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T. N. Lokhande[a]; G. B. Kolekar[a]; M. A. Anuse[a]; M. B. Chavan[a]
[a] ANALYTICAL CHEMISTRY LABORATORY, DEPARTMENT OF CHEMISTRY, SHIVAJI UNIVERSITY, KOLHAPUR, INDIA

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Extraction of Ruthenium(IV) from Hydrochloric Acid Medium with *N*-Octylaniline and Its Determination Spectrophotometrically with Pyrimidine-2-thiol

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T. N. LOKHANDE, G. B. KOLEKAR, M. A. ANUSE,* and
M. B. CHAVAN
ANALYTICAL CHEMISTRY LABORATORY
DEPARTMENT OF CHEMISTRY
SHIVAJI UNIVERSITY
KOLHAPUR-416004, INDIA

ABSTRACT

A novel method is proposed for the extraction of microgram level concentrations of ruthenium(IV) from halide medium with *N*-octylaniline dissolved in xylene as an extractant. The optimum conditions have been determined by making a critical study of acid concentration, extractant concentration, period of equilibration, and effect of solvent on the equilibria. The ruthenium(IV) from the organic phase is stripped with sodium chloride solution and determined spectrophotometrically with pyrimidine-2-thiol as a reagent. The method affords the binary separation of ruthenium(IV) from base metals such as iron(III), cobalt(II), nickel(II), and copper(II), and it is used for analysis of synthetic mixtures of associated metal ions and alloys. It can be successfully applied for the separation and determination of ruthenium(IV) from the constituent elements of a fuel used for Experimental Breeder Reactor II. The method is highly selective, simple, and reproducible.

INTRODUCTION

The abundance of ruthenium in the earth's crust is about 0.001 ppm. It is used as a hardening agent for palladium and platinum. Small amounts of this element greatly increase the corrosion resistance of titanium. It is a versatile catalyst, used in the selective reduction of carbonyl groups in organic com-

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* To whom correspondence should be addressed. FAX: 0091-0231-656133.

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pounds by hydrogen and the removal of hydrogen sulfide from oil refining and other industrial processes.

Solvent extraction of noble metals has been widely employed in chemistry and industry for many years. This technique has been used for the separation of platinum metals (1–3). These noble metals are recovered from a wide variety of sources because they can cause metallurgical problems of widely differing natures. The aqueous chemistry of these metals is extremely complex. The most prominent feature of their chemistry is the great tendency of the metals to form chlorocomplexes in chloride media. In addition, the stabilities of the full chlorocomplexes are widely different. In general, two effects are used to achieve separation by anion exchange (4): 1) the differing stabilities of chlorocomplex anions and 2) differences in structure, charge, and size among different chlorocomplexes. The first effect is most useful in separating the noble metals from base metals. In moderately weak chloride medium most base metals are present in solution in the cationic forms whereas the noble metal chlorocomplexes are stable (or inert to substitution) at fairly low chloride concentrations. The second effect is useful in achieving both group and individual noble metals separations.

Solvent extraction by high molecular weight amines (HMWA) has become increasingly popular in recent years for studying metal complexes. These are known as liquid anion exchangers which uniquely combine some of the advantages of liquid–liquid extraction and ion exchange. It was further observed that the acid binding properties of high molecular weight amines depend on the fact that acid salts of these bases are essentially insoluble in water while they are readily soluble in hydrocarbon solvents (5).

4-Octylaniline has been reported to be a group extractant for noble metals (6–10). Comparison has been made of the merits of *N*-octylaniline relative to 4-octylaniline as an extractant. Pohlandt has reported that the effectiveness of 4-octylaniline in these extractions depends on its method of preparation (9). Difficulties encountered in the extraction of noble metals are the formation of emulsions, extent of equilibration time (30 minutes), and requirement of a higher reagent concentration for the quantitative extraction of noble metals (7, 9). Further, the extraction method suffers from the need for multiple extraction for the quantitative recovery of the metal ion (7). The factors that remain to be examined include the effect of varying amounts of extractant, varying phase ratios, different diluents, and the use of mineral acids other than hydrochloric acid. Tri-iso-octylamine (11) has been used as a group extractant for the noble metals from 1 $\text{mol}\cdot\text{dm}^{-3}$ hydrochloric acid medium with 2 minutes of shaking. Other extractants reported for ruthenium(III) consist of the use of trioctylamine oxide (12), bis (2-ethylhexyl) amine (13), triphenylphosphine (14), di (2-ethylhexyl) phosphoric acid (15), tributyl phosphate (16), octyl (phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (17), and trinonylamine (18).

A novel extractant, *N*-octylaniline, has been used successfully as an extractant for the extraction separation of In(III), TI(III), Zn(II), Bi(III), and Ga(III) in our laboratory (19–21). Owing to their generally greater solubility, primary amines are used less frequently than secondary amines. For *N*-octylaniline, the presence of an octyl group attached to an amino group in aniline renders this amine less soluble in water. There is no emulsion formation and it has the potential of being prepared on a large scale. We have recently reported liquid–liquid extraction of palladium(II) (22) and platinum(IV) (23) with *N*-octylaniline from hydrochloric acid media. An extension of this work has shown that *N*-octylaniline can also be used for solvent extraction separation of ruthenium(IV) from hydrochloric acid media. The method we have developed for the extractive separation and determination of ruthenium(IV) from associated elements and alloys is reported below.

