

Reverse phase extraction chromatography of rhodium(III) with N-n-octylaniline

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Novel separation methods are developed for the extraction of rhodium(III) from aqueous chloride media with N-n-octylaniline (liquid anion exchanger) coated on silica gel. Rhodium(III) was quantitatively extracted from 0.1 mol/L hydrochloric acid, eluted with 1.0 mol/L hydrochloric acid and determined by spectrophotometrically. Different parameters, *viz.* effect of hydrochloric acid concentrations, N-n-octylaniline concentrations and flow rates of mobile phase were studied. The method was applied for separation of rhodium(III) from synthetic mixtures corresponding to alloys. It was free from interferences from a number of cations and anions. A separation scheme was developed for the mutual separation of rhodium(III), platinum(IV) and gold(III). The nature of the extracted species, ascertained by the log-log plot of N-n-octylaniline concentration *versus* distribution ratio, indicates that the probable extracted species is $[(RR'NH_2^+)_3, RhCl_3^{3-}]_6$.

Key words: Extraction chromatography, rhodium(III), separation, alloys

1. INTRODUCTION

The abundance of rhodium in the earth crust is only 0.001 ppb [1]. It has a wide range of applications in the production of alloys, optical instruments and jewelry. Recently it has been employed in automobile catalytic converters as a monitor to control NO_x emission [2]. Rhodium has a low abundance, high price and wide range of applications; hence the development of an innovative method for its separation would be of analytical merit.

Rhodium was separated from palladium by a reverse phase extraction chromatographic method using Bu_3PO_4 as a stationary phase [3], however, this method requires high concentration of mineral acid for the extraction. A column packed with silica treated with tri-n-octylammonium salt [4] was used for separation of platinum(IV), palladium(II), iridium(IV) and rhodium(IV) using hydrochloric and nitric acid media. The method requires high concentrations of mineral acids for the extraction and elution of the metals and it takes 2 hr. Extraction chromatography of platinum metals was carried out using Bu_3PO_4 coated on VAPEX [5]; the method requires high concentrations of mineral acids for the extraction. An alkylated 8-hydroxyquinoline extractant (Kelex 100) [6] was used for separation of rhodium chlorocomplexes by the supported liquid membrane technique. Rhodium

was extracted as rhodium chloride and was separated from palladium and platinum with trioctylamine or aliquat 336 in toluene [7]. The metal was stripped with concentrated hydrochloric acid. N, N'-dimethyl-N, N'-diphenyltetradecylmalonamide [8] was used for the solvent extraction of rhodium. The metal was stripped by a mixture of 4.0 mol/L hydrochloric acid in presence of 0.05 mol/L sodium hypochlorite. Alamine 336 in kerosene was used for the selective separation of iridium(III), ruthenium(III) and rhodium(III) from chloride media [9]. Cyanex 923 [10] was used for the extraction separation of iridium(III) and rhodium(III) from 5.0 to 8.0 mol/L hydrochloric acid media; the method was applied to the metal recovery from a synthetic solution corresponding to a spent catalyst. Rhodium(III) was extracted in acidic medium with bis-(2-ethylhexyl) phosphoric acid [11]; the method was used for the separation of some noble metals but it requires 4.0 mol/L hydrochloric acid for stripping. N-n-octylaniline and n-octylaniline were used for the extraction separation of zinc(II), cadmium(II), mercury(II) [12], copper(II), silver(I), gold(III) [13], gallium(III), indium(III), and thallium(III) [14]. N-octylaniline was also used for the extraction column chromatographic separation of gallium(III), indium(III) and thallium(III) [15]. Recently methods were developed for the extraction chromatographic separation of platinum(IV) [16], palladium(II) [17], ruthenium(III) [18], iridium(III) [19], molybdenum(VI) [20], manganese(II) [21],

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copper(II) [22], bismuth(III) [23], and gold(III) [24] using N-n-octylaniline as a stationary phase.

