Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Application of Solvent Extraction to the Refining of Precious Metals. II. Purification of Ruthenium

M. Ali Khan[a][b]; D. F. C. Morris[a]
[a] DEPARTMENT OF CHEMISTRY, BRUNEL UNIVERSITY, LONDON, ENGLAND [b] Institute of Chemistry, The Panjab University, Lahore, West Pakistan

To cite this Article Khan, M. Ali and Morris, D. F. C.(1967) 'Application of Solvent Extraction to the Refining of Precious Metals. II. Purification of Ruthenium', Separation Science and Technology, 2: 5, 635 — 644
To link to this Article: DOI: 10.1080/01496396708049727
URL: http://dx.doi.org/10.1080/01496396708049727

SEPARATION SCIENCE, 2(5), pp. 635–644, Nov., 1967

Application of Solvent Extraction to the Refining of Precious Metals. II. Purification of Ruthenium*

M. ALI KHAN† and D. F. C. MORRIS
DEPARTMENT OF CHEMISTRY
BRUNEL UNIVERSITY
LONDON, ENGLAND

Summary

A procedure for the purification of ruthenium based on its extraction as the tetroxide by carbon tetrachloride is described. Radiotracer studies have shown that the method provides an excellent quantitative separation of ruthenium from several other elements. It appears that advantages could ensue from the incorporation of a scaled-up version of the procedure in the process for the commercial refining of ruthenium.

At the Platinum Metals Refinery of International Nickel Limited at Acton, London, one of the most important steps in the separation and purification of ruthenium involves the distillation of the tetroxide RuO_4 (*2–4*). This procedure has certain drawbacks; many traps are required to assure complete recovery, a separation from osmium is not achieved, and great care is required to exclude organic matter from the system to avoid explosions. It was decided, therefore, to investigate the possibility of replacing the distillation by solvent extraction. Results of a preliminary laboratory-scale study are presented in this article. Carbon tetrachloride has been employed as the extractant for ruthenium(VIII) oxide. This solvent has been used previously on many occasions for extraction of RuO_4, particularly in radiochemical separations where a quantitative yield

---

[*] See Ref. (*1*).

[†] On leave from the Institute of Chemistry, The Panjab University, Lahore, West Pakistan.

is not required (5–8). For the present purpose it was desirable to devise a procedure giving complete recovery and this necessitates particular care to avoid loss of ruthenium(VIII) oxide by volatilization.

In our method, oxidation of ruthenium(VI) in solution to ruthenium(VIII) oxide is effected by addition of freshly prepared sodium hypochlorite solution and acidification. The tetroxide is extracted with carbon tetrachloride and subsequently the ruthenium is back-extracted from the organic phase into a cooled aqueous solution of 6 *M* hydrochloric acid saturated with sulfur dioxide. A quantitative recovery of ruthenium is easily achieved in this way and decontamination from other elements is good.

We have also carried out some experiments with Arklone (trichlorotrifluoroethane) as the organic extractant. This was found not to extract ruthenium(VIII) oxide so well as carbon tetrachloride but it has the general advantage of being less toxic than the latter compound. However, since other substances involved in the process are poisonous, there seemed little point in fully pursuing a study with Arklone.

EXPERIMENTAL

Solvent

Carbon tetrachloride of AnalaR quality was used without further purification.

General Procedure

Ruthenium metal powder, mingled with known amounts of various other elements, was mixed thoroughly with sodium peroxide in a silver crucible and heated at 500° for 10 min. After cooling, the resulting cake was leached with water and filtered using a sintered-glass disk. The filtrate was treated with 6 *M* hydrochloric acid until a precipitate just appeared. A volume of carbon tetrachloride corresponding to one-quarter of that of the aqueous solution was added and the mixture was kept cool (<20°). An excess of an ice-cold freshly prepared solution of sodium hypochlorite* was added, followed by dropwise addition of 6 *M* hydrochloric acid until the color changed to golden-yellow. The solution was adjusted to pH 5–7

---

* Prepared by saturating ice-cold 3.5 *M* sodium hydroxide with chlorine.

by addition of a few more drops of 6 *M* hydrochloric acid and the system agitated to bring about extraction of ruthenium tetroxide into the organic layer. The organic phase was then run off below the surface of a cooled solution of 6 *M* hydrochloric acid saturated with sulfur dioxide which back-extracts the ruthenium into aqueous medium. The extraction and back-extraction were repeated with two additional portions of carbon tetrachloride; the ratio (volume of organic phase/volume of aqueous phase) was 0.2 in each case. The resulting aqueous phase containing the purified ruthenium was separated and retained for assay.

