CROATICA CHEMICA ACTA
CCACAA **78** (4) 617–626 (2005)

ISSN-0011-1643
CCA-3055
Original Scientific Paper

Extraction of Ruthenium and Its Separation from Rhodium and Palladium with 4-Pyridone Derivatives

Vinka Drušković,[a] Vlasta Vojković,[b,]* and Tatjana Antonić[c]

[a]*Research & Development, Belupo Ltd. Pharmaceuticals & Cosmetics, Radnička cesta, 10000 Zagreb, Croatia*

[b]*Laboratory of Analytical Chemistry, Faculty of Science, University of Zagreb, Strossmayerov trg 14, 10000 Zagreb, Croatia*

[c]*Laboratory for the Synthesis of New Materials, Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia*

RECEIVED MARCH 2, 2004; REVISED MAY 3, 2005; ACCEPTED MAY 3, 2005

Keywords
extraction
gama-pyridone
palladium
rhodium
ruthenium
separation
spectrophotometry

Formation of a yellow chelate complex of ruthenium(III) with 3-hydroxy-2-methyl-1-phenyl--4-pyridone or 3-hydroxy-2-methyl-1-(4-tolyl)-4-pyridone in the aqueous phase and extraction of the chelates in dichloromethane were used for spectrophotometric determination of ruthenium. Beer's law was obeyed over the concentration range of 0.1–20.0 μg cm^{-3} ruthenium. Molar absorptivity was 1.35×10^4 mol^{-1} dm^3 cm^{-1} (organic phase, at 393 nm) and 1.29×10^4 mol^{-1} dm^3 cm^{-1} (aqueous phase, at 367 nm), irrespective of the reagent used. The method was successfully applied to the determination of ruthenium in synthetic mixtures. Extraction of a chelate complex of ruthenium(III) with 3-hydroxy-2-methyl-1-phenyl-4-pyridone proved to be a simple and efficacious method for the separation of ruthenium(III) from large amounts of palladium(II) and rhodium(III).

INTRODUCTION

Ruthenium is a scarce element that is found in about 10^{-8} % of the earth's crust. It is present in much larger amounts in chondrite and, especially, in iron meteorites ($(1\text{-}6) \times 10^{-4}$ %). It usually occurs in association with other platinum group metals.[1]

As one of the most effective hardeners in high-density alloys, ruthenium is widely used in the electronic industry. Alloyed with other platinum metals it serves to make electrical contacts for heavy wear resistance. Recently, platinum metals, especially ruthenium and its chlorocomplexes, have been much used in the catalytic oxidation of some organic compounds. Ruthenium and its alloys also have a widespread application in jewellery.[1]

In radiochemistry, the interest lies in the separation of rhodium from ruthenium since rhodium is a daughter of ruthenium by beta decay.[2]

The growing use of ruthenium in widely different fields has made it necessary to develop simple, inexpensive and sensitive methods for its determination. When ruthenium is present in various matrices in extremely low concentrations, direct determination is not successful without previous preconcentration and separation.

---

* Author to whom correspondence should be addressed. (E-mail: vlastavojkovic@yahoo.com)

Separation procedures (volatilization, coprecipitation, solvent extraction, sorption and chromatography) can be used to isolate and preconcentrate ruthenium from multi-component samples containing noble and base metals.[3]

A conventional method for the separation of ruthenium from the platinum metals is based on the distillation of volatile ruthenium tetroxide.[3,4] Different oxidants ($HClO_4$+H_2SO_4, $NaBiO_3$, $K_2Cr_2O_7$ and $KMnO_4$) for ruthenium have been used. This, however, is not an appropriate method for producing ruthenium on an industrial scale because it requires complicated manipulation and because of the explosive property of tetroxide at temperatures above 180 °C. Therefore, solvent extraction is preferred to distillation.[1] For metal preconcentration, the tetroxide can be extracted into carbon tetrachloride,[5-7] chloroform,[5] or mephasine.[8]

Precipitation methods are rarely used to isolate ruthenium from multi-component mixtures due to lack of selective precipitants.[3] However, ruthenium concentration can be achieved by the solvent flotation method.[9] The method is based on the ion associate formed by the anionic chloride complex of ruthenium $RuCl_6^{2-}$ with the basic dye Rhodamine 6G. It precipitates when the aqueous solution is shaken with toluene. The separated compound is soluble in acetone.

Various complexing agents (*e.g.,* di(2-ethylhexyl)-phosphonic acid,[10] carbamates,[3] dithizone,[3] and thiourea derivatives[3]) can be used in separation procedures to convert ruthenium into stable extractable species.

The chlorocomplexes of ruthenium are extractable by means of various organophosphorus compounds[11] and high-molecular-weight amines.[11,12] Amine, dissolved in an organic diluent, is transformed into organic cation (R_xNH^+) by reacting with the acid present in aqueous solution. The cation reacts with the anionic complex of the analyte in solution by forming an ion-pair, dissolved in the organic solvent used as diluent.

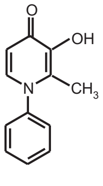
Ruthenium can be separated from platinum metals after its conversion into a thiocyanate complex.[13–17] A high distribution coefficient is achieved when polyurethane foam is applied in ruthenium extraction from thiocyanate media.[16] Surfactant extraction of ruthenium from thiocyanate media into Triton X-100 phase in the presence of Zephiramine has been investigated.[17]

Solvent-extraction processes are well established and efficient techniques for the separation of ruthenium from platinum and palladium,[12,18] rhodium,[14,18] osmium, and iridium.[18,19]

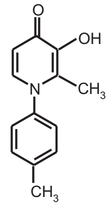
UV-VIS spectrophotometry is widely applied for the determination of microgram amounts of ruthenium. Extraction is the first step to be taken before spectrophotometric determination of ruthenium.[12, 20–31]

Recently, gamma-pyridone derivatives, 3-hydroxy-2-methyl-1-phenyl-4-pyridone (HX) or 3-hydroxy-2-methyl--1-(4-tolyl)-4-pyridone (HY), have been used as effective extracting spectrophotometric reagents to determine palladium(II),[32] and spectrophotometric or fluorimetric reagents to determine iridium(IV).[33,34]

In the present paper, we report the results of studies of the reaction between ruthenium(III) and HX(HY) with the intention to elucidate the spectrophotometric determination of ruthenium in the aqueous phase or in the organic phase after extraction with some organic solvents, and to use the data to open new possibilities for the separation of ruthenium from other platinum metals.



