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## Reversed phase extraction chromatographic separation of trivalent iridium using liquid anion exchanger

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### ABSTRACT

A simple, rapid and sensitive reversed phase chromatographic method was developed for separation of trivalent iridium using N-n-octylaniline (a liquid anion exchanger) coated on silica gel as a stationary phase. Iridium(III) was quantitatively extracted from 1.0 M hydrochloric acid, stripped with 2.0 M hydrochloric acid and determined by spectrophotometric method. Different parameter viz effect of hydrochloric acid concentration, N-n-octylaniline concentration and flow rate of mobile phase was studied. The method was applied for separation of iridium(III) from alloys and multicomponent mixtures. Method was free from large number of interferences from cations and anions. The nature of extracted species deduced by log-log plot of distribution ratio versus N-n-octylaniline concentration indicates that probable extracted species is  $[RR^3NH_2^+ \cdot IrCl_4]_{org}$ .

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### KEYWORDS

Extraction chromatography;  
Iridium(III);  
Separation;  
Alloys.

### INTRODUCTION

The abundance of iridium in earth's crust is only 0.001 ppm. It is most commonly used with platinum to impart additional corrosion resistance. Iridium, its alloys and complexes has wide range of application as catalyst, multipored spinters, balances, air craft engine parts, direct-ignition engine and flat panel displays. Due to wide range of application and trace amount of abundance of iridium there is a need to develop a more accurate, reliable and precise method for its separation is of great importance.

Reversed phase extraction chromatography was used for separation of non volatile noble metal using  $Bu_3PO_4$ <sup>[1]</sup> treated porasil C column. In a column platinum and iridium eluted with 0.1 M hydrochloric acid.

These metals were separated on screened column using reducing condition. Iridium was separated from gold using tri-n-octylamine salt<sup>[2]</sup> coated on silica in hydrochloric acid medium. In a method iridium was eluted using 5.0 M nitric acid. Amberlite LA-1 hydrochloride<sup>[3]</sup> impregnated on paper was used for quantitative chromatographic analysis of platinum metals and gold. Development of paper was carried out using 6.0 M hydrochloric acid. Platinum, palladium and iridium was separated using ion chromatography. The separation of platinum(IV), palladium(II) chlorocomplex was achieved from iridium(IV) and base metals by cation exchange. Iridium(IV) was eluted using mixture of 4.0 M hydrochloric acid and 0.015 M sodium perchlorate after reduction with hydroxylamine hydrochloride<sup>[4]</sup>. DEAE-cellulose and ECTEOLA-cellulose<sup>[5]</sup> ion ex-

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changer was used for thin layer chromatographic separation of rhodium(III), iridium(III) and iridium(IV) by using 5.0 M hydrochloric acid. Rhodium and iridium was separated using diethyl amino ethyl cellulose<sup>[6]</sup> anion exchanger in chloride form by thin layer chromatographic plate and developed using 2.0 N sulphuric acid. Aliquot 336<sup>[7]</sup> was used for solvent extraction of iridium in hydrochloric acid medium and was stripped with ammonia.

The use of *n*-octylaniline in the extraction of noble metals was described in number of papers<sup>[8-11]</sup>. *n*-Octylaniline in toluene was used as an extractant for iridium(III), but method requires prior separation of base metals<sup>[8]</sup>. The extraction of iridium(III) was carried out from 3.0 M hydrochloric acid in *n*-octylaniline in diisobutylketone (DIBK) and then determined by AAS<sup>[9,10]</sup>, but method suffers from interference from base metals. Iridium(III) was also extracted from *n*-octylaniline in diisobutylketone (DIBK) from 3.0 M hydrochloric acid solution<sup>[11]</sup>. Literature survey revealed that some of existing methods have drawbacks as the use of *n*-octylaniline in the extraction of noble metals was described in the literature<sup>[11-13]</sup>. The comparison can be made of the merits of *N*-*n*-octylaniline relative to *n*-octylaniline as an extractant for noble metal. The extraction depends upon method of preparation of the reagent. Some of the drawbacks of the method are emulsion formation, requirement of more elution time (30 min), higher reagent concentration and the need of multiple extractions. Reversed phase extraction chromatography is an extremely versatile technique and has been applied successfully for separation of various metals<sup>[14-18]</sup>. *N*-*n*-octylaniline was used for solvent extraction of various metals<sup>[19-21]</sup>.