EXPERIMENTAL

Equipment and Reagents

An Elico digital spectrophotometer model CL-27 with 1 cm quartz cells was used for absorbance measurements. pH measurements were carried out with an Elico digital pH meter model LI-120.

A stock solution of ruthenium(III) was prepared by dissolving 1 g ruthenium(III) chloride hydrate (Johnson Matthey, England) in dilute AnalaR hydrochloric acid (1 $\text{mol}\cdot\text{dm}^{-3}$) and diluting it to 1000 mL with distilled water and further standardizing it (3). A working solution of 100 μg/mL was made from it by diluting the stock solution with distilled water. Chlorine water was prepared following the standard procedure (24). *N*-Octylaniline was prepared by using the method of Gardlund (25), and its solutions (% v/v) were prepared in xylene.

Other standard solutions of different metals used to study the effect of foreign ions were prepared by dissolving weighed quantities of their salts in distilled water or dilute hydrochloric acid. Solutions of anions were prepared by dissolving the respective alkali metal salts in water. All the chemicals used were of AR grade. Doubly distilled water was used throughout.

General Procedure

An aliquot of solution containing 100 μg of ruthenium(III) was mixed with 5 mL of 0.1 $\text{mol}\cdot\text{dm}^{-3}$ chlorine water. The mixture was heated carefully to moist dryness. The hydrochloric acid and water were added to give a final concentration of 1 $\text{mol}\cdot\text{dm}^{-3}$ with respect to hydrochloric acid in a total volume of 10 mL. The solution was then transferred to a 125-mL separatory funnel and equilibrated with 10 mL of 5% *N*-octylaniline in xylene for 1 minute. The phases were allowed to separate. Ruthenium from the organic phase was stripped twice, once with 40 mL of 2% NaCl solution followed by 10 mL of the same solution after diluting the organic phase to 20 mL with xylene. The extracts were evaporated to suitable volumes and the ruthenium was estimated spectrophotometrically at 620 nm by using the reagent pyrimidine-2-thiol (26).

Recovery of Reagent

The residual organic phase was shaken two or three times with 10 mL portions of ammonia solution (sp.gr. 0.88, solution diluted 1:1 with water) and then with distilled water. The xylene was distilled off and *N*-octylaniline was treated with sodium hydroxide pellets to remove the last traces of water. After decantation, the reagent was distilled under reduced pressure before use.

RESULTS AND DISCUSSION

Extraction of Ruthenium(IV) as a Function of Acid Concentration

The extraction of ruthenium(III) as a function of acid concentration showed that there was 80, 56, 30, and 74.5% extraction in hydrochloric, hydrobromic, perchloric, and sulfuric acid media, respectively, while emulsion formation was observed in nitric acid. The extraction became quantitative when ruthenium(III) was oxidized to ruthenium(IV) in the presence of 5 mL of 0.1 $\text{mol}\cdot\text{dm}^{-3}$ chlorine water in acidic medium (27) and the mixture was heated carefully to moist dryness.

The extraction of ruthenium(IV) was carried out from different acid media with 5% *N*-octylaniline in xylene while keeping the aq:org volume ratio 1:1. The extraction was found to be complete from hydrochloric and sulfuric acid media (Fig. 1). It was incomplete in perchloric acid and hydrobromic acid, and no extraction could be achieved by using nitric acid. The extraction was quantitative in sulfuric acid medium in the 5–6 $\text{mol}\cdot\text{dm}^{-3}$ range, but third-phase formation took place above this range of acidity. Hence, the hydrochloric acid system was used for further studies.

Extraction of Ruthenium(IV) as a Function of *N*-Octylaniline Concentration

Ruthenium(IV) was extracted over the 0.2–10 $\text{mol}\cdot\text{dm}^{-3}$ acidity range with hydrochloric acid with varying concentrations of *N*-octylaniline. The reagent concentration was varied from 1 to 7%. It was observed that extraction increased with an increase in the acidity of the aqueous solution and became quantitative at 1 $\text{mol}\cdot\text{dm}^{-3}$ hydrochloric acid. It was found that 5% reagent in xylene was needed for quantitative extraction of metal ion from 1 $\text{mol}\cdot\text{dm}^{-3}$ hydrochloric acid (Table I).