3-Hydroxy-2-Methyl-1-Phenyl-4-Pyridone (HX)



3-Hydroxy-2-Methyl-1-(4-Tolyl)-4-Pyridone (HY)

EXPERIMENTAL

Reagents

A stock solution of ruthenium(III) (1×10^{-2} mol dm^{-3}) was prepared by dissolving $(NH_4)_2RuCl_5 \cdot H_2O$ (Johnson Matthey, New York, USA) in 1 mol dm^{-3} HCl. The solution was standardized spectrophotometrically with thiourea[35] and checked with the ruthenium atomic absorption standard solution (Johnson Matthey).

Rhodium(III) and palladium(II) stock solutions (0.02 and 0.01 mol dm^{-3}) were prepared from $RhCl_3$ or $PdCl_2$ (Fluka, Buchs, Switzerland) in 0.05 mol dm^{-3} HCl. The solutions were standardized gravimetrically[36] with the dimethylglyoxime (palladium) and zinc (rhodium). Working solutions were obtained by appropriate dilution of the stock solution with deionized water.

3-Hydroxy-2-methyl-1-phenyl-4-pyridone (HX), and 3-hydroxy-2-methyl-1-(4-tolyl)-4-pyridone (HY) were synthesized as described previously.[37] Solutions were prepared by dissolving weighed amounts of HX in water (heating time 15 minutes at about 80 °C) and of HY in 96 % (v/v) ethanol.

Thiourea, 10 %, w/v aqueous solution.

A solution of alkali metal salts and a solution of different metals were used to study ion interference.

All the chemicals used were of analytical-reagent grade.

Apparatus

A Varian double-beam spectrophotometer, model Cary 3, equipped with 1-cm quartz cells, was used for absorption measurements. Determination of palladium, ruthenium and rhodium in the aqueous phase after extraction was performed on a Perkin Elmer atomic absorption spectrometer, model 3030B. Operating conditions are given in Table I.

TABLE I. Operating conditions for ruthenium, rhodium and palladium determination by AAS

R.f. generator	50/60 Hz, operating power 500 W
Gas flow	air: 45 dm^3/min; acetylene: 20 dm^3/min
Ruthenium	0.57 mol dm^{-3} HCl; 0.15 mol dm^{-3} HNO_3; 0.5 % $LaCl_3$; 349.9 nm
Rhodium	2.7 mol dm^{-3} HCl; 0.07 mol dm^{-3} Na_2SO_4; 343.5 nm
Palladium	0.5 mol dm^{-3} HCl; 244.8 nm

A Griffin flask shaker with a time switch served for extraction. The pH of the aqueous phase was measured with a Radiometer PHM 85 precision pH-meter.

General Extraction Procedure

A known volume of the working ruthenium solution and a given amount of HX(HY) were mixed and diluted to about 6 cm^3. The pH was adjusted to 6.5 (Ru^{III}-HX) or 7.0 (Ru^{III}--HY) with the addition of NaOH. The solution was transferred quantitatively to a 10-cm^3 standard flask, heated at 75 °C for 15 minutes, cooled to room temperature in ice water and finally diluted to volume. An aliquot was used for absorbance measurement at 367 nm. Another aliquot (5 cm^3) was shaken with an equal volume of dichloromethane in a 50-cm^3 conical flask with a mechanical shaker for 20 min. After the phases were separated by gravity for each experimental point, aliquots of the organic and aqueous phases were used for absorbance measurements at 393 and 367 nm.

Ruthenium(III) concentrations in the aqueous phase were determined by atomic absorption spectrometry (AAS) after appropriate dilution. The difference between the initial ruthenium concentration and its final concentrations in the aqueous phase after extraction was assumed to be equal to its concentration in the organic phase. The distribution coefficient was calculated from the concentration ratio of the metal in the organic phase to the metal left in the water solution.

Procedure for Palladium Separation from Ruthenium

Separation of palladium(II) from ruthenium(III) was carried out at room temperature by shaking equal volumes (10 cm^3) of HX in chloroform and the aqueous phases with a mechanical shaker in a 50-cm^3 conical flask for 35 minutes. The aqueous phase consisted of $1 \cdot 10^{-4}$ mol dm^{-3} Pd^{II} and ruthenium(III) in the corresponding excess (see Table VIII). The pH was adjusted to 2.5 by addition of sulphuric acid and sodium sulphate (μ = 0.2 mol dm^{-3}). After the phases were separated by gravity for each experimental point, their aliquots were used. Concentrations of the metals that remained in the aqueous phase were determined by atomic absorption spectrometry (AAS) after dilution, as described above. The experiments were carried out in duplicate.

Procedure for Ruthenium Separation from Rhodium

A known volume of the working ruthenium solution with the corresponding excess of rhodium(III) (see Table VIII), and a given amount of HX were mixed and diluted to about 15 cm^3. The pH was adjusted to 6.5 by addition of NaOH. The solution was transferred quantitatively to a 25-cm^3 standard flask, heated at 75 °C for 15 minutes, cooled to room temperature in ice water and finally diluted to volume. The final ruthenium(III) and HX concentrations were $5 \cdot 10^{-5}$ mol dm^{-3} and $4.5 \cdot 10^{-3}$ mol dm^{-3}.

An aliquot (10 cm^3) was shaken with an equal volume of dichloromethane in a 50-cm^3 conical flask with a mechanical shaker for 20 min. Concentrations of the metals that remained in the aqueous phase were determined by atomic absorption spectrometry (AAS) after dilution, as described above. The experiments were carried out in duplicate.