In our laboratory *N*-*n*-octylaniline was used for extraction chromatographic separation of palladium(II)<sup>[22]</sup>. In continuation to our previous work deals with extraction of iridium(III) from hydrochloric acid media with *N*-*n*-octylaniline (liquid anion exchanger) coated on silica gel as a stationary phase was developed.

### EXPERIMENTAL

**Apparatus:** An Elico spectrophotometer model SL-159 with 10 mm path length quartz cell was used for absorbance measurements.

**Reagents:** A stock solution of iridium(III) was prepared by dissolving 1.0 g iridium trichloride ( $\text{IrCl}_3 \cdot \text{H}_2\text{O}$ ) (Loba. Chem. Laboratories and fine chemical. India) in 1.0 M hydrochloric acid, diluted to 250 ml with distilled water and standardized using gravimetrically<sup>[23]</sup>. A working solution of iridium(III), 50  $\mu\text{g}/\text{ml}$  was made from it by diluting the stock solution with distilled water. Other standard solutions of different metals used to study were prepared by dissolving respective salt with distilled water and dilute hydrochloric acid. *N*-*n*-octylaniline was prepared by method reported by Gardlund<sup>[24]</sup>. The stock solution of *N*-*n*-octylaniline was prepared in chloroform.

**Preparation of anion exchange material:** Silica gel (60-120 mesh) obtained from BDH was dried at 120<sup>o</sup> C for 2-3 h. and stored in desiccators. It was packed in U tube through which a stream of nitrogen was bubbled through a small durand bottle containing 20.0 ml of dimethyldichlorosilane (DMCS) (Acros Organics. New Jersey. USA). The passage of DMCS vapor continued for 4 h. The silica gel was then washed with anhydrous methanol and dried. A portion of 5.0 g of silanated silica gel was soaked with 2.0% (v/v) *N*-*n*-octylaniline previously equilibrated with 1.0 M hydrochloric acid. The solvent was then evaporated to get nearly dried gel. The slurry of *N*-*n*-octylaniline coated silica gel was prepared in distilled water by centrifugation at 2000 rpm and coated silica gel was packed into chromatographic column to give a bed height of 6.0 cm. The bed was then covered with glass wool plug.

**General procedure:** An aliquot of the solution containing 40  $\mu\text{g}$  of iridium(III) was made 1.0 M in hydrochloric acid in 25 ml volumetric flask. The solution was passed through the *N*-*n*-octylaniline coated silica gel column at the flow rate of 1.0 ml/min. The extracted iridium(III), was eluted with 20 ml of 2.0 M hydrochloric acid. The fraction collected was analyzed for iridium(III) spectrophotometrically by stannous chloride hydrobromic acid method<sup>[25]</sup>.

### RESULT AND DISCUSSION

**Effect of acidity:** Trivalent iridium was extracted with hydrochloric acid in concentration range of 0.75 to 1.0 M on column coated with 2.0% *N*-*n*-octylaniline as the stationary phase on silica gel. Distribution ratio of

iridium(III) decreases with increasing the concentration of hydrochloric acid. It was observed that the extraction was quantitative in a range of 0.75 to 1.0 M hydrochloric acid, further increased in acid concentration extraction of iridium(III) was decreases Figure 1.

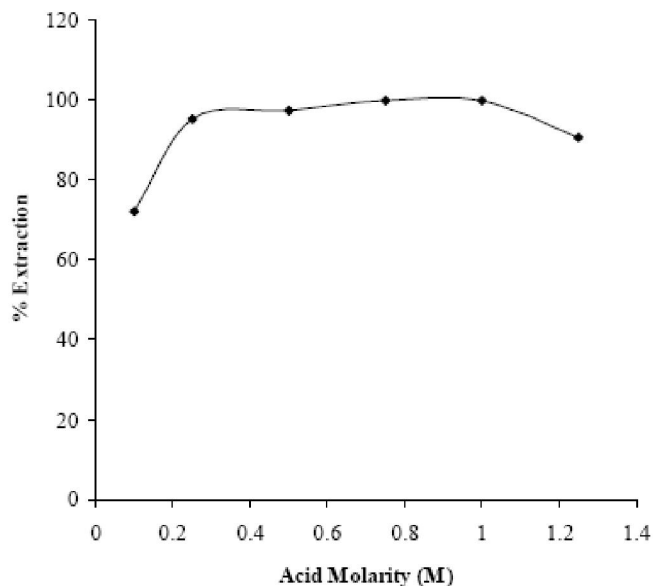


Figure 1 : Extraction behavior of iridium(III) as a function of hydrochloric acid concentration with 2.0% N-n-octylaniline in chloroform.

