

## Reverse phase extraction chromatographic separation of osmium(VIII) with N-*n*-octylaniline

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A trace level concentration of osmium(VIII) has been quantitatively extracted from 1.0 M hydrochloric acid with 0.087 M N-*n*-octylaniline as a stationary phase on silica gel. Osmium(VIII) has been eluted with 5.5 M, 25 mL hydrochloric acid and determined by spectrophotometric method. Various parameters influencing the extraction, such as acid concentration, reagent concentration and flow rate have also been studied to determine the optimum conditions for the quantitative separation of osmium(VIII). This method is free from large number of interferences from cations and anions. This method has been effectively applied for the separation of osmium(VIII) from neuyanskite and osmiridium alloy. Osmium(VIII) has also been separated from rhodium(III), ruthenium(III) and base metals such as iron(III), copper(II) and lead(II). The method is found to be simple, rapid and reproducible.

**Keywords:** Extraction chromatography, Osmium(VIII), Multicomponent mixture, N-*n*-octylaniline

The abundance of osmium in earth crust is only 0.001 ppm. It has wide range of applications as a catalyst, hardening agent of alloys, polymer staining and buckminster fullerene adducts. Osmium occurs in association with platinum group metals and base metals, it has electronic, industrial and environmental importance. Hence, the separation of osmium(VIII) is an analytical merit.

Reversed phase extraction chromatography (RPEC) is an extremely versatile technique and has been applied successfully for the separation of various metals and organic compounds<sup>1-4</sup>. The literature survey reveals that osmium(VIII) was extracted with trioctyl phosphine oxide<sup>5</sup> as the stationary phase (silica gel as support) in a hydrochloric acid media. In this method, elution of metal requires thiourea and it suffers from interference of cations like thallium(III), gallium(III) and indium(III). Extraction and spectrophotometric determination of osmium(VIII) was carried out using the tetra methyl thiuram disulphide<sup>6</sup> in a toluene but quantitative extraction of osmium(VIII) using this method requires higher concentration of hydrochloric acid. Bu<sub>3</sub>PO<sub>4</sub>, tri-*n*-octylphosphine oxide, aliquot 336 or their mixture<sup>7</sup> was used for the extraction chromatographic

separation of platinum metals and gold. Method requires 6.0-8.0 M hydrochloric acid as a mobile phase. Osmium(III), Osmium(IV) and Osmium(V) were extracted on a paper impregnated with tributylphosphate and amberlite LA-1 hydrochloride<sup>8</sup>, this method required 2 h duration for development of paper. Platinum group metal (PGM) and gold(III) were quantitatively separated on paper impregnated with amberlite LA-1 hydrochloride<sup>9</sup>. This method required 6.0 M hydrochloric acid for development of paper. Trioctylamine<sup>10</sup> had been used for the extraction chromatography of noble metals using mixture of hydrochloric acid and nitric acid as a developing solvent, Rf value of osmium(IV) was less than other platinum group metals. Osmium(VIII) was extracted from its acidic solution with bis-2-ethylhexyl phosphoric acid<sup>11</sup> and was stripped with mixture of hydrochloric acid and thiourea. Platinum group metals were extracted with cyanex 925<sup>12</sup> in toluene from aqueous chloride media, on addition of tin(II) chloride, the extraction of osmium(VIII) decreases. Presence of ruthenium, osmium and iridium was observed from Ni-Cr-PGE minerals but the separation study has not been carried out<sup>13</sup>.

The use of *n*-octylaniline for the extraction of noble metals has been described in the literature<sup>14,15</sup>. The comparison can be made of the merits of

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*N-n*-octylaniline relative to *n*-octylaniline as an extractant of noble metal. 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.