Synthetic Mixtures

Different amounts of metal salts, including those of ruthenium, were mixed. A mixture (about 0.5 g) was dissolved in 1 cm^3 concentrated hydrochloric acid by heating. After cooling to room temperature, it was diluted with deionized water to 25.0 cm^3 in a calibrated flask. Aliquots of sample solution were analyzed for ruthenium as described above.

RESULTS AND DISCUSSION

Optimum Conditions for Ruthenium Extraction

The extraction process consisted of two steps – the formation of a complex between ruthenium(III) and HX or HY in the aqueous phase, and the extraction of the complex in dichloromethane. As ruthenium(III) formed a complex with 4-pyridone derivatives quantitatively only under heating, the effect of temperature and the heating time on the formation of the Ru^{III}-HX(HY) complex in the aqueous phase and on its extraction in dichloromethane was determined by heating the aqueous phase before extraction. The optimal heating time was 10 minutes at 65 °C (Figure 1).

The effect of acidity on the formation and extraction of the Ru^{III}-HX(HY) complex into organic solvent was investigated at different pH values. Extraction of ruthenium(III) with HX(HY) was carried out over the pH range from 2 (the initial pH as a result of stock solution acidity) to 8.5 (adjusted by the addition of NaOH). The efficiency of ruthenium extraction at one stage was about 80–82 % at pH 5.5–8.5 (for Ru^{III}-HX) and pH 6–8.5 (for Ru^{III}-HY) (Table II). Therefore, in subsequent studies a pH of 6.5 (7.0) was maintained throughout the experiment. For complete formation of the complex in the aqueous phase and its extraction in the organic phase, the minimum molar ratio of ligand to ruthenium was HX(HY) : Ru^{III} = 70 : 1 (Figure 2).

To test the feasibility of developing a ruthenium recovery process based on the HX(HY) reagent, the back--extraction properties of the Ru^{III}-HX(HY) complex from dichloromethane were studied using various mineral acids

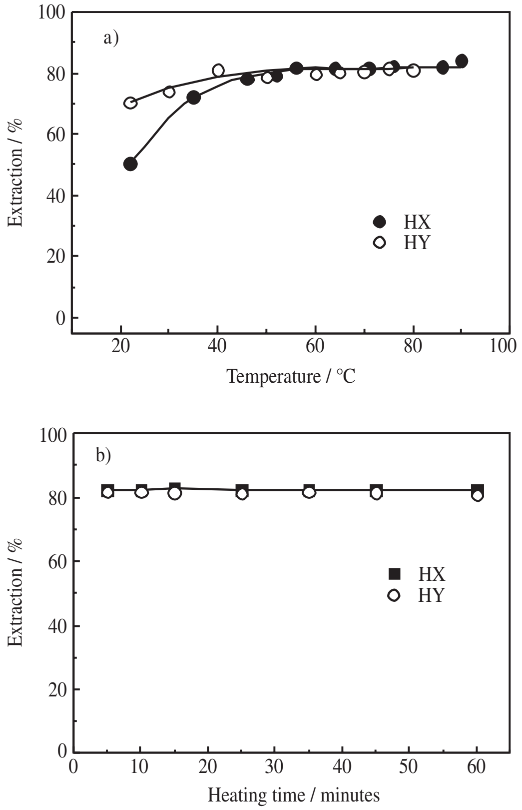


Figure 1. Effect of temperature (a) and heating time (b) of the aqueous phase on percent extraction of Ru^{III}-HX(HY) complexes: $c(Ru^{III}) = 5 \times 10^{-5}$ mol dm^{-3}; $c(HX) = 4.5 \times 10^{-3}$ mol dm^{-3}; $pH_{aqueous\ phase} = 6.5$ or $c(Ru^{III}) = 5 \times 10^{-5}$ mol dm^{-3}; $c(HY) = 4.5 \times 10^{-3}$ mol dm^{-3}; $pH_{aqueous\ phase} = 7.0$; $\varphi(EtOH) = 30$ %. a) heating time = 15 minutes; b) temperature = 75 °C.

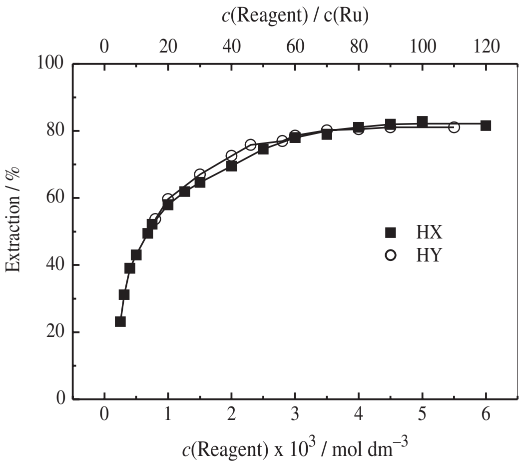


Figure 2. Dependence of percent extraction of Ru^{III}-HX(HY) on the initial reagent concentrations: $c(Ru^{III}) = 5 \times 10^{-5}$ mol dm^{-3}; pH = 6.5; varied HX or $c(Ru^{III}) = 5 \times 10^{-5}$ mol dm^{-3}; $\varphi(EtOH) = 30$ %; pH = 7.0; varied HY.

as stripping reagents. Percentages of the stripped ruthenium, extracted under optimal conditions, were 96 with ≥ 5 mol dm^{-3} H_2SO_4 and 88 with 5 mol dm^{-3} HCl.

TABLE II. Dependence of the percent of Ru^{III}-HX(HY) complex extraction on the initial pH

pH	Extraction / %	
	HX	HY
2.0	1.5	0.6
2.5	2.7	0.9
3.0	4.9	2.9
3.5	9.5	20.7
4.0	16.6	34.1
4.5	36.5	52.7
5.0	58.7	71.3
5.5	81.8	76.8
6.0	81.0	79.4
6.5	82.5	80.4
7.1	82.4	82.2
7.5	81.9	80.4
8.0	80.8	81.9
8.5	82.1	80.5

$c(Ru) = 5 \times 10^{-5}$ mol dm^{-3}; $c(HX\ or\ HY) = 4.5 \times 10^{-3}$ mol dm^{-3}

Spectrophotometric Measurements

The Ru^{III}-HX(HY) complex was used for spectrophotometric determination of ruthenium in the aqueous phase, or in the organic phase after extraction with dichloromethane.

