organic volume ratio could be tolerated for the successfully extraction of ruthenium(III) by 4-HAP under optimum condition. The results showed that for aqueous, organic volume ratio up to 50:10 is favorable for the quantitative extraction of ruthenium(III); beyond that, the percentage extraction of ruthenium(III) get decreases as aqueous, organic ratio increases from 100:10 to 150:10.

3.9. Nature of Extracted Species

Stoichiometry of the extracted species was determined by plotting the graph of $\log D_{[\text{Ru(III)}]}$ Vs $\log C_{[4\text{-HAP}]}$ at fixed sodium malonate concentration (0.04 M). The graphs are found to be linear and having the slopes of 0.95 and 0.92 at pH 4.0 and 5.0, respectively (Figure 5). Similarly, $\log D_{[\text{Ru(III)}]}$ versus $\log C_{[\text{malonate}]}$ at fixed 4-HAP concentration (0.07 M) plotted. The plots were linear, and the slope values are found to be 1.76 and 1.79 at pH 4.0 and 5.0, respectively (Figure 6). The stoichiometry of the extracted species is calculated to be 1:2:1 (metal:acid:extractant).

The extraction efficiency of system depends on the amount of free electron pair in 4-HAP that can shared with the metal to form a complex compound. The possible mechanism of the extracted species appears to be protonated 4-HAP which forms cationic species as 4-HAPH^+ , while malonate combine with ruthenium(III) to form anionic species as

Table 2: Effect of stripping agent.

Strippant ruthenium	Concentration	Percentage extraction (%E)	Distribution ratio (D)
Ammonia	1-10 M	38.4	1.5
	(2 × 10 mL)		
Water	(2 × 10 mL)	0.0	-
NH_4Cl	2%	31.9	1.17
	(2 × 10 mL)		
Ammonia + NH_4Cl	2 M + 3M	50.5	2.55
	(2 × 10 mL)		
HCl	Concentrated (2 × 10 mL)	100	∞
HBr	Concentrated (2 × 10 mL)	100	∞
2% $\text{NaCl} + 1 \text{ M HCl}^*$	40 mL + 10 mL	100	∞
NaOH	1-5 M	38.1	1.54
	(2 × 10 mL)		
KOH	1-5 M	34.1	1.29
	(2 × 10 mL)		

Ruthenium(III)=200 μg , $\text{pH}=2.5$, aqueous organic ratio=2.5:1, sodium malonate=0.04 M, extractant=0.07 M 4-HAP in xylene. *Recommended for general extraction procedure. 4-HAP=4-heptylaminopyridine

$\text{Ru}(\text{C}_3\text{H}_2\text{O}_4)_2^-$, and both of them associate to form ion-pair of the type $[\text{4-HAPH}^+ \cdot \text{Ru}(\text{C}_3\text{H}_2\text{O}_4)_2^-]_{\text{org}}$ which being neutral constitutes extractable species.

The probable extraction mechanism is as follows:

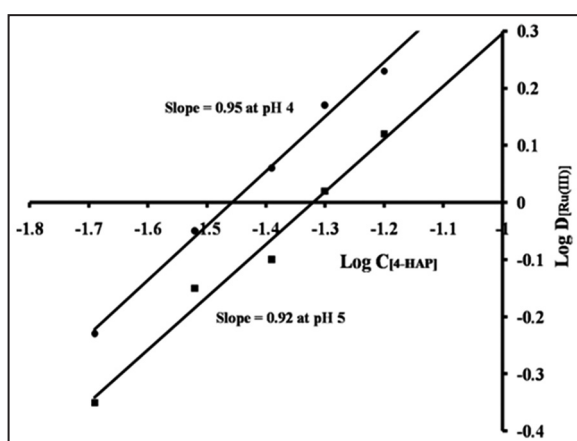
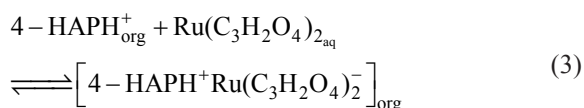
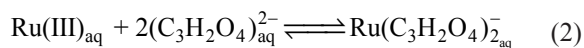
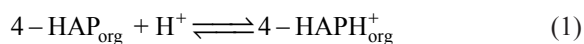


Figure 5: Log-log plot of $\text{Log } D_{[\text{Ru(III)}]}$ versus $\text{Log } C_{[\text{4-heptylaminopyridine}]}$ at fixed malonate concentration. Conditions: Ruthenium(III)=200 μg , pH=4.0 and 5.0, sodium malonate=0.04 M, equilibrium time=5.0 min, aqueous organic=2.5:1.0, strippant=2% NaCl + 1 M HCl (4:1).