The work has also been reported on separation of osmium(VIII) using *N-n*-octylaniline<sup>16</sup> by solvent extraction method. But the method suffers from drawbacks such as interferences from anions like ascorbate, iodide, thiosulphate, thiocyanate and cations like iron, mercury, bismuth and platinum. Their interferences must be removed prior to extraction of osmium. Recently, the *N-n*-octylaniline has been used for the extraction chromatographic separation of palladium(II)<sup>17</sup>, platinum(IV)<sup>18</sup>, iridium(III)<sup>19</sup>, manganese(II)<sup>20</sup>, ruthenium(III)<sup>21</sup>, molybdenum(VI)<sup>22</sup>, gold(III)<sup>23</sup>, and copper(II)<sup>24</sup> using silica gel as supports towards stationary phase. The silica gel is the best among the various supporting material because it is colourless, porous, with large surface area and physically and chemically more stable. Its surface chemistry can be modified by silane devitization procedures. In present communication, extraction chromatographic separation of a trace level concentration of osmium(VIII) at 1.0 M hydrochloric acid is reported.

## Experimental Procedure

### Apparatus

An Elico spectrophotometer model SL-159 with 10 mm path length quartz cell and Control dynamic pH meter were used for absorbance and pH measurements respectively.

### Preparation of standard osmium(VIII) solution

A stock solution of osmium(VIII) was prepared by dissolving 1.0 g osmium tetroxide [OsO<sub>4</sub>] (Loba. Chem.Pvt. Ltd. Mumbai) in 1.0 M hydrochloric acid and diluted to 250 mL with distilled water. It was standardized using gravimetric method<sup>25</sup>. A working solution of 25 µg/mL osmium(VIII) was made by diluting stock solution with distilled water.

### Preparation of *N-n*-octylaniline solution

*N-n*-octylaniline was prepared by using a method reported by gardlund<sup>26</sup>. The stock solution of *N-n*-octylaniline was prepared in chloroform. Other standard solutions of different metal ions were prepared by dissolving respective salt in distilled water and dilute hydrochloric acid. All other chemicals used were of A. R. Grade.

### Preparation of ion-exchange material

Silica gel (60-120 mesh), obtained from British Drug House Pvt. Ltd. India, was dried at 120°C for 2-3 h and stored in desiccator. Some of the silica gel was packed in a U-tube, through which a stream of dry nitrogen that had been bubbled through a small Durand bottle containing 20.0 mL of dimethyldichlorosilane (DMCS) (Acros Organics. New Jersey. USA), was passed. The passage of DMCS vapour was continued for 3-4 h. The silica gel was then washed with anhydrous methanol and dried. A 5.0 g portion of the silanated silica gel was soaked in 5 mL 0.087 M *N-n*-octylaniline in chloroform previously equilibrated with hydrochloric acid (1.0 M) for 10 min. The solvent was then evaporated till the gel was nearly dry.

A slurry of coated silica gel in distilled water was prepared by centrifugation at 2000 r/min and then packed into chromatographic column made up of a borosilicate glass tube, bore 8 mm, length 30 cm, fitted with glass-wool plug at the bottom to give a bed height of 6.0 cm. The voids present in the column were removed by pressing gently with a glass rod. The bed was then covered with a glass wool plug.

### General procedure

An aliquot (25.0 mL) of a solution containing 25 µg of osmium(VIII) was made by adjusting concentration of hydrochloric acid 1.0 M. The solution was passed through the coated silica gel column with 0.087 M *N-n*-octylaniline at 1.0 mL/min flow rate. After extraction, the metal ion was eluted with 25.0 mL hydrochloric acid (5.5 M). The solution was evaporated to moist dryness. The residue was dissolved in minimum amount of 1.0 M hydrochloric acid and separated osmium(VIII) was determined by spectrophotometric method<sup>27</sup>.

## Results and Discussion

### Effect of acid concentration

25 µg osmium(VIII) in 25 mL aqueous solution was extracted in 0.2-1.2 M hydrochloric acid with 0.087 M *N-n*-octylaniline as the stationary phase on silica gel. The percentage extraction of osmium(VIII) initially increases and becomes quantitative at 1.0 M hydrochloric acid Fig. 1. There is incomplete extraction found in hydrobromic (84.9%), sulphuric (55.1%), perchloric (45.5%) and nitric (26.6%) acid. Hence, the use of hydrochloric acid is recommended for further study.

