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Separation of Osmium(VIII) from Platinum Group Metals by Extraction with Liquid Ion Exchangers

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NOTE

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Abstract

A method is developed for the extraction and separation of osmium from palladium, platinum, ruthenium, rhodium, and iridium with tri-*n*-octyl amine either from hydrochloric or hydrobromic acid solutions. The extracted species is $(R_3NH^+)_2OsCl_6^{2-}$. The method is shown to be applicable to synthetic mixtures.

A liquid ion exchanger such as tri-*n*-octyl amine (TOA) has been used as an extractant in this laboratory for the selective separations of copper (*1*), mercury (*2*), and tin (*3*). This paper describes systematic studies on its use for separation of osmium from platinum group metals such as palladium(II), platinum(IV), ruthenium(III), rhodium(III), and iridium. A 5% solution of TOA in benzene extracts osmium quantitatively from 5 *M* HCl or HBr solutions. The metal ion from the organic phase is back-stripped with sodium hydroxide solution (2 × 5 ml of 1 *M* NaOH) and subsequently determined photometrically with thiourea (*4*).

The literature on the separation of osmium is somewhat scanty and has been reviewed by De et al. (*5*) and Korkisch (*6*) in their monographs. Short- and long-chain amines (*7*) have been used for extraction studies of osmium but no attempts were made to separate osmium from platinum group metals. The proposed method for the extraction of osmium permits its separation from metal ions such as Pd, Pt, Ru, Rh, and Ir.

EXPERIMENTAL

Apparatus and Reagents

Absorbance measurements were taken on a Zeiss Spectrophotometer (German) using 1 cm quartz cells.

The stock solution of osmium(VIII) was prepared by dissolving 1 g OsO_4 (Johnson Matthey and Co., London) in 0.1 *N* H_2SO_4, standardized and diluted as required for working solution.

A 5% w/v solution of TOA (Kochlight, England) in benzene was equilibrated for 10 min with equal volumes of 4 *M* HCl or 2 *M* HBr solution before use.

All other chemicals used were of GR grade.

Extraction Procedure for Osmium

Take 300 μg of osmium and add hydrochloric or hydrobromic acid to make its concentration 5 *M* in a total volume of 10 ml. Transfer the solution to a separating funnel and extract twice (shaking period, 5 min each) with 5 ml of 5% TOA in benzene. Collect the organic phase and back-strip osmium by equilibrating with 1 *M* NaOH solution (2 × 5 ml). The combined aqueous phase is shaken with 5 ml of benzene to remove traces of TOA. Finally, osmium is determined photometrically with thiourea (*4*).

RESULTS AND DISCUSSION

The extraction behavior of osmium with varying acid and TOA concentration is shown in Table 1. Five percent TOA extracts osmium quantitatively from 5 *M* HCl or HBr solutions. The log-log plot of distribution ratio vs $[TOA]_{org}$ at fixed acid concentration (2 and 3 *M* HCl) gave a slope of 1.73 (Fig. 1), indicating that the metal: amine ratio in the extractable species is 1:2. The high molecular weight amine reacts with HCl according to

$$[R_3N]_0 + H^+ + Cl^- \rightleftarrows \underset{\text{amine salt}}{[R_3NH^+Cl^-]_0}$$

where $R = -CH_2 \cdot (CH_2)_6 \cdot CH_3$.

The amine salt thus formed acts as a liquid anion exchanger and reacts with the halometallic complex:

$$2(R_3NH^+Cl^-)_0 + H_2OsCl_6 \rightleftarrows (R_3NH^+)_2OsCl_6^{2-} + 2HCl$$

The extracted species is thus $(R_3NH^+)_2OsCl_6^{2-}$.

TABLE 1

Extraction Behavior of Osmium(VIII) as a Function of Acid Concentration and TOA Concentration[a]

Initial acid concentration	1% TOA (0.025 *M*)		2% TOA (0.055 *M*)		3% TOA (0.083 *M*)		4% TOA (0.11 *M*)		5% TOA (0.14 *M*)	
	%*E*	*D*	%*E*	*D*	%*E*	*D*	%*E*	*D*	%*E*	*D*
HCl										
1	40.8	1.73	66.2	3.918	80.7	8.2	83.3	9.9	86.1	12.3
2	45.1	1.64	70.7	4.6	83.3	9.97	88.8	16.18	92.0	23.0
3	51.0	2.00	75.0	6.0	86.7	13.2	91.0	20.18	98.2	27.3
4	77.6	6.9	87.2	13.5	88.8	16.2	92.7	25.3	99.0	198.0
5	89.8	17.8	93.4	28.8	95.5	44.4	96.7	58.8	100	∞
HBr										
1	56.4	2.6	69.0	4.3	74.9	5.9	78.0	70.0	81.0	8.5
2	59.3	2.8	70.7	4.6	76.7	6.6	80.5	8.2	83.3	9.9
3	66.6	3.4	72.0	5.1	77.7	6.9	91.7	22.0	94.4	33.7
4	78.0	7.0	80.5	8.2	81.5	8.8	93.4	28.3	98.5	131.1
5	81.0	8.5	83.3	9.9	84.3	10.9	94.4	33.7	100	∞

[a] Os(VIII) = 300 μg; extracting solution = 2 × 5 ml of 5% TOA.