The absorption spectra in the aqueous and organic layers were measured against a reagent blank. The absorption maximum of the yellow complex in the aqueous and organic phases depended on the acidity of the aqueous phase (Figure 3), on its heating temperature and on ligand concentration. For a simpler illustration, the absorption spectra of the Ru^{III}-HX complex are presented.

The spectra had a constant maximum at 367 nm (aqueous phase) and 393 nm (organic phase) if the pH was in the 4.5–8.5 range, heating temperature 50 °C or higher, and molar ratio HX(HY) : Ru^{III} = 15(10) : 1 and higher. As the blank did not show a measurable absorbance at 367 nm and 393 nm, measurements could be made against the solvent.

The optimum pH ranges for constant absorbance in the aqueous and organic layers were 5.5-8.5 (Ru^{III}-HX) and 6.0–8.5 (Ru^{III}-HY) (Figure 4). At pH = 6.5(7.0), the Ru^{III}-HX(HY) complex failed to show any significant change in absorbance for up to 20 hours at room temperature.

To prevent ruthenium hydrolysis, the effect of ethyleneglycol on the colour reaction of Ru^{III} was studied. In the presence of 0.1–1 cm^3 ethyleneglycol, at an optimal pH value, the absorption of the chromogenic system increased only from one to four percent. Accordingly,

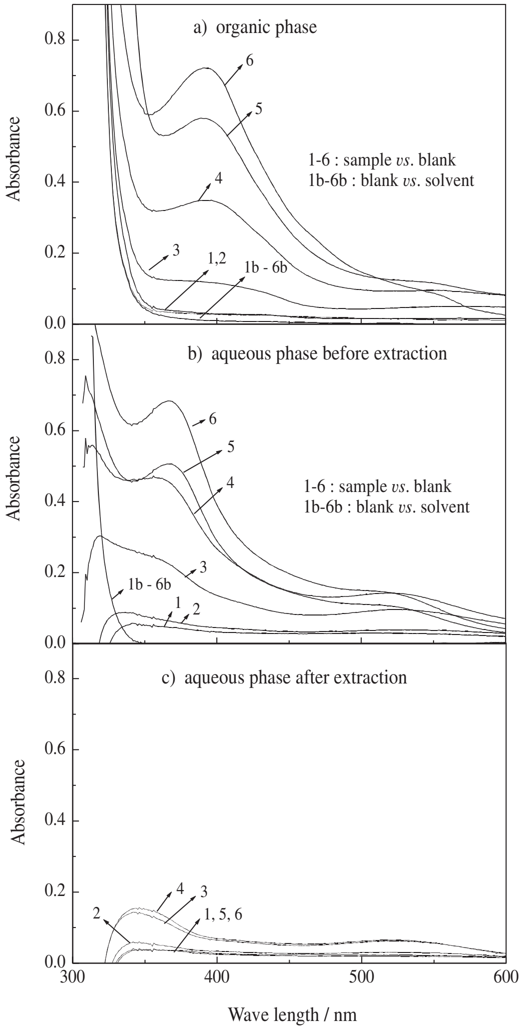


Figure 3. Effect of the aqueous phase pH on absorption spectra of the Ru^{III}-HX complex: c(Ru^{III}) = 5 × 10^{-5} mol dm^{-3}; c(HX) = 4.5 × 10^{-3} mol dm^{-3}. pH: (1) 2.0; (2) 3.0; (3) 3.3; (4) 4.3; (5) 4.8; (6) ≥5.5.

all further measurements were without the addition of ethyleneglycol.

In contrast to HX, which is soluble in hot water, HY is soluble in ethanol. Thus, before extraction the aqueous phase consisted of 15 % EtOH as a result of addition of the HY solution. The effect of ethanol in the 15-65 % range on the extraction and spectrophotometric determination of ruthenium(III) with HY was investigated. The relationships between the absorbance value and the C_2H_5OH yield are shown in Figure 5. At a lower ethanol yield, up to 30 (v/v) %, the absorbance was maximal and constant. The absorbance in the aqueous and organic phases decreased with an increasing percentage of ethanol.

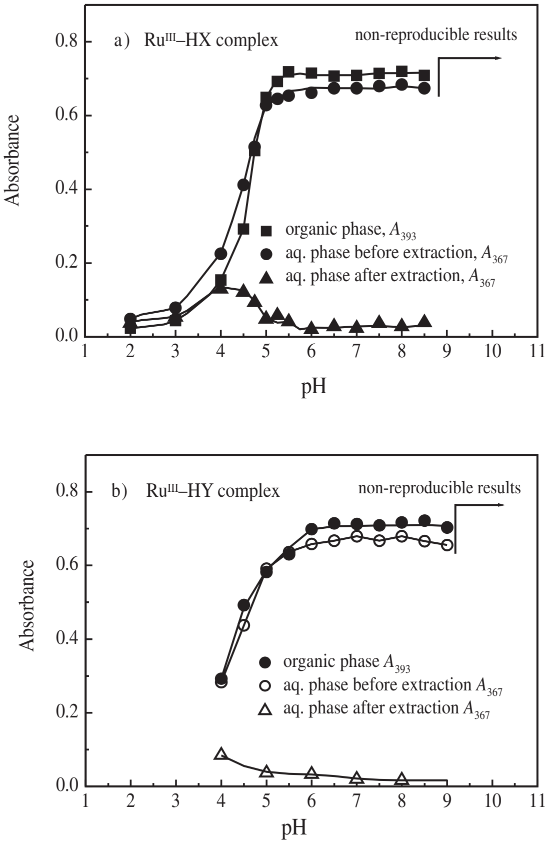


Figure 4. Effect of pH on the formation of Ru^{III}-HX(HY) complex and its extraction in dichloromethane: c(Ru^{III}) = 5 × 10^{-5} mol dm^{-3}; c(HX) = 4.5 × 10^{-3} mol dm^{-3} or c(Ru^{III}) = 5 × 10^{-5} mol dm^{-3}; c(HY) = 4.5 × 10^{-3} mol dm^{-3}; φ(EtOH) = 30 %.