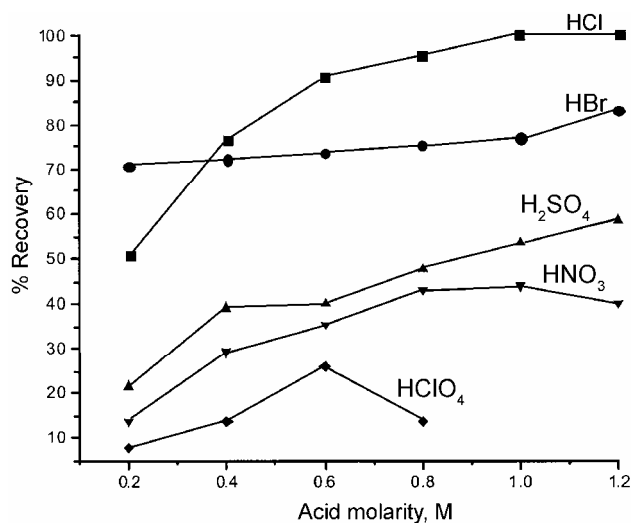
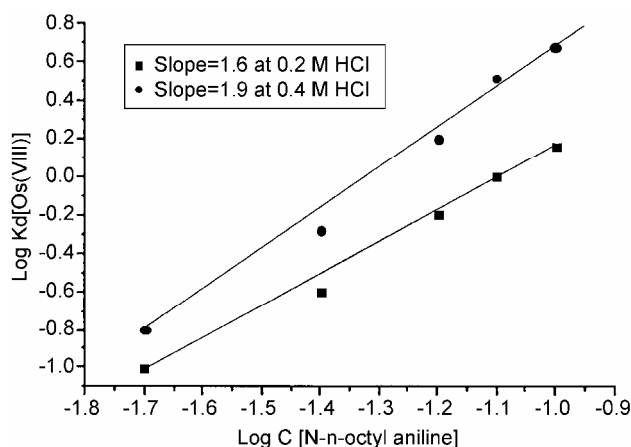


Fig. 1—Effect of acid concentration on % recovery

Fig. 2—log-log plots of *N-n*-OA conc. vs. log  $K_d$ 

#### Effect of flow rate on extraction

The effect of flow rate on percentage extraction of osmium(VIII) was studied from 0.5 mL/min to 3.0 mL/min. It is observed that the increase in flow rate is inversely proportional to percentage extraction. It is quantitative up to 1.0 mL/min. Hence, normal flow rate is kept 1.0 mL/min.

#### Effect of *N-n*-octylaniline concentration

Effect of different concentrations (0.022-0.109 M) of *N-n*-octylaniline over hydrochloric acid range (0.2 -1.2 M) was studied on extraction of osmium(VIII). Extraction of osmium(VIII) was quantitative with 0.087 M *N-n*-octylaniline in 1.0 M hydrochloric acid media. The extraction of osmium(VIII) increases with the increase in concentration of *N-n*-octylaniline.  $\text{Log}K_{d[\text{Os(VIII)}]}$  versus  $\text{Log}C_{[\text{N-n-octylaniline concentration}]}$  (Fig. 2) at 0.2 M and 0.4 M hydrochloric acid gives slope value of 1.6

Table 1—Effect of diverse ion  
[Os(VIII) 25  $\mu\text{g}$ , hydrochloric acid 1.0 M, *N-n*-octylaniline 0.087 M, eluent 25.0 mL 5.5 M hydrochloric acid and flow rate 1.0 mL/min]

Foreign ion	Tolerance limit, $\mu\text{g}$	Foreign ion	Tolerance limit, $\mu\text{g}$
Mn(II)	200	Mg(II)	100
Cd(II)	100	Pb(II)	100
Fe(III)	200	V(V)	50
Hg(II)	50	U(VI)	250
Bi(III)	50	Co(II)	250
Ni(II)	250	Ce(IV)	100
Cu(II)	400	Ca(II)	400
Be(II)	400	Mo(VI)	200
Ba(II)	400	Sr(II)	100
Al(III)	200	Tl(III)	50
Sb(III)	100	Zr(IV)	200
Cr(III)	100	Pd(II)	200
Zn(II)	200	Ir(III)	100
Pt(IV)	100	Rh(III)	100
Ru(III)	100	Succinate	1000
Au(III)	100	Salicylate	1000
Persulphate	1000	Citrate	1000
E.D.T.A.	100	Malonate	1000
Oxalate	1000	Bromide	1000

Table 2—Analysis of synthetic mixture corresponding to alloy

Alloy sample composition $\mu\text{g}$	Amount taken $\mu\text{g}$	Amount found $\mu\text{g}$	% Recovery <sup>a</sup>	% Relative standard deviation
Neuyanskite (Os 650, Pt 400, Ru 50, Rh 100, Ir 3100)	50	49.9	99.8	0.20
Osmiridium (Os 325, Pt 100, Ru 80, Rh 110, Ir 450, Au 10)	50	49.8	99.6	0.40

<sup>a</sup>Average of three determinations.

and 1.9 respectively. The probable composition of extracted species calculated to be 1:2 (metal: amine) ratio.