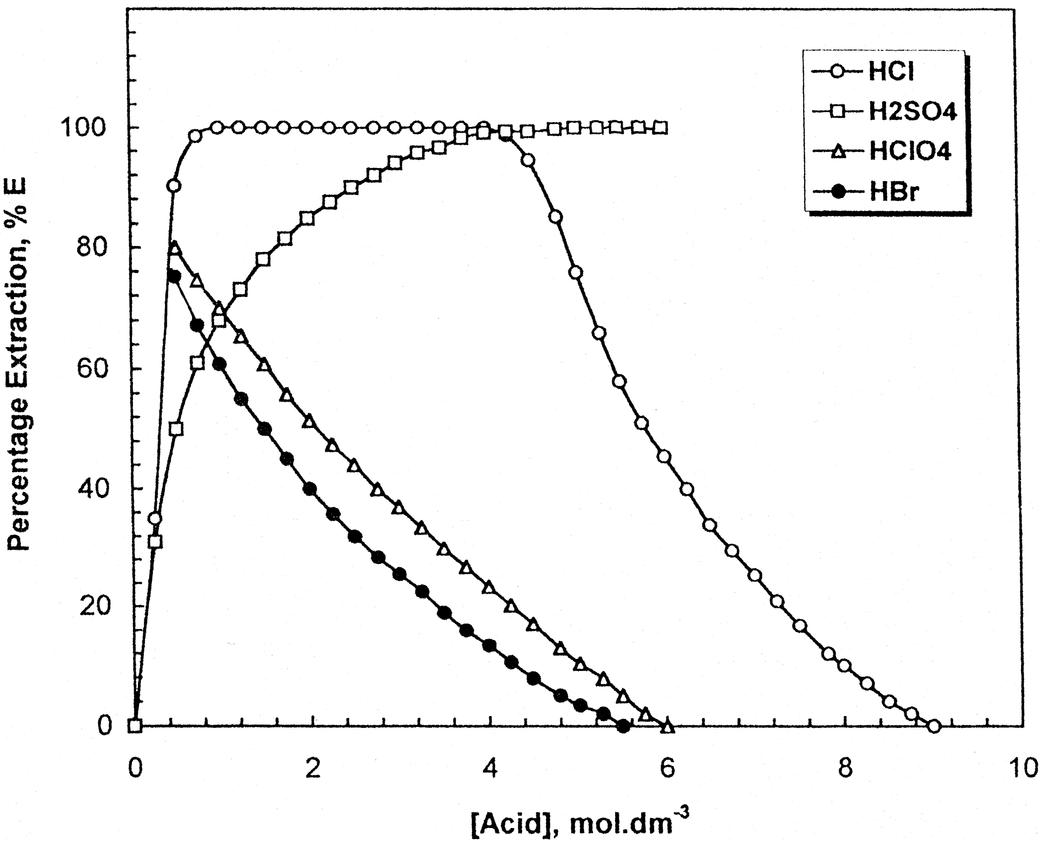

FIG. 1 Extraction of Ru(IV) with 5% *N*-octylaniline in xylene as a function of acid concentration. Ru(IV) = 100 μg.

Effect of Equilibration Time

Variation of the shaking period from 5 seconds to 15 minutes showed that a minimum of 30 seconds equilibration time was adequate for quantitative extraction of ruthenium(IV) from both hydrochloric acid and sulfuric acid media. As a general procedure, 1 minutes of equilibration time is recommended in order to ensure the complete extraction of a metal ion from hydrochloric acid medium. However, a prolonged shaking up to 15 minutes has no adverse effect on the extraction.

Effect of Stripping Agents

In order to strip extracted ruthenium from the organic phase, strippents like mineral acids, alkali, salts, and buffer solutions were used. It was found that concentrated HBr, 1 mol·dm^{-3} NaOH, and 1 mol·dm^{-3} KOH provided quantitative stripping of ruthenium without dilution of the organic phase. Concentrated hydrochloric acid and 2% NaCl quantitatively strip ruthenium

TABLE 1
Extraction of Ruthenium(IV) as a Function of *N*-Octylaniline Concentration
[Ru(IV) = 100 μg; aqueous:organic = 10:10]

HCl (mol·dm^{-3})	*N*-Octylaniline (% v/v)	Extraction (%)	Distribution ratio (*D*)
0.5	1.0	21.6	0.27
	2.0	60.0	1.50
	3.0	75.5	3.08
	4.0	85.7	5.99
	5.0	90.2	9.20
	7.0	95.5	21.20
1.0	1.0	44.3	0.80
	2.0	79.0	3.76
	3.0	91.5	10.76
	4.0	99.9	999.00
	5.0	99.9	999.00
	7.0	99.9	999.00
2.0	2.0	53.1	1.13
	3.0	99.9	999.00
	4.0	99.9	999.00
	5.0	99.9	999.00
	7.0	99.9	999.00
3.0	2.0	50.5	1.02
	3.0	70.2	2.36
	4.0	81.9	4.52
	5.0	99.9	999.00
	7.0	99.9	999.00
4.0	2.0	43.3	0.76
	3.0	64.1	1.79
	4.0	76.6	3.27
	5.0	99.9	999.00
	7.0	99.9	999.00
5.0	2.0	23.2	0.30
	3.0	39.4	0.65
	4.0	54.0	1.17
	5.0	69.0	2.20
	7.0	77.8	3.50

after the organic phase is diluted to 20 mL with xylene. Stripping was incomplete in the presence of salts like potassium chloride, ammonium chloride, and some buffer solutions (Table 2). However, strippents like hydroxides are not suitable for separation studies of platinum metals and gold. Very careful handling is required if concentrated acids are used as strippents.