TABLE III. Effect of the solvent nature on the absorbance of the Ru^{III}-HX(HY) complex organic layer

Solvent	Dielectric constant (~20 °C)[39]	A_{393}	
		HX	HY
Toluene	2.4	0.037	0.036
Benzene	2.3	0.028	0.031
Cyclohexane	2.0	0.043	0.039
Chloroform	5.1	0.714	0.715
Dichloromethane	9.08	0.715	0.718
1,2-Dichloroethane	10.5	0.629	0.731
1-Octanol	10.8	0.603	0.661
MIBK	13.1	0.052	0.065
Isoamyl alcohol	15.8	0.043	0.041
Butanol	17.8	0.024	0.021

c(Ru^{III}) = 5.0 × 10^{-5} mol dm^{-3}; shaking time 20 min;
c(HX) = 4.5 × 10^{-3} mol dm^{-3}; pH$_{\text{aqueous phase}}$ = 6.5, or
c(HY) = 3.5 × 10^{-3} mol dm^{-3}; pH$_{\text{aqueous phase}}$ = 7.0; φ(EtOH) = 30 %

Different organic solvents were employed for extraction of the Ru^{III}-HX(HY) complex. The results (Table III) show that the complex extraction varied with the nature of the diluent, and that ruthenium extraction was enhanced with diluents such as chloroform, dichloromethane, dichloroethane, 1-octanol having middle dielectric constants. On the other hand, diluents having lower or higher dielectric constants led to lower ruthenium(III) extraction with both reagents. For commercial

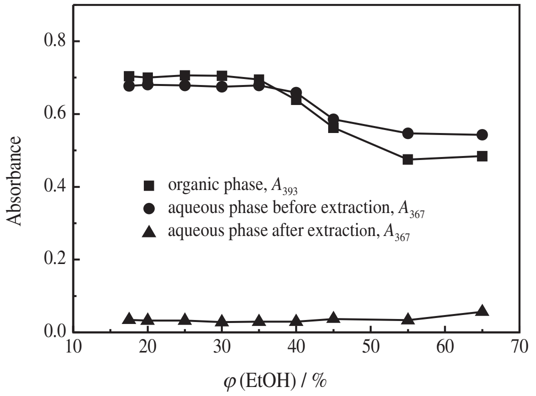


Figure 5. Effect of ethanol on the formation of Ru(III)-HY complex and its extraction in dichloromethane: c(Ru^{III}) = 5 × 10^{-5} mol dm^{-3}; c(HY) = 4.5 × 10^{-3} mol dm^{-3}; pH = 7.0.

purposes, chloroform or dichloromethane may be replaced by 1-octanol.

The ratio of ruthenium to HX and HY was determined by a logarithmic method[38] and was 1:1 in the aqueous and organic layers.

A calibration graph for ruthenium(III) determination was constructed using the optimal conditions. Linear calibration graphs were obtained in the range 0.1–20.2 μg/cm^3 of ruthenium(III). The calibration lines for ruthenium(III) determination fit the equations:

Ru^{III}-HX(HY)	Org. phase	$A = 0.0338 + 0.1350\ C$	$n = 11$	$R = 0.999$
	Aq. phase	$A = 0.0261 + 0.1291\ C$	$n = 11$	$R = 0.993$

C – ruthenium concentration (μg cm^{-3})

Molar absorptivity was 1.35×10^4 mol^{-1} dm^3 cm^{-1} (organic phase) and 1.29×10^4 mol^{-1} dm^3 cm^{-1} (aqueous phase) for both reagents. To examine the accuracy and precision of the method, ten successive measurements were carried out with the standard solution containing 0.509 μg cm^{-3} ruthenium(III) (Table IV). The results showed the system to be accurate and to have a relatively good reproducibility.

To assess the usefulness of the proposed method, the effects of diverse ions that often associate with ruthenium(III) were studied. Ruthenium(III) was determined as the Ru^{III}-HX(HY) complex under the optimal conditions, as described in Experimental, *General Extraction Procedure*. Tolerance to foreign ions was tested with solutions containing 5.05 μg ruthenium(III) per cm^3. The tolerance limit was taken to be the amount that caused ± 3 % change in absorbance. Table V shows the tolerance limits.

TABLE IV. Accuracy and precision of the spectrophotometric determination of ruthenium(III) with HX(HY)

Parameter	Ru^{III}–HX		Ru^{III}–HY	
	Organic phase	Aqueous phase	Organic phase	Aqueous phase
$\bar{x}$ / μg Ru cm^{-3}	0.509	0.503	0.513	0.508
95 % CL / μg cm^{-3}	±0.003	±0.002	±0.005	±0.004
RSD / %	0.78	0.48	1.21	0.91

c(HX) = 4.5 × 10^{-3} mol dm^{-3}; $pH_{aqueous\ phase}$ = 6.5 or
c(HY) = 4.5 × 10^{-3} mol dm^{-3}; $pH_{aqueous\ phase}$ = 7.0; φ(EtOH) = 30 %
CL-confidence limit; (n = 10)

TABLE V. Tolerance limits for ruthenium in presence of foreign ions

Foreign ions	Tolerance limit [Ion] / [ruthenium(III)]
Na^I, K^I, Li^I, chloride	5000
Bromide	2500
Sulphate, NH_4^+	1000
Perchlorate	500
Acetate	250
Ba^{II}, Ca^{II}, Mg^{II}	100
Zn^{II}, Cd^{II}, nitrate, carbonate	50
Cr^{III}, Al^{III}	20
Os^{VIII}, Mn^{II}, Co^{II}	10
Citrate, tartarate, thiocyanate	1
Fe^{III}, Os^{IV}, arsenate, oxalate	<1

c(Ru^{III}) = 5 × 10^{-5} mol dm^{-3}; c(HX) = 4.5 × 10^{-3} mol dm^{-3};
$pH_{aqueous\ phase}$ = 6.5 or
c(HY) = 4.5 × 10^{-3} mol dm^{-3}; $pH_{aqueous\ phase}$ = 7.0; φ(EtOH) = 30 %;

Studies of the use of gama-pyridone derivatives in the extraction and spectrophotometric determination of metal ions in the presence of HY showed a synergistic effect, and some metal ions were extracted from more acidic solutions than in the presence of HX.[39–47] In this work, the effect of HX was found to be comparable to that of HY. However, extraction of the ruthenium-HY complex was carried out from a mixed water-ethanol solution. For simplicity, same HX was used throughout the experiment.