The present work deals with the extraction chromatographic separation of rhodium(III) from aqueous chloride media with N-n-octylaniline (liquid anion exchanger) coated on silica gel. Rhodium(III) was quantitatively extracted from 0.10 mol/L hydrochloric acid, eluted with 1.0 mol/L hydrochloric acid and was determined spectrophotometrically [25]. The method was applied to the separation of rhodium(III) from binary mixtures and synthetic mixtures corresponding to alloys. Mutual separation scheme was developed for separation of rhodium(III), platinum(IV) and gold(III).

2. EXPERIMENTAL

Apparatus

An Elico digital spectrophotometer model SL-159 with 1-cm quartz cells was used for the absorbance measurements. The pH measurements were carried out on an Elico digital pH meter model LI-120.

Reagents

Rhodium(III) solution. A standard stock solution of rhodium(III) was prepared by dissolving 1.0 g of rhodium trichloride (Loba Chemie) in 1.0 mol/L hydrochloric acid and diluting to 250 mL with distilled water. The solution was standardized gravimetrically [26]. A working solution containing 25 µg of rhodium(III) was made by diluting the stock solution with distilled water. The N-n-octylaniline solution was prepared using a method reported by Gardlund [27]. The stock solution of N-n-octylaniline was prepared in chloroform. Standard solutions of different metal ions were prepared by dissolving the corresponding salt with distilled water and dilute hydrochloric acid. All other chemicals used were of A.R. grade.

Preparation of anion exchange material

The preparation of silanated silica gel was described earlier [16]. A portion (5.0 g) of silanated silica gel was soaked in 5.0% (v/v) N-n-octylaniline previously equilibrated with hydrochloric acid (0.10 mol/L) for 10 min. The solvent was evaporated almost to dryness. The slurry of N-n-octylaniline coated silica gel was prepared in distilled water by centrifugation at 2000 r/min. This slurry was packed in the chromatographic column to give a bed height of 6.0 cm. The bed was covered with a glass wool plug.

General procedure for extraction of rhodium(III)

An aliquot of a solution containing 25.0 µg of rhodium(III) was made up to 25.0 mL by adjusting the concentration of hydrochloric acid to 0.10 mol/L. This solution was passed through the column containing silica coated with 5.0% (v/v) N-n-octylaniline with a flow rate of 0.5 mL/min. After extraction, rhodium(III) was eluted with 25.0 mL of 1.0 mol/L hydrochloric acid. The solution was evaporated to a moist residue. The latter was dissolved in a minimum amount of 1.0 mol/L hydrochloric acid and rhodium(III) was determined by a spectrophotometric method [25].

3. RESULTS AND DISCUSSION

Effect of hydrochloric acid concentration

An amount of 25 µg of rhodium(III) in 25 mL aqueous solution was extracted by varying the acid concentration from 0.05 to 0.25 mol/L hydrochloric acid with 5.0% N-n-octylaniline on silica gel as the stationary phase. The percent extraction of rhodium(III) initially increases, becomes quantitative at 0.1 mol/L hydrochloric acid and then it decreases (Fig. 1).

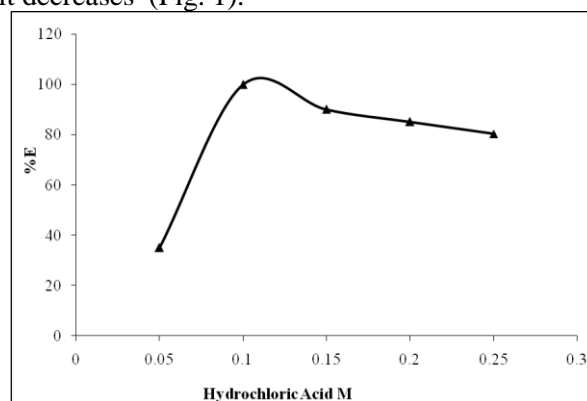


Fig. 1. Extraction behavior of rhodium(III) as a function of hydrochloric acid concentration.