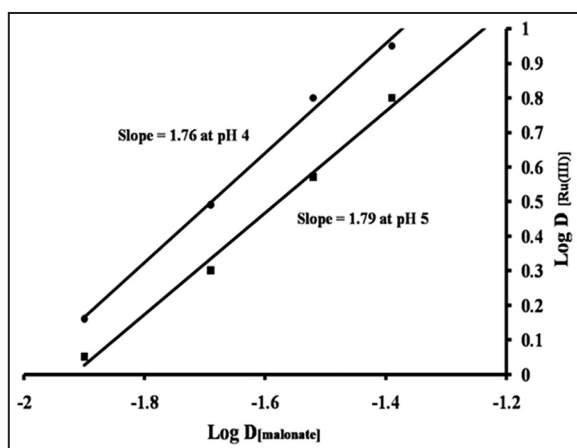


Figure 6: Log-log plot of $\text{Log } D_{[\text{Ru(III)}]}$ versus $\text{Log } C_{[\text{malonate}]}$ at fixed 4-heptylaminopyridine (4-HAP) concentration. Conditions: Ruthenium(III)=200 μg , pH=4.0 and 5.0, organic=0.07 M 4-HAP in xylene, equilibrium time=5.0 min, aqueous organic=2.5:1.0, strippant=2% NaCl + 1 M HCl (4:1).

3.10. Effect of Foreign Ions

The effect of the presence of various cations and anions on the extraction of ruthenium(III) was studied by carrying out the extraction of ruthenium(III) in the presence of various ions. A detailed study of the interference effect on the solvent extraction of ruthenium(III) was performed. Ions were considered to be noninterfering when they produced an error of less than $\pm 2\%$ in the analyte determination. Tolerance limit for the ions tested is given in Table 3. The results showed that Pd(II) and Rh(III) were masked with 25 mg tartrate and Au(III) with 45 mg bromide. Ir(III) was masked with 45 mg oxalate. In the presence of thiourea, thiosulfate, and thiocyanate, citrate extraction of ruthenium(III) was not possible.

3.11. Applications

3.11.1. Separation of ruthenium(III) from binary mixtures

The suitability of the extraction method of ruthenium(III) was studied by applying it to the separation and determination of ruthenium(III) from binary mixtures containing Pt(IV), Fe(III), Os(VIII), Co(II), Cu(II), Te(IV), Se(IV), and Ni(II). The separation of these associated metal ions from ruthenium(III) was achieved by taking advantage of the difference in the extraction condition of metals. All the added metal ions were remained quantitatively in aqueous phase from which they were determined spectrophotometrically by standard methods [33-38]. Ruthenium(III) from organic phase was stripped and estimated spectrophotometrically by thiourea method (Table 4).

During extraction of ruthenium(III) from binary mixture, some metals such as Au(III), Rh(III), Pd(II),

Table 3: Effect of foreign ions.

Tolerance limit, mg	Foreign ion added
50	Oxalate, bromide, EDTA
25	Fe (III), tartrate, fluoride
15	Mg (II), Ce (IV), Ni (II), Co (II), U (VI), acetate, iodide
10	Zn (II), Mo (VI), Se (IV), Ba (II), Hg (II)
5	Pb (II), Ca (II), Al (III), Cr (III)
3	Cu (II), Bi (III), Te (IV), Cd (II), Tl (I)
2	Cr (VI)
1	Ag (I), Ir (III) ^b , Au (III) ^c , phosphate
0.5	Pt (IV), Os (VIII), Rh (III) ^a , Pd (II) ^a

Ruthenium (III)=200 μg , pH=2.5, sodium malonate=0.04 M, aqueous organic ratio=2.5:1, extractant=0.07 M 4-HAP in xylene, strippant=2% NaCl+1 M HCl (4:1). ^aMasked by 25 mg tartrate, ^bmasked by 45 mg oxalate, ^cmasked by 45 mg bromide. EDTA=Ethylenediaminetetraacetic acid

Table 4: Separation of ruthenium(III) from binary mixtures.