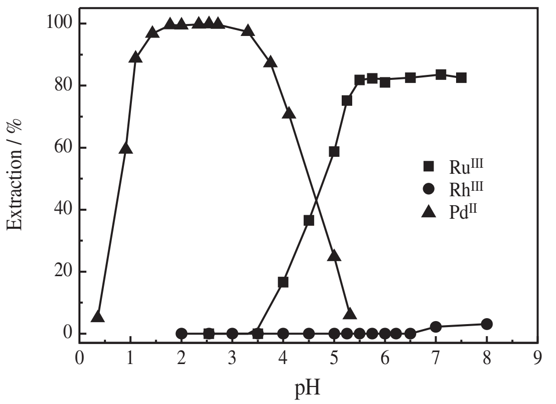


Figure 6. Effect of pH on the extraction of Ru^{III}-HX, Pd^{II}-HX and Rh^{III}-HX complexes: c(Ru^{III}) = 5 × 10^{-5} mol dm^{-3}; $c(HX)_{aqueous\ phase}$ = 4.5 × 10^{-3} mol dm^{-3} or c(Rh^{III}) = 5 × 10^{-5} mol dm^{-3}; $c(HX)_{aqueous\ phase\ or\ dichloromethane}$ = 4.5 × 10^{-3} mol dm^{-3} or c(Pd^{II}) = 4 × 10^{-5} mol dm^{-3}; $c(HX)_{dichloromethane}$ = 1.6 × 10^{-3} mol dm^{-3}.

TABLE VI. Comparison of the proposed spectrophotometric determination of ruthenium with other methods

Reagent	pH	λ_{max} / nm	medium	Heating temp. / °C	Heating time / minutes	ε / $dm^3 mol^{-1} cm^{-1}$	Ref.
1-(4'-Tolyl) 4:4:6 trimethyl-pyrimidine-2-thiol / CTAB	1.0–2.5	390	water	without heating	without heating	7.1×10^3	49
6-Amino-5-nitroso-2,4-pyrimidynethiol	1.0–3.5	530	water	100	40	1.2×10^4	50
Benzyltributyl-ammonium chloride	6.5–7.8	342 380	$CHCl_3$	without heating	without heating	1.26×10^4 1.04×10^4	25
Tetraphenylarsonium or Tetraphenylphosphonium chloride / SCN^-	2.0–3.0	575	$CHCl_3$	85	45	8.4×10^3	13
Cetylpyridinium chloride or Cetyltrimethylammonium bromide / SCN^-	2.0–4.0	568	$CHCl_3$	85	45	8.4×10^3	13
Zephiramine / SCN^-	1.6	565	TRITON X-100	80	80	1.16×10^4	17
3-Chloro-1-nitroso-2-naphthol	~2	595	MIBK	Boiling water bath	30	8.6×10^3	20
2,4,6-tris(2′-pyridyl)-1,2,3-triazine	2.0–7.0	510	DCE	90	60	3.4×10^5	24
4,7-Diphenyl-1,10-phenanthroline	4.0–6.0	466	DCE	90	60	1.88×10^4	32
1-Phenyl-2-methyl-3-hydroxy-4-pyridone	5.5–8.5	367 393	H_2O CH_2Cl_2	75	15	1.28×10^4 1.33×10^4	This work
1-(4-Tolyl)-2-methyl-3-hydroxy-4-pyridone	6.0–8.5	367 393	H_2O CH_2Cl_2	75	15	1.28×10^4 1.33×10^4	This work

DCE: 1,2-Dichloroethane; MIBK: Methyl isobutyl ketone; CTAB: Cetyltrimethylammonium bromide

TABLE VII. Determination of ruthenium in some synthetic mixtures

Sample / μg cm^{-3}	Ru / μg cm^{-3}	
	Spectrophotometry	AAS
Mixture 1: Ru(80), Pd(10), Rh(10), Mo(32)	80.8 ± 0.2	78.8 ± 1.2
Mixture 2: Pd(35), Rh(400), Ru(400)	400.0 ± 4.8	401.6 ± 5.2
Mixture 3: Ru(100), Rh(60), Pd(50)	103.0 ± 4.1	102.5 ± 3.1
Mixture 4: Ru(96.5), Rh(0.72), Pd(1.43), Pt(0.42), Ir(0.93)	96.8 ± 1.4	93.5 ± 2.8

Average of four determinations

Table VI summarizes the analytical characteristics of the proposed method along with some other spectrophotometric methods for ruthenium determination. Comparison shows the molar absorptivity in the present approach to be about twice as high as that of some other proposed methods.[13,20,49] Some methods are time-consuming because reactions take place at higher temperatures and longer heating time.[13,17,20,24,32]

Application of the Method to Synthetic Mixtures

The method was applied for the determination of ruthenium in synthetic mixtures. Sample treatment of synthetic mixtures is described in Experimental, *Synthetic Mixtures*. Results of the analyses were in good agreement with those obtained by the AAS method (Table VII).