#### Effect of diverse ion

Various amounts of foreign ions were added to fixed amount of osmium(VIII) (25  $\mu\text{g}$ ) to study the effect of presence of foreign ions according to recommended procedure. The tolerance limit was set at the amount require to cause  $\pm 1.5\%$  error in the metal recovery (Table 1). It is observed that method

Table 3—Separation of osmium(VIII) from multicomponent mixtures

Mixture	Chromogenic ligand	Acid conc.	Eluent	Recovery <sup>a</sup> , %	RSD, % (n=3)
Ru(III)	Thiourea	-	Aqueous phase	99.9	0.10
Os(VIII)	Thiourea	1.0 M HCl	5.5 M HCl	99.7	0.30
Rh(III)	SnCl <sub>2</sub> + KI	-	Aqueous phase	99.8	0.20
Os(VIII)	Thiourea	1.0 M HCl	5.5 M HCl	99.4	0.60
Au(III)	SnCl <sub>2</sub>	-	0.25 M ammonia	99.8	0.20
Os(VIII)	Thiourea	1.0 M HCl	5.5 M HCl	99.7	0.30
Fe(III)	Thiocyanate	-	Aqueous phase	99.7	0.30
Os(VIII)	Thiourea	1.0 M HCl	5.5 M HCl	99.8	0.20
Mo(VI)	Thiocyanate	-	Distilled water	99.2	0.80
Os(VIII)	Thiourea	1.0 M HCl	5.5 M HCl	99.4	0.60
Cu(II)	Rubbanic Acid	-	Aqueous phase	99.6	0.40
Os(VIII)	Thiourea	1.0 M HCl	5.5 M HCl	99.8	0.20
Pb(II)	4-(2-Pyridylazo) Resorcinol	-	Aqueous phase	99.9	0.10
Os(VIII)	Thiourea	1.0 M HCl	5.5 M HCl	99.7	0.30

<sup>a</sup>Average of three determination.

Table 4—Statistical analysis of osmium(VIII)

Amount found <sup>a</sup> µg	Difference	(Difference) <sup>2</sup>	Results
24.70	-0.21	0.0441	Mean = 24.91
24.90	-0.01	0.0001	Median =24.95
24.85	-0.06	0.0036	Average deviation =0.0043
25.01	0.10	0.0100	Average deviation of mean =0.0016
24.95	0.04	0.0016	Standard deviation =0.105
24.95	0.04	0.0016	Standard deviation mean =0.040
24.98	0.07	0.0049	Coefficient variation =0.42%

<sup>a</sup>Average of three determinations.

was free from large number of interferences from cations and anions.

#### Analysis of synthetic mixture corresponding to alloy

The solution of synthetic mixture corresponding to composition of 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 are found to be reproducible and in agreement with labelled amount (Table 2). The proposed method gives quite encouraging results at trace levels.

#### Separation of osmium(VIII) from multicomponent mixture

The osmium(VIII) was separated from rhodium(III), ruthenium(III) and base metals such as

iron(III), copper(II) and lead(II). Under optimum condition of the extraction all added metals remain in aqueous phase. These ions are determined by spectrophotometrically using standard methods<sup>27</sup>. Osmium(VIII) from the stationary phase was eluted with 25 mL 5.5 M hydrochloric acid and estimated by thiourea method. Osmium(VIII) is separated from gold(III), molybdenum(VI) by using different elution conditions (Table 3).