Metal ions	Amount taken, µg	Average recovery*, %	Chromogenic ligand	References
Ru (III)	200	99.7	4'-bromo PTPT	33
Te (IV)	40	99.9		
Ru (III)	200	99.5	4'-bromo PTPT	34
Se (IV)	400	99.6		
Ru (III)	200	99.9	Thiocyanate	36
Fe (III)	60	99.8		
Ru (III)	200	99.8	4'-chloro PTPT	35
Cu (II)	40	99.9		
Ru (III)	200	99.6	DMG method	36
Ni (II)	40	99.9		
Ru (III)	200	99.8	Thiocyanate method	36
Co (II)	300	99.7		
Ru (III)	200	99.9	Stannous chloride	30
Au (III) ^c	100	99.7		
Ru (III)	200	99.6	Thiourea method	30
Os (VIII)	300	99.9		
Ru (III)	200	99.7	KI method	36
Rh (III) ^a	200	99.9		
Ru (III)	200	99.7	Stannous chloride	36
Ir (III) ^b	40	99.6		
Ru (III)	200	99.9	4'-chloro PTPT	37
Pd (II) ^a	100	99.9		
Ru (III)	200	99.9	Stannous chloride	36
Pt (IV)	300	99.7		

*Average of six determination. ^aMasked by 25 mg tartrate, ^bmasked by 45 mg oxalate, ^cmasked by 45 mg bromide.
DMG: Dimethylglyoxime

and Ir(III) were co-extracted. Palladium(II) and Rh(III) were masked with 25 mg tartrate. Gold(III) masked with 45 mg bromide, and Ir(III) masked with 45 mg oxalate. All the masked metal ions remained in the aqueous phase.

3.11.2. Separation of ruthenium(III) from ternary mixture

The selectivity of the developed method was examined by applying it to the separation and determination of ruthenium(III) from variety of ternary mixture containing PGMs and some base metal ions. The ternary mixture of Ir(III), Co(II); Cu(II), Ni(II); Os(VIII), Se(IV); Co(II), Cu(II); Pd(II), Fe(III); Rh(III), Au(III);

Rh(III), Te(IV); Au(III), Te(IV); Fe(III), Os(VIII); and Co(II), Pt(IV) were resolved by developed extraction method of ruthenium(III) (Table 5). The PGMs are masked by suitable masking agents, and the extraction of ruthenium(III) was carried out. All the PGMs are unextracted with 10 mL 0.07 M 4-HAP in xylene and 0.04 M sodium malonate at pH 2.5.

3.11.3. Analysis of ruthenium(III) in synthetic mixture corresponding to the composition of alloys

The validity of the developed method was checked by applying it to the synthetic mixture of alloys for ruthenium content. Numbers of alloy samples were analyzed for ruthenium content, namely, ruthenium

Table 5: Separation of ruthenium(III) from ternary mixture.

Composition of mixture, μg	Amount of ruthenium (III) found, μg	Percentage recovery of ruthenium (III) (%R)*	RSD, %
Ru (III) 200	199.8	99.9	0.1
Ir (III) ^b 40			
Co (II) 300			
Ru (III) 200	199.5	99.7	0.25
Cu (II) 40			
Ni (II) 40			
Ru (III) 200	198.7	99.3	0.65
Os (VIII) 300			
Se (IV) 400			
Ru (III) 200	198.4	99.2	0.8
Co (II) 300			
Cu (II) 40			
Ru (III) 200	198.4	99.2	0.8
Pd (II) ^a 100			
Fe (III) 60			
Ru (III) 200	199.9	99.9	0.05
Rh (III) ^a 200			
Au (III) ^c 100			
Ru (III) 200	199.3	99.6	0.35
Rh (III) ^a 200			
Te (IV) 40			
Ru (III) 200	198.2	99.1	0.9
Au (III) ^c 100			
Te (IV) 40			
Ru (III) 200	198.8	99.4	0.6
Fe (III) 60			
Os (VIII) 300			
Ru (III) 200	199.6	99.8	0.2
Co (II) 300			
Pt (IV) 300			