**Effect of flow rate on percentage extraction:** The effect of flow rate on percentage extraction of iridium(III) was studied from 0.5 ml/min to 3.0 ml/min. It was observed that the increase in flow rate was in-

versely proportional to percentage extraction. Therefore normal flow rate was kept 1.0 ml/min for furtherer extraction studies.

**Effect of N-n-octylaniline concentration:** The concentration of N-n-octylaniline in chloroform varied from 0.1% to 2.0% over hydrochloric acid range 0.1 to 1.25 M at 1.0 ml/min flow rate. The extraction of iridium(III) was quantitative at 2.0% (v/v) N-n-octylaniline with flow rate 1.0 ml/min. An increase in N-n-octylaniline concentration percentage extraction of iridium(III) increases. Log-log plot of N-n-octylaniline concentration versus distribution ratio Figure 2 at 0.1 M and 0.25 M of hydrochloric acid gave a slope 1.2 and 1.3 respectively. The probable composition of metal to amine ratio is 1:1 indicating that the probable extracted species was  $[RR'NH_2^+ \cdot IrCl_4^-]_{org.}$

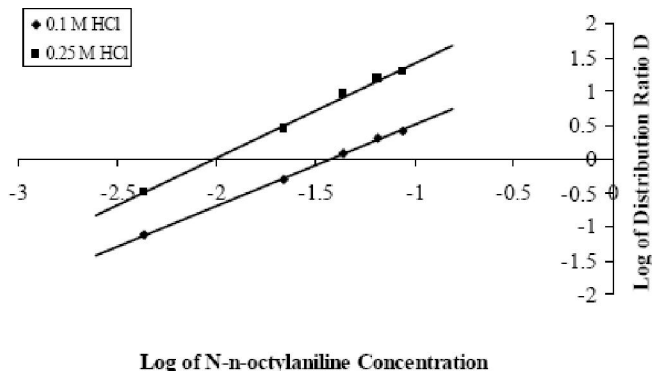


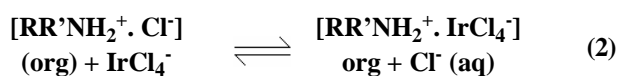
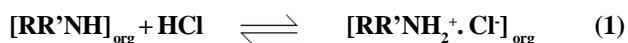
Figure 2 : Log-log plot of distribution ratio versus N-n-octylaniline concentration at 0.10 mol/L and 0.25 mol/L HCl.

TABLE 1 : Separation of iridium(III) from binary mixtures

Foreign Ion	Added as	Tolerance limit / $\mu\text{g}$	Foreign Ion	Added as	Tolerance limit / $\mu\text{g}$
Pd(II)	$\text{PdCl}_2 \cdot x\text{H}_2\text{O}$	300	Os(VIII)	$\text{OsO}_4$	500
Au(III)	$\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$	300	Zn(II)	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	500
Rh(III)	$\text{RhCl}_3$	200	V(V)	$\text{V}_2\text{O}_5$	500
Ru(III)	$\text{RuCl}_3$	400	Cd(II)	$3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$	200
U(VI)	$\text{UO}_2 \cdot (\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	400	Fe(II)	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	500
Mn(II)	$\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$	450	Tl(I)	$\text{TlNO}_3$	200
Pb(II)	$\text{Pb}(\text{NO}_3)_2$	400	Ga(III)	$\text{GaCl}_3$	200
Sn(II)	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	200	In(III)	$\text{InCl}_3$	250
W(IV)	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	300	Mg(II)	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	250
Hg(II)	$\text{HgCl}_2$	250	Bi(III)	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	250
Cr(VI)	$\text{K}_2\text{Cr}_2\text{O}_7$	250	Al(III)	$\text{AlCl}_3$	250
Fe(III)	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	250	Ni(II)	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	250
Cu(II)	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	250	Salicylate	$\text{HOC}_6\text{H}_4\text{COONa}$	1000
Ti(IV)	$\text{K}_2\text{TiF}_6 \cdot \text{H}_2\text{O}$	250	Oxalate	$(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$	1000
Co(II)	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	250	Acetate	$\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$	1000

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The extraction mechanism can be explained as follows



Where  $\text{R} = -\text{C}_6\text{H}_5$ ,  $\text{R}' = -\text{CH}_2(\text{CH}_2)_6\text{CH}_3$ .