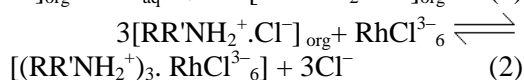
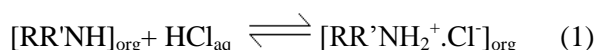
Effect of flow rate

The effect of flow rate on the percent extraction of rhodium(III) was studied in the range from 0.5 mL/min to 3.0 mL/min. It was observed that the increase in flow rate was inversely proportional to the percent extraction. Optimum extraction was observed at flow rates from 0.5 to 1.0 mL/min.

Effect of N-n-octylaniline concentration

The effect of different concentrations (1.0 to 5.0%) of N-n-octylaniline on the extraction of rhodium(III) over hydrochloric acid concentrations in the range from 0.05 to 0.25 mol/L was studied. Extraction of rhodium(III) was quantitative with

5.0% of N-n-octylaniline in 0.10 mol/L hydrochloric acid medium. The extraction of rhodium(III) increases with an increase in the concentration of N-n-octylaniline. The nature of the extracted species was determined by a log-log plot of the distribution coefficient versus N-n-octylaniline concentration at 0.05 and 0.15 mol/L hydrochloric acid, which gave a slope of 2.58 and 2.67, respectively (Fig. 2). This indicated that the metal-to-amine ratio in the extracted species is 1:3 and the probable extracted species is $[(RR'NH_2^+)_3, RhCl_6^{3-}]$. The extraction mechanism can be explained as follows:



where R = $-C_6H_5$ R' = $-CH_2(CH_2)_6CH_3$.

Effect of the eluting agent

It was evident from the data that all acid eluents employed in the present investigation were effective and the optimum elution of rhodium(III) was in the concentration range 1.0 to 4.0 mol/L (hydrochloric, nitric, sulphuric, hydrobromic and perchloric acids), Table 1. Water elutes only 45% of rhodium(III). In the actual process 1.0 mol/L hydrochloric acid was used for elution of rhodium(III).

Table 1. Effect of eluting agents: rhodium(III) 25 µg; stationary phase 5.0% N-n-octylaniline.

Molarity (mol/L)	HCl Recovery (%)	HNO ₃ Recovery (%)	H ₂ SO ₄ Recovery (%)	HBr Recovery (%)	HClO ₄ Recovery (%)
0.5	89.0	91.0	87.0	90.2	92.0
1.0	99.8	99.7	99.8	99.7	99.8
2.0	99.8	99.7	99.8	99.7	99.8
3.0	99.8	99.7	99.8	99.6	99.8
4.0	99.8	99.7	99.8	99.6	99.8

Statistical analysis of the results for rhodium(III)

Statistical analysis was carried out for interpretation of the results. The magnitudes of mean, median, average deviation, average deviation of mean, standard deviation, standard deviation of mean and coefficient of variation were determined. The values obtained indicated that the proposed method offers reproducible results, Table 3.

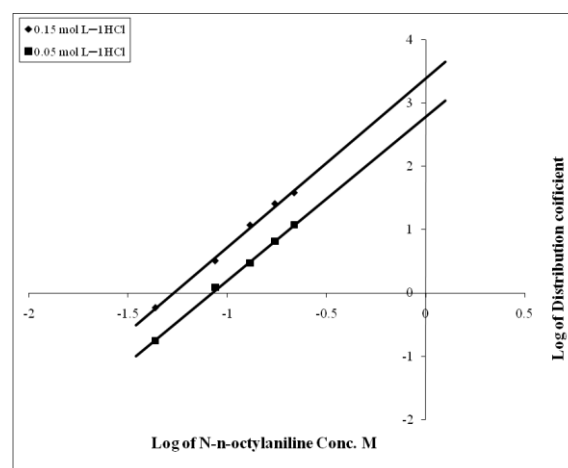


Fig. 2. Log-log plot of the distribution ratio versus N-n-octylaniline concentration at 0.05 mol/L and 0.15 mol/L hydrochloric acid.