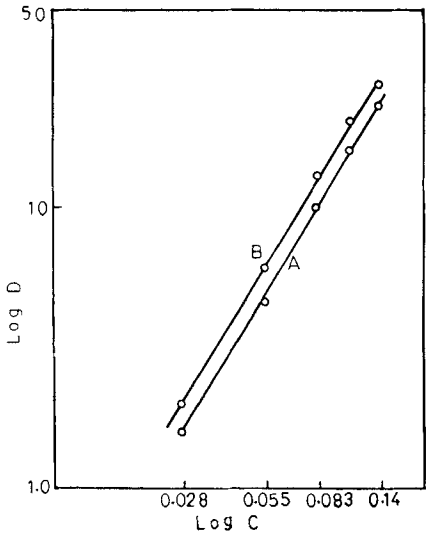

FIG. 1. Log-log plot of distribution ratio vs $[TOA]_{org}$ at 2 *M* HCl (A) and 3 *M* HCl (B).

TABLE 2
Effect of Diverse Ions (Os = 300 μg)

Ions added	Tolerance limit (μg)
Palladium	None
Platinum(IV)	4000
Ruthenium (III)	None
Rhodium(III)	4000
Iridium(III)	2000
Copper	None
Selenium(IV)	5000
Tellurium(IV)	5000
Phosphate	5000
Thiocyanate	None
Tartrate	5000
Citrate	5000
EDTA	5000
Ascorbate	5000

An interference study showed that of the ions tested (Table 2), only palladium, ruthenium, copper, and thiocyanate seriously affect the extraction and determination of osmium(VIII). Procedures are described below for the separation of osmium from palladium and ruthenium.

Separation of Osmium from Rhodium, Iridium, Palladium, and Platinum

The extraction of osmium from a 5 *M* HCl solution with 5% TOA in benzene facilitates its separation from rhodium, iridium, palladium, and platinum. Rhodium and iridium remain in the aqueous extract (determined by known methods) whereas palladium and platinum coextract with osmium. From the organic layer, palladium and platinum are back-stripped with 2.5 *M* HNO_3 (2 × 5 ml) and 3 *M* HNO_3 (2 × 5 ml) solutions, respectively, and estimated in the aqueous extract (*4*). Finally, osmium from the TOA layer is removed and estimated as described in the general procedure. The results for various synthetic mixtures are reported in Table 3.

Separation of Osmium and Ruthenium

Separation of osmium from ruthenium is achieved by its extraction from 5 *M* HBr solution into TOA. Under this condition, ruthenium quantita-

TABLE 3

Analysis of Synthetic Mixtures (all analyses were carried out in triplicate)

Composition of mixture and amounts taken (μg)	Osmium recovered (%)	Relative error (%)	Percentage recovery of added ions	Relative error (%)
Os, 300; Pd, 200	99.7	0.3	99.2	0.8
Os, 300; Pt, 300	99.7	0.3	98.9	1.1
Os, 300; Ru, 300	99.0	1.0	98.9	1.1
Os, 300; Rh, 300	99.5	0.5	99.2	0.8
Os, 300; Ir, 300	99.5	0.5	99.4	0.6
Os, 300; Pd, 300; Pt, 300	99.2	0.8	—	—
Os, 300; Pd, 600; Pt, 600	99.2	0.8	—	—
Os, 300; Rh, 300; Ir, 300	99.5	0.5	—	—
Os, 300; Rh, 1000; Ir, 1000	99.5	0.5	—	—

tively retains in the aqueous phase. The TOA phase is washed with NaOH (2 *M*) to remove osmium in the aqueous extract and then determined as described earlier. Ruthenium is estimated by the thiourea method (*4*). The separation results are reported in Table 3.

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REFERENCES

1. P. S. Patil and V. M. Shinde, *Mikrochim. Acta, II*, 207 (1977).
2. P. S. Patil and V. M. Shinde, *Indian J. Chem., 14A*, 1030 (1977).
3. P. S. Patil and V. M. Shinde, *Sep. Sci. Technol., 14*, 247 (1979).
4. E. B. Sandell, *Colorimetric Metal Analysis*, 3rd ed., Interscience, New York, 1958.
5. A. K. De, S. M. Khopkar, and R. A. Chalmers, *Solvent Extraction of Metals*, Van Nostrand, London, 1970.
6. J. Korkisch, *Modern Methods for the Separation of Rare Metal Ions*, Pergamon, New York, 1969.
7. H. Meier, E. Zimmerhackl, W. Albrecht, D. Bosche, W. Wecker, P. Menge, A. Ruckdeschel, E. Unger, and G. Zeitler, *Mikrochim. Acta, 1969*, 826.

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