*Average of six determination. ^aMasked by 25 mg tartrate, ^bmasked by 45 mg oxalate, ^cmasked by 45 mg bromide.
RSD=Relative standard deviation

mineral, osmiridium alloys, platinum alloy, and hexamolybdenum mineral. Real samples such as alloys of ruthenium are not available at this working place. Therefore, the composition of each alloy was prepared synthetically, and from which known, amount of ruthenium(III) was added and the determination of ruthenium(III) in alloys from sodium malonate media at 2.5 pH was carried out by developed method (Table 6).

3.11.4. Analysis of ruthenium(III) in water samples

To check the usefulness of the above-developed method, it was applied for the determination of

ruthenium(III) in environmental water samples collected from different sources. The water samples collected were filtered through Whatman filter paper No. 40 to remove suspended matter, impurities, etc., and then boiled for 5 min to remove chlorine and dissolved gases. Then, water samples were spiked with 200 µg of ruthenium(III), and the developed method is applied for determination of ruthenium(III) in spiked and unspiked water samples. The results were in good agreement with the amount added as shown in Table 7.

Table 6: Analysis of ruthenium(III) in synthetic mixture corresponding to the composition of alloys.

Alloy	Amount of ruthenium (III) taken, µg	Amount of ruthenium (III) found, µg	% recovery (%E)*	RSD, %
Ruthenium mineral				
Ir-41.99	200	199.4	99.7	0.34
Os-13.85				
Ru-44.16				
Osmiridium alloy				
Rh-110, Os-325	200	199.2	99.6	0.4
Pt-100, Ru-80				
Ir-400, Au-10				
Platinum alloy				
Pt-850, Ru-100	200	199.7	99.8	0.15
Pt-750, Ru-100, Ir-100	200	198.7	99.3	0.65
Hexamolybdenum mineral				
Fe-4.29, Ni-0.56, Mo 51.64	200	199.2	99.6	0.4
Ir-12.93, Os-5.48, Ru-23.32, W-1.77				

*Average of six determination. RSD=Relative standard deviation

Table 7: Analysis of ruthenium(III) in water samples.

Sample	Ruthenium (III) spiked (µg)	Ruthenium (III) found (µg)	Average recovery ^a (%)	RSD (%)
Tap water ^b	ND ^d	-	-	-
	200	199.5	99.7	0.25
Distilled water ^b	ND ^d	-	-	-
	200	199.9	99.9	0.05
Waste water ^b	ND ^d	-	-	-
	200	199.7	99.8	0.15
Rain water ^b	ND ^d	-	-	-
	200	198.9	99.4	0.55
River water ^c	ND ^d	-	-	-
	200	198.5	99.2	0.75

^aAverage of six determinations, ^bDepartment of Chemistry, Shivaji university, Kolhapur, ^cPanchganga river Kolhapur, dnot detected. RSD=Relative standard deviation

4. CONCLUSION

- I. The newly proposed reagent 4-HAP has been proved to be a potential analytical reagent for extraction of ruthenium(III)
- II. Proposed liquid-liquid extraction method is simple, sensitive, and precise with selectivity enhanced using suitable masking agents
- III. No sophisticated instruments required and quantitative extraction achieved using simple equipment such as spectrophotometer, separatory funnel, and pH meter
- IV. Method permits enhanced applicability with analysis of binary and ternary mixtures, synthetic alloy, and water samples which has been developed.

5. ACKNOWLEDGMENTS

Authors are thankful to UGC New Delhi for research funding to corresponding author (Minor Research Project).

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