TABLE 2

Effect of Different Stripping Agents on Stripping of Ruthenium(IV) [ruthenium(IV) = 100 µg]

Stripant	Concentration	%*E*
HCl	Concentrated (2 × 10 mL)	99.9
HBr	Concentrated (2 × 5 mL)	99.9
NaOH	1 $mol \cdot dm^{-3}$ (2 × 5 mL)	99.9
KOH	1 $mol \cdot dm^{-3}$ (2 × 5 mL)	99.9
Na_2CO_3 + $NaHCO_3$ buffer solution	pH 9 (2 × 10 mL)	55.8
HCl + KCl buffer solution	pH 1.3 (2 × 10 mL)	11.2
CH_3COOH + CH_3COONH_4 buffer solution	pH 4.7 (2 × 10 mL)	63.5
KCl	5% (2 × 10 mL)	72.6
NH_4Cl	5% (2 × 10 mL)	20.5
NaCl	2% (40 mL, 10 mL)	99.9

Thus a 2% sodium chloride solution (40 mL, 10 mL) is a suitable strippent for ruthenium.

Extraction with Various Diluents

Different diluents with varying dielectric constant values were used for the extraction of ruthenium(IV) from chloride medium by using the proposed method. It was found that a 5% (v/v) solution of *N*-octylaniline in benzene, toluene, xylene, and carbon tetrachloride provides quantitative extraction of ruthenium(IV). The extraction of ruthenium(IV) was found to be incomplete in amyl acetate (50%) and *n*-butyl acetate (67%) and yielded zero extraction in chloroform, amyl alcohol, *n*-butyl alcohol, 4-methyl-2-pentanol, and methyl isobutyl ketone. Xylene is preferred as the diluent because it has minimum toxicity and offers better phase separation.

Effect of Aqueous to Organic Volume Ratio on Extraction

Ruthenium(IV) was extracted from the aqueous phase in the 10 to 150 mL range at 1 $mol \cdot dm^{-3}$ hydrochloric acid with 10 mL of 5% *N*-octylaniline in xylene. Ruthenium was stripped with 2% sodium chloride solution and estimated as described in the procedure. It was found that the extraction of ruthenium(IV) was quantitative when the aqueous to organic phase volume ratio was 1:1 to 1.5:1, while it decreased when the ratio was changed from 1.5:1 to 15:1. Hence, the aqueous to organic volume ratio recommended in the procedure is 1:1.

The loading capacity of 10 mL of 5% *N*-octylaniline is 5.0 mg of ruthenium(IV).