Separation of Ruthenium(III) from Palladium(II) and Rhodium(III)

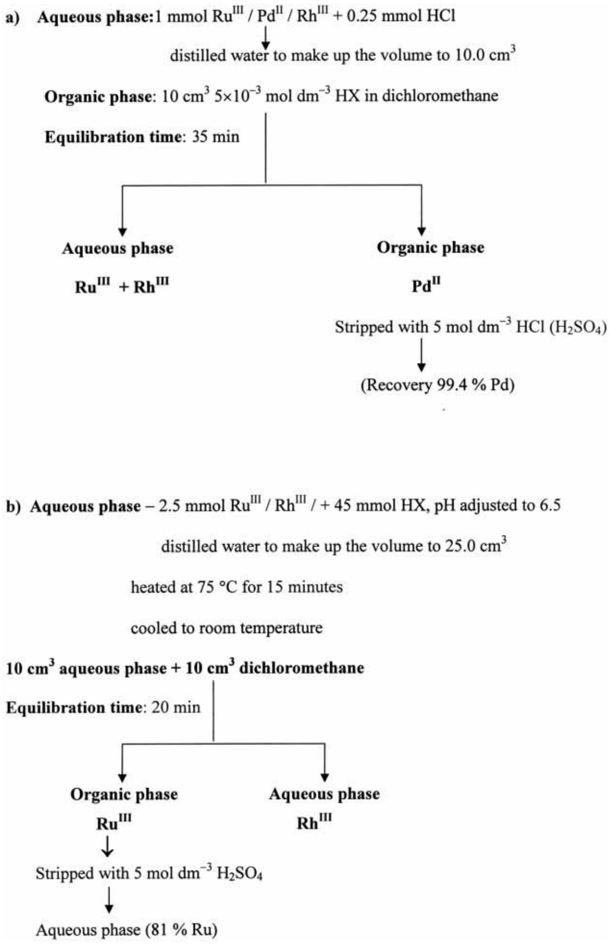


Figure 7. Schematic flow diagram for separation of ruthenium from palladium (a) and rhodium (b).

Ruthenium is usually found in association with other platinum group metals, as intermetallic solid solutions that also contain gold, silver, iron, copper, nickel and cobalt.[1]

Separation of ruthenium from the platinum group metals is of large practical importance in the field of analytical chemistry and high purity ruthenium technology. Separation of ruthenium(III), palladium(II) and rhodium(III) from their mixtures was based on their different extraction and stripping conditions with respect to HX.

TABLE VIII. Separation of ruthenium from a) rhodium and b) palladium

a)

c(Rh) / c(Ru)	Extraction / %	
	Ru	Rh
1	83.1	0,0
10	82.5	0.0
50	90.6	0.0
100	83.3	0.0
500	82.3	0.0
1000	84.0	0.0

b)

c(Ru) / c(Pd)	Extraction / %	
	Ru	Pd
1	0.0	95.2
10	0.0	94.9
25	0.0	94.8
50	1.0	95,3
100	0.0	96.3
160	0.0	94.2

a) pH = 6.5; c(Ru^{III}) = 1.0 × 10^{-4} mol dm^{-3}; c(HX) = 1.0 × 10^{-2} mol dm^{-3} in aqueous phase
b) pH = 2.0, c(Pd^{II}) = 1.0 × 10^{-4} mol dm^{-3}; c(HX) = 5.0 × 10^{-3} mol dm^{-3} in dichloromethane

Palladium(II) was quantitatively extracted with HX dissolved in dichloromethane or chloroform in the pH range 1.5–3.0[32] while ruthenium(III) remained in the aqueous phase (Figure 6).

The Rh^{III}-HX complex extraction in dichloromethane and chloroform was investigated in the pH range 2–8. Under these conditions, rhodium(III) was not extracted and remained in the aqueous phase (Figure 6). The diagram depicting ruthenium separation from palladium and rhodium is given in Figure 7.

The effects of large amounts of ruthenium on palladium(II) extraction and of large amounts of rhodium on ruthenium(III) extraction were studied. Results confirmed that palladium(II) extraction was not affected, regardless of the ruthenium(III) concentrations present. The molar ratio of rhodium to ruthenium was 1 : 1000, and that of ruthenium(III) to palladium was 1 : 160 (Table VIII).

CONCLUSIONS

The proposed method has the following advantages:

– Extraction occurs in two steps and ruthenium recovery is about 82 per cent.

– Ruthenium(III) can be separated from palladium(II) and rhodium(III).

– The method can be used for the spectrophotometric determination of ruthenium in the aqueous phase or in the organic phase after extraction with dichloromethane. The method is fast, reproducible, and accurate.

Acknowledgement. – The authors are grateful to the Ministry of Science, Education and Sports of the Republic of Croatia for financial support to Research Projects Nos. 0119641 and 0098060.