Effect of foreign ions

The extraction of rhodium(III) in presence of cations and anions was carried out according to the recommended procedure to examine the interferences. The tolerance limit was set at the amount required to cause $\pm 2\%$ error in the recovery of rhodium(III), Table 2. Interferences only from thiocyanate and tartrate anions are registered.

4. APPLICATIONS

Analysis of synthetic mixtures corresponding to alloys and to a catalyst

The validity of the method was verified by applying the proposed method for extraction of rhodium(III) from synthetic mixtures corresponding to alloys and to a catalyst. The compositions were laboratory-prepared for iridium alloy, jewelry alloy, neuyanskite alloy, osmiridium alloy, platinum-rhodium thermocouple wire and platinum-palladium-rhodium catalyst and were

Table 2. Effect of foreign ions: rhodium(III) 25 µg; stationary phase 5.0% N-n-octylaniline; mobile phase 1.0 mol/L HCl

Foreign Ion	Added as	Tolerance limit, µg	Foreign Ion	Added as	Tolerance limit, µg
Mo(VI)	(NH ₄) ₆ MO ₂ O ₂₄	200	Iodide	KI	1000
Cr(VI)	K ₂ Cr ₂ O ₇	200	Fluoride	NaF	1000
Al(III)	AlCl ₃	200	Bromide	KBr	1000
Cd(II)	CdCl ₂ . 2H ₂ O	100	Malonate	CH ₂ (COONa) ₂	1000
Sn(II)	SnCl ₂ . 2H ₂ O	100	Succinate	(CH ₂ COONa) ₂ . 6H ₂ O	1000
Zn(II)	ZnSO ₄ . 7H ₂ O	100	Persulfate	K ₂ S ₂ O ₈	1000
V(V)	V ₂ O ₅	100	Oxalate	(COOH) ₂ . 2H ₂ O	1000
U(VI)	UO ₂ (NO ₃) ₂ . 6H ₂ O	100	Salicylate	HOC ₆ H ₄ COONa	1000
Ca(II)	CaCl ₂ . 2H ₂ O	250	Au(III)	HAuClO ₄ . H ₂ O	100
Ni(II)	NiCl ₂ . 6H ₂ O	200	Ag(I)	AgNO ₃	50
Ti(IV)	TiO ₂	200	Ir(III)	IrCl ₃ . xH ₂ O	100
Mg(II)	MgCl ₂ . 6H ₂ O	400	Ru(III)	RuCl ₃ . xH ₂ O	100
Cu(II)	CuSO ₄ . 5H ₂ O	400	Pt(IV)	H ₂ PtCl ₆	100
Pb(II)	Pb(NO ₃) ₂	400	Os(VIII)	OSO ₄	100
Fe(II)	FeSO ₄ . 7H ₂ O	400	Pd(II)	PdCl ₂ . xH ₂ O	100
Hg(II)	HgCl ₂	50			

Table 3. Statistical analysis of the results: rhodium(III) added 25.0 µg

Amount Found [µg]	Difference	(Difference) ²	Results
25.02	0.00	0.0000	M = 25.02
25.06	0.04	0.0016	M = 25.02
24.98	-0.04	0.0016	d = 0.0014
24.97	-0.05	0.0025	D = 0.0005
25.11	0.09	0.0081	s = 0.0508
24.98	-0.04	0.0016	S = 0.019
25.03	0.01	0.0001	C.V = 0.20%

analyzed by the proposed method. The results of the analysis reveal the good agreement between the added and the found values, Table 4.