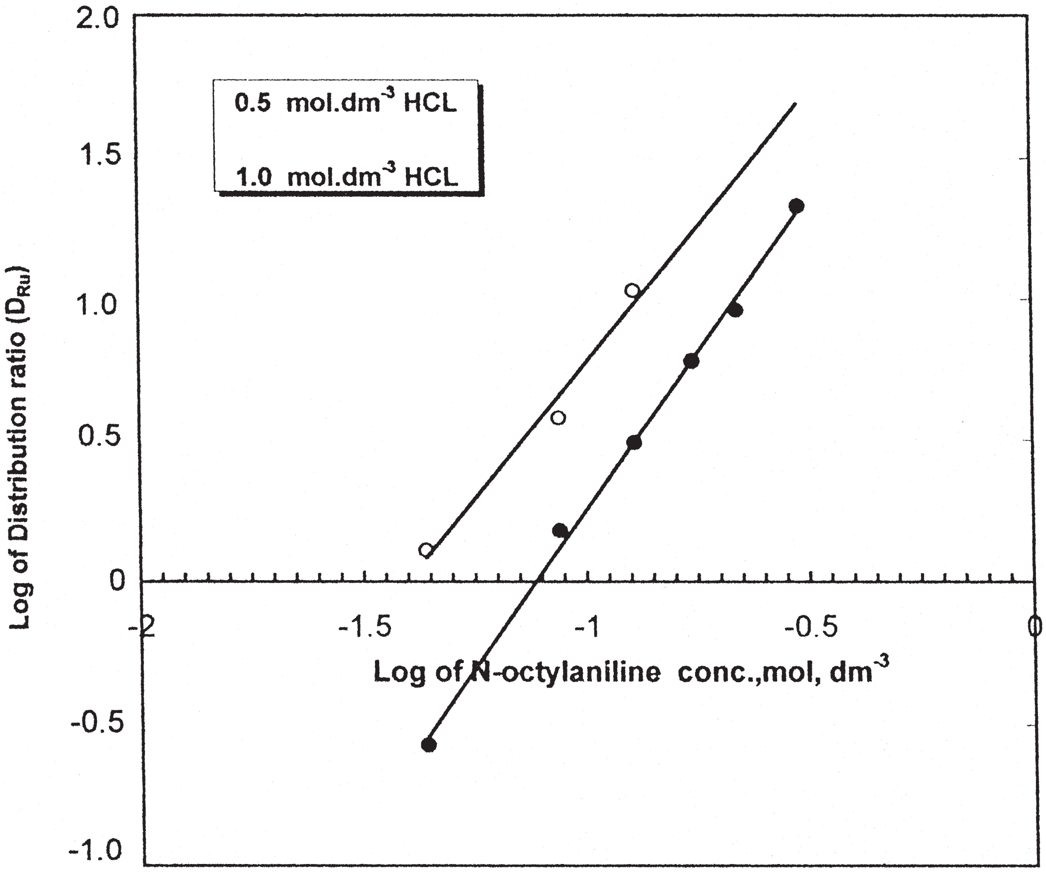

FIG. 2 Log-log plot of distribution ratio (D_{Ru}) versus *N*-octylaniline concentration at 0.5 mol·dm^{-3} HCl and 1.0 mol·dm^{-3} HCl.

Nature of Extracted Species

A log-log plot of the distribution ratio versus *N*-octylaniline concentration (see Fig. 2) at 0.5 and 1.0 mol·dm^{-3} hydrochloric acid showed slopes of 2.2 and 2.4, respectively, indicating that the metal-to-amine ratio in the extracted species is 1:2. Hence the probable extracted species is $[(RR'NH_2^+)_2RuCl_6^{2-}]$ where R = —C_6H_5 and R′ = —$CH_2(CH_2)_6CH_3$. The extraction mechanism is as follows;

$$[RR'NH]_{(org)} + HCl_{(aq)} = [RR'NH_2^+Cl^-]_{(org)}$$

$$2[RR'NH_2^+Cl^-]_{(org)} + [RuCl_6^{2-}]_{(aq)} = [(RR'NH_2^+)_2RuCl_6^{2-}]_{(org)} + 2Cl^-_{(aq)}$$

Effect of Foreign Ion

Ruthenium(IV) was extracted in the presence of a large number of foreign ions. The tolerance limit was set as the amount of foreign ion causing a ±2%

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error in the recovery of ruthenium(IV). It was observed that the method is free from interference from a large number of transition and nontransition metal ions and anions (Table 3). The only species showing interference in the procedure are ascorbate, iodide, thiosulfate, thiocyanate, and thiourea. Of the cations examined, only iron(II), lead(II), cadmium(II), manganese(II), bismuth(III), cerium(IV), and tellurium(IV) interfered. The interference of lead(II), cadmium(II), and cerium(IV) was eliminated by masking with citric acid and that of manganese(II) and tellurium(IV) with tartaric acid. The interference of iron(II) was overcome by oxidizing iron(II) to iron(III) with chlorine water. Bismuth(III) was coextracted and removed by stripping with 4 mol·dm^{-3} hydrochloric acid.

TABLE 3

Effect of Foreign Ions on the Extraction of 0.100 mg of Ruthenium(IV) from 1 mol·dm^{-3} HCl with 5% *N*-Octylaniline Dissolved in Xylene

Foreign ion	Added as	Amount tolerated (mg)	Foreign ion	Added as	Amount tolerated (mg)
Mn(II)[a]	$MnCl_2\cdot 6H_2O$	5	Rh(III)	$RhCl_3\cdot 3H_2O$	0.5
Cd(II)[b]	$CdCl_2\cdot 2^1/_2H_2O$	5	Au(III)	$HAuCl_4\cdot 4H_2O$	0.5
Mg(II)	$MgCl_2\cdot 6H_2O$	20	Ag(I)[e]	$AgNO_3$	10
Fe(II)[c]	$FeSO_4\cdot 7H_2O$	5	Se(IV)	SeO_2	15
Fe(III)	$FeCl_3$	20	Te(IV)[a]	Na_2TeO_3	5
Pb(II)[b]	$Pb(NO_3)_2$	5	Al(III)	$AlCl_3$	20
Hg(II)	$HgCl_2$	5	Sr(II)	$Sr(NO_3)_2$	5
V(V)	$NH_4VO_3\cdot H_2O$	5	Sb(III)	Sb_2O_3	5
U(VI)	$UO_2(NO_3)_2\cdot 6H_2O$	20	Ti(IV)	$K_2TiF_6\cdot H_2O$	10
Ni(II)	$NiCl_2\cdot 6H_2O$	20	Cr(III)	$CrCl_3$	5
Co(II)	$CoCl_2\cdot 6H_2O$	20	In(III)	$InCl_3$	10
Cu(II)	$CuCl_2\cdot 2H_2O$	20	Zr(IV)	$ZrOCl_2\cdot 8H_2O$	20
Bi(III)[d]	$Bi(NO_3)_2\cdot 5H_2O$	5	Tartrate	$C_6H_6O_6$	100
Tl(I)[e]	$TINO_3$	5	Fluoride	NaF	100
Ce(IV)[b]	$Ce(SO_4)_2$	5	Citrate	$C_6H_8O_7\cdot H_2O$	100
Be(II)	$BeSO_4\cdot 4H_2O$	20	Oxalate	$(COOH)_2\cdot 2H_2O$	100
Ca(II)	$CaCl_2$	20	Acetate	CH_3COONa	100
Ba(II)	$BaCl_2\cdot 2H_2O$	20	EDTA	EDTA (disodium salt)	50
Mo(VI)	$(NH_4)_6Mo_7O_{24}\cdot 2H_2O$	20	Malonate	Malonic acid	100
Pd(II)	$PdCl_2\cdot xH_2O$	2.0	Bromide	KBr	50
Pt(IV)	H_2PtCl_6	1.0	Succinate	$HO_2CCH_2CH_2CO_2H$	100
Os(VIII)	OsO_4	1.0	Persulfate	$K_2S_2O_8$	100
Ir(III)	$IrCl_3\cdot xH_2O$	5.0	Salicylate	HOC_6H_4COONa	100