REFERENCES

1. J. A. Rard, *Chem. Rev.* **85** (1985) 2.
2. *International Directory of Radioisotopes*, 2nd Ed.; International Atomic Energy Agency, Vienna, 1962.
3. M. Balcerzak, *Crit. Rev. Anal. Chem.* **32** (2002) 181–226.
4. F. E. Beamish, *Talanta* **5** (1960) 1–35.
5. R. D. Sauerbrunn and E. B. Sandell, *Anal. Chim. Acta* **9** (1953) 86–90.
6. F. S. Martin, *J. Chem. Soc*. (1954) 2564–2570.
7. J. W. Meadows and G. M. Matlack, *Anal. Chem.* **34** (1962) 89–91.
8. W. Smulek, *Radiochem. Radioanal. Lett*. **2** (1969) 265–271.
9. M. Balcerzak, *Mikrochim. Acta II* (1985) 389–400.
10. G. L. Yan and J. Alstad, *J. Radioanal. Nucl. Chem*. **196** (1995) 287–293.
11. H. Meier, D. Bosche, E. Zimmerhackl, W. Albrecht, W. Hecker, P. Menge, A. Ruckdeschel, E. Undre, and G. Zeitler, *Mikrochim. Acta*, (1969) 1083–1096, 1107–1113.
12. J. Lingen, L. Shiyan, L. Guangcheng, S. Jingxuan, and R. Manchang, *Solvent Extr. Ion Exch*. **7** (1989) 613–624.
13. B. B. Tamhina, V. Vojković, and N. Brajenović, International Solvent Extraction Conference, *Solvent Extraction for the 21st Century*, Vol. 2, Proceedings of ISEC' 99, M. Valiente and M. Aguilar (Eds.), Barcelona, 2001. pp. 1167–1172.
14. Z. Marczenko and M. Balcerzak, *Anal. Chim. Acta* **109** (1979) 123–127.
15. S. Jaya and T. V. Ramakrishna, *Bull. Chem. Soc. Jpn*. **57** (1984) 267–270.
16. S. J. Al-Bazi and A. Chow, *Talanta* **31** (1984) 189–193.
17. S. Tagashira, Y. Murakami, M. Nishiyama, N. Harada, and Y. Sasaki, *Bull. Chem. Soc. Jpn*. **69** (1996) 3195–3199.
18. M. A. Anuse and M. B. Chavan, *Chem. Anal*. (Warszaw) **29** (1984) 409–419.
19. A. Mhaske and P. Dhadke, *Hydrometallurgy* **63** (2002) 207–214.
20. B. S. Mohite and V. M. Shinde, *J. Indian Chem. Soc*. **60** (1983) 1006–1007.
21. A. K. Das and J. Das, *Chem. Anal*. (Warszaw) **29** (1984) 403–407.
22. P. G. P. Mezarapus, I. S. Kunicka, and E. U. Jansons, *Zh. Anal. Khim* **41** (1986) 99–103.
23. A. K. Malik and A. Lj. Rao, *J. Anal. Chem.* **55** (2000) 746–749.
24. A. Morales, M. I. Toral, P. Richter, and M. Silva, *Anal. Lett*. **25** (1992) 1765–1778.
25. M. S. El-Shahawi, A. Z. Abuzuhri, and S. M. Aldaherio, *Fresenius' J. Anal. Chem*. **350** (1994) 674–677.
26. M. S. El-Shahawi and M. Almehdi, *J. Chromatogr. A* **697** (1995) 185–190.
27. M. Balcerzak and E. Wyrzykowska, *Analusis* **27** (1999) 829–834.
28. T. Lokhande, G. B. Kolekar, M. A. Anuse, and M. B. Chavan, *Sep. Sci. Technol*. **35** (1999) 153–168.
29. R. K. Sharma, *Bull. Chem. Soc. Jpn*. **66** (1993) 1084–1085.
30. M. I. Toral, P. Richter, A. E. Tapia, and J. Hernandez, *Talanta* **50** (1999) 183–191.
31. A. S. Amin, *Spectrochim. Acta, Part A* **58** (2002) 1831–1837.
32. V. Vojković and V. Drušković, *Croat. Chem. Acta* **76** (2003) 87–92.
33. V. Drušković and V. Vojković, *Croat. Chem. Acta* **76** (2003) 49–54.
34. V. Drušković, V. Vojković, and S. Miko, *Talanta* **62** (2004) 489–495.
35. G. H. Ayres and F. Young, *Anal. Chem*. **22** (1950) 1277–1280.
36. N. H. Furman, *Standard Methods of Chemical Analysis*, D. Van Nostrand Company, Inc., Princenton, New Jersey, 1963. pp. 883, 902.
37. K. Jakopčić, B. Tamhina, F. Zorko, and M. J. Herak, *J. Inorg. Nucl. Chem*. **39** (1977) 1201–1203.
38. H. E. Bent and C. L. French, *J. Am. Chem. Soc*. **63** (1941) 568–572.
39. B. Tamhina, V. Vojković, and M. J. Herak, *Croat. Chem. Acta* **48** (1976) 183–188.
40. V. Vojković, B. Tamhina, and M. J. Herak, *Z. Anal. Chem.* **276** (1975) 377–379.
41. B. Tamhina and V. Vojković, *Mikrochim. Acta* I (1986) 135–145.
42. V. Vojković, B. Tamhina, and M. J. Herak, *Z. Anal. Chem.* **285** (1977) 226–267.
43. B. Tamhina and V. Vojković, *Analysis* **16** (1988) 151–154.

44. V. Vojković, A. Gojmerac Ivšić, and B. Tamhina, *Croat. Chem. Acta* **70** (1997) 667–677.
45. V. Vojković, I. Juranović, and B. Tamhina, *Croat. Chem. Acta* **74** (2001) 467–477.
46. B. Tamhina, and M. J. Herak, *J. Inorg. Nucl. Chem.* **39** (1977) 391–393.
47. B. Tamhina and N. Brajenović, in: T. Sekine (Ed.) *Proceeding of ISEC'90*, Part A, Elsevier Science Publishers, Amsterdam, 1992, pp. 1027–1032.
48. CRC, *Handbook of Chemistry and Physics*. 55th Ed., CRC Press, Inc. USA, 1974–1975. pp. E55–E58.
49. A. J. D. Sharma and A. L. J. Rao, *Indian J. Chem., Sect. A* **35** (1996) 166–167.
50. S. R. Sindhu and R. P. Singh, *J. Indian Chem. Soc*. **62** (1985) 80–81.

SAŽETAK

Ekstrakcija rutenija s derivatima 4-piridona i njegovo odvajanje od rodija i paladija

Vinka Drušković, Vlasta Vojković i Tatjana Antonić

U reakciji rutenija(III) s 1-fenil-3-hidroksi-2-metil-4-piridonom odnosno 3-hidroksi-2-metil-1-(4-tolil)-4-piridonom nastaju žuto obojene kompleksne vrste koje se iz vodenih otopina ekstrahiraju diklormetanom. Organska i vodena faza mogu se primijeniti za spektrofotometrijsko određivanje rutenija(III). Sustavi slijede Beerov zakon u rasponu koncentracija 0.1–20.0 μg $\mathrm{Ru^{III}}$ $\mathrm{cm^{-3}}$. Molarne apsorptivnosti iznose 1.35×10^4 $\mathrm{mol^{-1}\ dm^3\ cm^{-1}}$ (organska faza, pri 393 nm) i 1.29×10^4 $\mathrm{mol^{-1}\ dm^3\ cm^{-1}}$ (vodena faza, pri 367 nm), neovisno o uporabljenome reagensu. Opisana spektrofotometrijska metoda može se koristiti za određivanje rutenija u sintetskim smjesama. Ekstrakcija kelatnoga kompleksa rutenija(III) s 1-fenil-3-hidroksi-2-metil-4-piridonom temelj je jednostavne i efikasne metode za odvajanje rutenija(III) od većih količina rodija(III) i paladija(II).