#### Statistical analysis of osmium(VIII)

The statistical analysis was carried out for interpretation of results. The magnitude of mean, median, average deviation, average deviation of mean, standard deviation, standard deviation mean and coefficient variation was calculated. The value obtained for the magnitude of mean (24.91), median (24.95), average deviation (0.0043), average deviation of mean (0.0016), standard deviation (0.105), standard deviation mean (0.040) and coefficient variation (0.425%) was indicating that proposed method offers reproducible results (Table 4).

#### Conclusion

Reversed phase extraction chromatography offers a promising separation of osmium(VIII) at tracer concentration from the other elements. It requires low reagent concentration. Reliability of method is verified by analyzing synthetic mixture corresponding to alloys. This method is found to be tolerating large number of diverse ions. It is simple, rapid and reproducible. Supporting material used has its higher stability towards stationary phase.

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### References

- 1 Mandal B & Ghosh N, *Indian J Chem Sec A*, 48A(2009) 668.
- 2 Heddur R B & Khopkar S M, *Chemia Analityczna* (Warsaw Poland), 31(2)(1986) 201.
- 3 Aher H R & Kuchekar S R, *Indian J Chem Technol*, 15(2008) 403.
- 4 Rokade M D & Dhadke P M, *Indian J Chem Sec A*, 40(2001) 1243.
- 5 Rokade M D, Iyer J N & Dhadke P M, *Chem Environ Res*, 10(2001)101.
- 6 Uttarwar R M & Joshi A P, *Microchemica Acta*, 67(5-6) (1977) 421.
- 7 Przeszlakowski S & Flieger A, *Chemia Analityczna* (Warsaw, Poland), 22(3)(1977) 431.
- 8 Przeszlakowski S & Flieger A, *Talanta*, 23(1976) 844.
- 9 Przeszlakowski S & Flieger A, *J Chromatography*, 81(1) (1973)129.
- 10 Przeszlakowski S & Flieger A, *Talanta*, 26(12) (1979) 1125.
- 11 Sherikar A V, Phalke P N & Dhadke P M, *Indian J Chem Technol*, 4(1997) 59.
- 12 Mhaske A & Dhadke P M, *Sep Sci Technol*, 37 (2002) 1861.
- 13 Sunder raju P V, Merkle R K W, Graser P, Botha A, Mohanthy S K & Classen M, *Current Sci*, 93(6) (2007) 851.
- 14 Pohlandt C, *Talanta*, 26 (1979) 199.
- 15 Gedye R N, Bozic J, Durbano P M & Williamson B, *Talanta*, 36 (1989) 1055.
- 16 Lokhande T N, Anuse M A & Chavan M B, *J Saudi Chem Soc*, 4 (2000) 1.
- 17 Kokate S J, Aher H R & Kuchekar S R, *Bulgarian Chem Communi*, 41(3) (2009) 272.
- 18 Kokate S J & Kuchekar S R, *Chinese J Chromatography*, 27(6) (2009) 809.
- 19 Kokate S J, Aher H R & Kuchekar S R, *Analyt Chem-An Indian J*, 8(4) (2009) 575.
- 20 Phule S R, Shelar Y S & Kuchekar S R, *Analyt Chem-An Indian J*, 9(2) (2010) 260.
- 21 Kokate S J & Kuchekar S R, *J Saudi Chem Soc*, 41 (2010) 14.
- 22 Gavande A A, Vikhe V K, Kokate S J, Aher H R & Kuchekar S R, *Indian J Chem Technol*, 17(2010) 154.
- 23 Kokate S J, Aher H R & Kuchekar S R, *Bulgarian Chem Commun*, 43(3) (2011) 406.
- 24 Phule S R, Kokate S J & Kuchekar S R, *J Saudi Chem Soc*, 15 (2011) 209.
- 25 Furman, *Standard Method of Chemical Analysis*, 6<sup>th</sup> edn, Vol.I, edited by N Howell Furmans & Robert E Krieger (Publication Company, Malabar, Florida), 1962, 905.
- 26 Gardlund Z G, Curtis R J & Smith G W, *Liq Crystals Ordered Fluids*, 2 (1973) 544.
- 27 Sandell E B, *Colorimetric Determination of Traces of Metals*, 3<sup>rd</sup> edn., edited by B L Clarke, P J Elving & I M Kolthoff (Interscience Publishers, INC, New York), 1965, 443, 524, 563.