[a] Masked with tartrate.

[b] Masked with citric acid.

[c] Oxidized by Cl_2 water.

[d] Bismuth(III) was backstripped with 4 mol·dm^{-3} HCl (2 × 10 mL).

[e] Centrifuged.

APPLICATIONS

Binary Separation of Ruthenium(IV) from Base Metals

The method permits the separation and determination of ruthenium(IV) from binary mixtures containing either iron(III), cobalt(II), nickel(II), or copper(II).

Ruthenium(IV) is separated from iron(III), cobalt(II), nickel(II) and copper(II) by its extraction with 5% *N*-octylaniline in xylene from 1 mol·dm^{-3} hydrochloric acid (separation scheme). Under this condition all the base metals remain quantitatively in the aqueous phase in the cationic form where they were determined spectrophotometrically with thiocyanate (28), α-nitroso-β-naphthol (28), DMG (28), and pyrimidine-2-thiol (29), respectively. The results were confirmed by the atomic absorption spectroscopic method (AAS). The organic phase was diluted to 20 mL with xylene. Ruthenium was stripped with 2% sodium chloride solution (40 mL, 10 mL). The extracts were combined and evaporated to moist dryness. The residue was leached with 1 mol·dm^{-3} hydrochloric acid to obtain the solution. Ruthenium(IV) was estimated spectrophotometrically with pyrimidine-2-thiol. The recovery of ruthenium(IV) and that of the added ions was 99.3%. The results are reported in Table 4.

Separation of Ruthenium(IV) from Multicomponent Synthetic Mixture

In its natural occurrence ruthenium is always associated with the noble and base metals, hence its separation from these metals is of great importance. The proposed method allows the selective separation and determination of ruthenium from many metal ions (Table 5).

TABLE 4
Extraction Separation of Ruthenium(IV) from Base Metals

Composition of metal ion (μg)	Recovery of ruthenium(IV)[a] (%)	RSD (%)	Recovery of added metal ion[a] (%)	RSD (%)
Ru, 200; Fe, 10,000	99.0	0.23	99.2	0.27
Ru, 200; Co, 10,000	99.4	0.24	99.4	0.26
Ru, 200; Ni, 10,000	99.2	0.21	99.5	0.24
Ru, 200; Cu, 10,000	99.2	0.22	99.4	0.26

[a] Average of six determinations.