**Effect of foreign ion:** The extraction of iridium(III) in presence of cations and anions was carried out according to recommended procedure to examine their interferences. The tolerance limit was set at the amount required to cause  $\pm 2\%$  error in recovery of iridium(III) TABLE 1. Only anions showing the interferences were EDTA, tartarate, thiocyanate thiosulphate and thiourea.

**Analysis of synthetic mixture corresponding to alloy:** The composition of synthetic mixture corresponding to alloys was prepared in laboratory. The proposed method was applied for the analysis of neuyanskite alloy and osmiridium alloy under the optimized condition. The results obtained were reproducible and in agreement with labeled amount TABLE 2.

**TABLE 2 : Analysis of synthetic mixtures corresponding to alloy**

Alloys sample Composition, $\mu\text{g}$	Amount Taken / $\mu\text{g}$	Amount Found / $\mu\text{g}$	Recovery/ % (n=3)	RSD/ % (n=3)
Neuyanskite alloy (Os 650, Pt 400, Ru 50, Rh 100, Ir 3100)	650	647.4	99.6	0.40
Osmiridium alloy (Os 325, Pt 100, Ru 80, Rh 110, Ir 450, Au 10)	325	324.4	99.8	0.20

**Separation of iridium(III) from multicomponent mixture:** Iridium(III) was separated from rhodium(III), ruthenium(III) and base metals such as iron(III), copper(II). Under optimum condition of the extraction all added metals are remains in aqueous phase. These ions were determined by spectrophotometrically by standard methods. Iridium(III) from the organic phase was stripped with 20 ml 2.0 M hydrochloric acid and estimated by stannous chloride hydrobromic acid method. Iridium(III) is separated from osmium(VIII), palladium(II) and molybdenum(VI) by using different stripping conditions TABLE 3.

**TABLE 3 : Multicomponent separation of iridium(III)**

Mixture	Chromogenic ligand	Acid Conc.	Stripping Agents	Recovery/%	RSD/ % (n=3)
Ru(III)	Thiourea	-	Aqueous Phase	99.2	0.80
Ir(III)	$\text{SnCl}_2 + \text{HBr}$	1.0 M HCl	2.0 M HCl	99.7	0.30
Rh(III)	$\text{SnCl}_2 + \text{KI}$	-	Aqueous Phase	99.3	0.70
Ir(III)	$\text{SnCl}_2 + \text{HBr}$	1.0 M HCl	2.0 M HCl	99.4	0.60
Os(VIII)	Thiourea	-	5.5 M HCl	98.3	0.70
Ir(III)	$\text{SnCl}_2 + \text{HBr}$	1.0 M HCl	2.0 M HCl	99.7	0.30
Pd(II)	N-N-Dimethylaniline	-	7.0 M Ammonia	98.8	0.20
Ir(III)	$\text{SnCl}_2 + \text{HBr}$	1.0 M HCl	2.0 M HCl	99.7	0.30
Fe(III)	Thiocyanate	-	Aqueous Phase	99.7	0.30
Ir(III)	$\text{SnCl}_2 + \text{HBr}$	1.0 M HCl	2.0 M HCl	99.8	0.20
Fe(II)	1,10 Phenanthroline	-	Aqueous Phase	99.1	0.90
Ir(III)	$\text{SnCl}_2 + \text{HBr}$	1.0 M HCl	2.0 M HCl	99.8	0.20
Mo(VI)	Thiocyanate	-	Distilled water	99.2	0.80
Ir(III)	$\text{SnCl}_2 + \text{HBr}$	1.0 M HCl	2.0 M HCl	99.4	0.60
Cu(II)	Rubbanic Acid	-	Aqueous Phase	99.6	0.40
Ir(III)	$\text{SnCl}_2 + \text{HBr}$	1.0 M HCl	2.0 M HCl	99.8	0.20

## CONCLUSIONS

Method is simple, rapid and reproducible. Extraction of iridium(III) requires low concentration of N-n-octylaniline. Method is free from large number of for-

eign ions. Method gives separation of iridium(III) from alloys.

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