Mutual separation of rhodium(III), platinum(IV) and gold(III)

The separation of rhodium(III), platinum(IV) and gold(III) from one another was carried out by quantitatively extracting platinum(IV) from 0.015 mol/L ascorbic acid, pH 1.0 using 1.5% N-n-

octylaniline coated on silica gel. Rhodium (III) and gold (III) remained in the aqueous phase. The extracted platinum (IV) was eluted with a 20 mL portion of distilled water from the column and was determined by a spectrophotometric method [25]. The aqueous phase containing rhodium(III) and gold(III) was evaporated almost to dryness; after addition of water the solution was adjusted to 0.10 mol/L hydrochloric acid and was passed through the column containing silica coated with 5.0% N-n-octylaniline at a flow rate of 0.5 mL/min. After extraction, rhodium(III) was eluted with 25.0 mL of 1.0 mol/L hydrochloric acid. The eluted fraction was evaporated almost to dryness and rhodium(III) was determined using a spectrophotometric method. The aqueous phase containing gold(III) was evaporated almost to dryness and gold(III) was determined by a spectrophotometric method [25]. The results of the analysis are presented in Table 5.

Table 4. Analysis of synthetic mixtures corresponding to alloys and catalyst: stationary phase 5.0% N-n-octylaniline; mobile phase 1.0 mol/L HCl. *Average of three determinations.

Alloy composition (µg)	Rhodium		E (%)	Relative error (%)
	added equivalent to(µg)	Rhodium found (µg)*		
Iridium alloy [Rh 7.0; Pd 3.5; Cu 8.01; Pt 55.51; Fe 3.51; Ir 28.01]	100	99.6	99.6	0.40
Jewelry alloy [Rh 1.0; Ru 4.0; Pd 95.0]	50	49.9	99.8	0.20
Neuyanskite alloy [Rh 100; Os 650; Pt, 400; Ru 50; Ir 3100]	100	99.6	99.6	0.40
Osmiridium alloy [Rh 110; Os 325; Pt 100, Ru 80; Ir 450; Au 10]	100	99.7	99.7	0.30
Pt-Rh wire [Rh 13; Pt 87]	50	49.9	99.8	0.20
Pt-Pd-Rh catalyst [Rh 0.005-0.05; Pd 0.03-0.15; Pt 0.03-0.20]	25	24.9	99.7	0.30

Table 5. Mutual separation of rhodium(III), platinum(IV) and gold(III).

Metal ion	Amount added (μg)	Amount found* (μg)	Chromogenic ligand	E (%)	RSD** (%)
Pt(IV)	50	49.90	SnCl_2	99.8	0.20
Rh(III)	25	24.92	$\text{SnCl}_2 + \text{KI}$	99.7	0.30
Au(III)	100	99.80	SnCl_2	99.8	0.20

*Average of three determinations.

**RSD (%) = (amount added – amount found/ amount added) \times 100.

4. CONCLUSIONS

The method permits the mutual separation of rhodium(III), platinum(IV) and gold(III). The reliability of the method is verified by analyzing a synthetic mixture corresponding to various alloys and a catalyst. The method is free from interference by a large number of cations and anions. It is simple, rapid and reproducible.

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ОБРАТНОФАЗОВА ЕКСТРАКЦИОННА ХРОМАТОГРАФИЯ НА РОДИЙ(III) С N-N-ОКТИЛАНИЛИН

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(Резюме)

Предложен е нов метод за екстракционно разделяне на родий(III) от солнокисели разтвори с N-n-октиламин (течен йонообменник), нанесен върху силициев оксид. Родий(III) се екстрахира количествено из 0.1 mol/L солна киселина, елуира се с 1.0 mol/L солна киселина и се определя спектрофотометрично. Изследвано е влиянието на концентрацията на солната киселина и N-n-октиламина, както и скоростта на мобилната фаза. Методът е приложен за разделяне на родий(III) от синтетични смеси, съответстващи на различни сплави. Установено е, че голям брой катиони и аниони не пречат. Разработена е схема за разделянето на родий(III), платина(IV) и злато(III) един от друг. От двойнологаритмичната зависимост между концентрацията на N-n-октиламина и коефициента на разпределение е установено, че вероятният състав на екстрахираната форма е $[(RR'NH_2^+)_3 \cdot RhCl_6^{3-}]$.