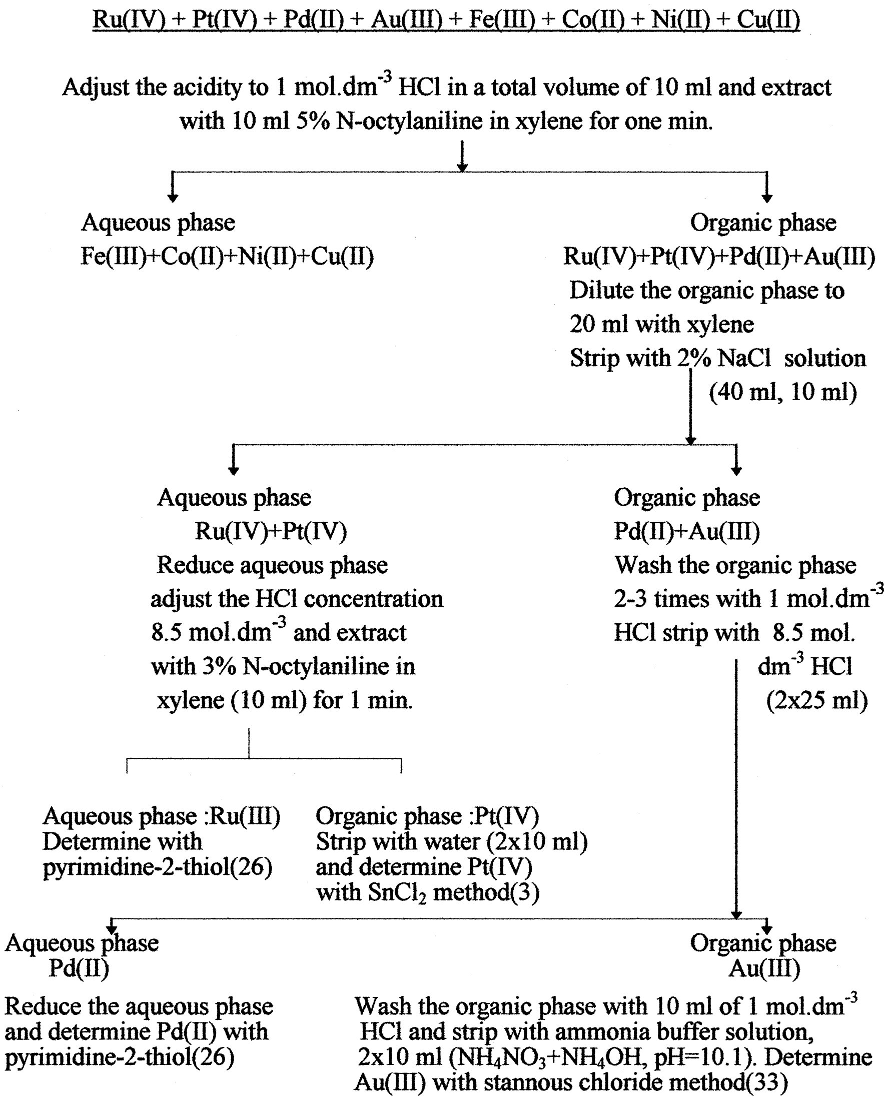
TABLE 5
Analysis of Synthetic Mixtures

Composition (μg)	Ruthenium(IV) found[a] (μg)	Recovery (%)	RSD (%)
Ru, 200; Pd, 1000	199.2	99.6	0.20
Ru, 200; Pt, 1000	198.4	99.2	0.19
Ru, 200; Os, 1000	198.2	99.1	0.21
Ru, 200; Rh, 500	198.0	99.0	0.17
Ru, 200; Ir, 1000	197.8	98.9	0.22
Ru, 200; Au, 1000	198.2	99.1	0.21
Ru, 200; Pt, 500; Pd, 500	198.0	99.0	0.24
Ru, 200; Pt, 500; Au, 500	197.6	98.8	0.23
Ru, 200; Pd, 500; Au, 500	198.0	99.0	0.23
Ru, 200; Os, 500; Ir, 500	197.4	98.7	0.22
Ru, 200; Os, 500; Rh, 500	197.6	98.8	0.24
Ru, 200; Ir, 500; Rh, 500	198.0	99.0	0.21
Ru, 200; 10,000 μg each Fe, Co, Ni, and Cu	198.0	99.0	0.20
Ru, 200; Au, 200; Pt, 200; Pd, 200; Os, 200; Rh, 200; Ir, 200	197.4	98.7	0.22
Ru, 200; Au, 200; Pt, 200; Pd, 200; Os, 200; Rh, 200; Ir, 200; 10,000 each Fe, Co, Ni, and Cu	197.8	98.9	0.23

[a] Average of six determinations.

Extraction Scheme for Separation of Ruthenium(IV), Platinum(IV), Palladium(II), Gold(III), and Base Metals and Its Application to Alloys

The extraction study showed that it is possible to separate ruthenium(IV) from platinum(IV), palladium(II), gold(III), and the base metals from one another. Under the optimum conditions for ruthenium(IV), separation there is quantitative extraction of platinum(IV), palladium(II), gold(III), and osmium(VIII), and no extraction of iridium(IV), rhodium(III), and the base metals. Hence the separation can be achieved by the use of different stripants. The extraction scheme is presented in the form of a flow sheet (Fig. 3). Real samples were not available at the working site, which forced us to use synthetic mixtures containing ruthenium(IV), platinum(IV), palladium(II), gold(III), and the base metals corresponding to the various alloys. A complete list is given in Table 6.



Ru(IV) + Pt(IV) + Pd(II) + Au(III) + Fe(III) + Co(II) + Ni(II) + Cu(II)

Adjust the acidity to 1 mol.dm^{-3} HCl in a total volume of 10 ml and extract with 10 ml 5% N-octylaniline in xylene for one min.

Aqueous phase
Fe(III)+Co(II)+Ni(II)+Cu(II)

Organic phase
Ru(IV)+Pt(IV)+Pd(II)+Au(III)
Dilute the organic phase to 20 ml with xylene
Strip with 2% NaCl solution (40 ml, 10 ml)

Aqueous phase
Ru(IV)+Pt(IV)
Reduce aqueous phase adjust the HCl concentration 8.5 mol.dm^{-3} and extract with 3% N-octylaniline in xylene (10 ml) for 1 min.

Organic phase
Pd(II)+Au(III)
Wash the organic phase 2-3 times with 1 mol.dm^{-3} HCl strip with 8.5 mol. dm^{-3} HCl (2x25 ml)

Aqueous phase :Ru(III)
Determine with pyrimidine-2-thiol(26)

Organic phase :Pt(IV)
Strip with water (2x10 ml) and determine Pt(IV) with $SnCl_2$ method(3)

Aqueous phase
Pd(II)
Reduce the aqueous phase and determine Pd(II) with pyrimidine-2-thiol(26)

Organic phase
Au(III)
Wash the organic phase with 10 ml of 1 mol.dm^{-3} HCl and strip with ammonia buffer solution, 2x10 ml (NH_4NO_3+NH_4OH, pH=10.1). Determine Au(III) with stannous chloride method(33)

* Ru(IV), 200 μg +Pt(IV), 200 μg + Pd(II), 200 μg + Au(III), 200 μg + 5000 μg each of Fe(III), Co(II), Ni(II) and Cu(II).

FIG. 3 Separation scheme flow sheet.

Extraction Separation and Determination of Ruthenium in Fissium Alloy

If a fissium alloy is to be analyzed, it should be dissolved according to a standard procedure (30). The proposed method permits the extraction, separation, and determination of ruthenium(IV) in a synthetic mixture containing ruthenium(III), uranium(VI), zirconium(IV), palladium(II), rhodium(III), and molybdenum(VI). This mixture has a composition (30) similar to a fissium al-

TABLE 6
Extraction Separation and Determination of Platinum Metals and Gold in Synthetic Mixture Corresponding to Alloys and Mineral
(mean values of six determinations)

	Palladium		Osmium		Ruthenium		Platinum		Rhodium		Iridium		Gold	
Mixture	Taken (µg)	Recovery (%)	Taken (µg)	Recovery (%)	Taken (µg)	Recovery (%)	Taken (µg)	Recovery (%)	Taken (µg)	Recovery (%)	Taken (µg)	Recovery (%)	Taken (µg)	Recovery (%)
Neuyanskite alloy	—	—	650	—	50	99.2	400	99.5	100	—	3100	—	—	—
	—	—	700	—	50	99.0	600	99.4	150	—	3250	—	—	—
Osmiridium alloy	—	—	200	—	25	99.1	60	99.2	125	—	400	—	10	99.0
	—	—	325		80	99.0	100	99.4	110	—	450	—	10	99.0
Jewelery	500	99.5			24	99.4								
	1000	99.6			48	99.5								
	1200	99.4			57	99.2								

TABLE 7
Extraction, Separation, and Determination of Ruthenium in Synthetic Mixture Corresponding to Fissium Alloy

Metal ion added (μg)[a]						Ru(IV)[b] recovery (%)	RSD (%)	Added ion[b] recovery (%)	RSD (%)
U^{I}	Zr^{II}	Pd^{III}	Rh^{IV}	Mo^{V}	Ru				
10,000	—	—	—	—	200	99.2	0.20	99.7	0.29
—	200	—	—	—	200	99.4	0.21	99.6	0.25
—	—	500	—	—	200	99.6	0.20	99.2	0.26
—	—	—	200	—	200	99.5	0.19	99.9	0.24
—	—	—	—	500	200	99.2	0.23	99.8	0.28
1,900	1	1	1	50	40	99.3	0.22	—	—
3,800	2	2	2	100	80	99.0	0.20	—	—
5,700	3	3	3	150	120	99.5	0.23	—	—
7,600	4	4	4	200	160	99.4	0.24	—	—
9,500	5	5	5	250	200	99.2	0.24	—	—

[a] Determined spectrophotometrically with i) PAR (31) ii) xylenol orange (32) iii) pyrimidine-2-thiol (26), iv) stannous chloride (33), v) thiocyanate (32).
[b] Average of six determinations.

loy which is used as a fuel for Experimental Breeder Reactor II. The results of binary and various synthetic mixtures of ruthenium(IV) with the above elements are reported in Table 7. Under the optimum extraction condition of ruthenium(IV), there is quantitative extraction of palladium(II) and no extraction of uranium(VI), zirconium(IV), molybdenum(VI), and rhodium(III). Coextracted palladium(II) was separated by the separation scheme and all the added metal ions were estimated from the aqueous phase by applying standard procedures.

CONCLUSIONS

The results of the experiment indicate that *N*-octylaniline in chloride form extracts ruthenium(IV) in chloride media. The extraction mechanism corresponds to an anion exchange in which a complex of stoichiometric formula $[(RR'NH_2^+)_2RuCl_6^{2-}]$ is formed in the organic phase while at the same time liberating Cl^- ions in the aqueous phase. The use of nontoxic solvents like xylene was favorable. The method permits the separation of ruthenium(IV) from base metals, other platinum group metals, and gold, which are commonly associated with its natural occurrence. *N*-Octylaniline can be synthesized at low cost, with high yield, in the best purity, and recovered for reuse without loss of extraction efficiency. The time needed for equilibration is short for *N*-octylaniline, namely 30 seconds, as compared to 10 minutes for 4-octylaniline.

The method is applicable to the analysis of ruthenium(IV) in synthetic mixtures with compositions corresponding to alloys. The method is simple, rapid, selective, and reproducible, requiring only 30 minutes for separation and determination.

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