Osmium in the final organic phase was subsequently transferred to aqueous solution by equilibrating the carbon tetrachloride extract with 3 *M* sodium hydroxide.

Tests of the Efficiency of the Procedure

The yield of ruthenium obtained with the procedure was determined in most experiments by measuring the concentration of the element in the solution of sodium ruthenate and in the final aqueous solution by a spectrophotometric method based on that of Ayres and Young (9). In some cases the yield was elucidated radiochemically by use of ruthenium labeled with ^{106}Ru–^{106}Rh. Spectrophotometric and radiochemical analyses gave results in excellent agreement.*

The efficiency of separation of a number of other elements from ruthenium was determined radiochemically. A known weight of a particular element, labeled with an appropriate radioisotope, was mixed with ruthenium and passed through the procedure. The elements studied and the corresponding radionuclides used as tracers are listed in Table 1.

RESULTS

Results for the separation of ruthenium from various elements effected by the procedure are shown in Tables 2–10. Measurements with ^{106}Ru indicate that extraction of RuO_4 with the three batches of carbon tetrachloride is complete. It will be noted from Table 2 that ruthenium is separated from more than 90% of original osmium

---

* Attention must be given to the fact that ruthenium produced in recent years is contaminated with ^{106}Ru–^{106}Rh originating from "fallout" (*10,11*). The ruthenium metal used in our tests was shown to be free from radioactivity.

TABLE 1

Radionuclides Used as Tracers for the Several Elements

Ruthenium	^{106}Ru	Platinum	^{197}Pt
Osmium	^{191m}Os + ^{193}Os	Gold	^{198}Au
Rhodium	^{105}Rh	Silver	^{110m}Ag
Palladium	^{109}Pd	Iron	^{59}Fe
Iridium	^{192}Ir	Tin	^{113}Sn

TABLE 2

Separation of Ruthenium from Osmium

Element taken, mg		Element in final solution, mg		Os lost in Na_2O_2 fusion, mg	Os recovered from organic extract, mg
Ru	Os	Ru	Os		
35.0	0.39	35.0	0.039	0.09	0.22
46.3	0.20	46.3	0.015	0.06	0.12
53.3	0.30	53.3	0.024	0.09	0.17
53.6	0.27	53.5	0.023	0.07	0.16
67.0	0.20	66.9	0.024	0.01	0.14

TABLE 3

Separation of Ruthenium from Rhodium

Element taken, mg		Element in final solution, mg	
Ru	Rh	Ru	Rh
53.8	0.32	53.6	0.0002
60.7	0.32	60.5	0.0003
68.8	0.32	68.8	0.0002
74.1	0.48	74.0	0.0001
57.6	0.64	57.5	0.0002

TABLE 4

Separation of Ruthenium from Palladium

Element taken, mg		Element in final solution, mg	
Ru	Pd	Ru	Pd
45.5	0.094	45.5	0.00005
54.0	0.094	54.0	0.0005
58.5	0.094	58.5	0.0004
66.2	0.094	66.2	0.0003
72.7	0.094	72.5	0.0002

TABLE 5

Separation of Ruthenium from Iridium

Element taken, mg		Element in final solution, mg	
Ru	Ir	Ru	Ir
50.5	0.30	49.9	0.00002
59.4	0.30	59.3	0.00002
46.1	0.54	45.8	0.00005
68.6	5.82	68.3	0.0012

TABLE 6

Separation of Ruthenium from Platinum

Element taken, mg		Element in final solution, mg	
Ru	Pt	Ru	Pt
59.9	0.96	59.8	0.004
67.7	0.96	67.5	0.006
48.7	0.48	48.6	0.0004
63.8	0.48	63.8	0.0014
65.0	0.48	65.0	0.0045

TABLE 7

Separation of Ruthenium from Gold

Element taken, mg		Element in final solution, mg	
Ru	Au	Ru	Au
36.7	0.19	36.7	0.00017
42.7	0.19	42.6	0.00040
46.7	0.19	46.6	0.00019
48.2	0.19	48.1	0.00008
50.7	0.19	50.6	0.00011

TABLE 8

Separation of Ruthenium from Silver[a]

Element taken		Element in final solution	
Ru, mg	Ag, μg	Ru, mg	Ag, μg
52.4	3.0	51.8	0.0005
53.7	3.0	53.9	0.0004
54.5	3.0	54.5	0.0001
64.9	3.0	64.9	0.0006
66.5	3.0	66.5	0.0007

[a] In these tests the sodium peroxide fusion was carried out in nickel crucibles.

TABLE 9

Separation of Ruthenium from Iron

Element taken, mg		Element in final solution, mg	
Ru	Fe	Ru	Fe
61.4	0.20	61.4	0.0009
71.1	0.20	71.1	0.0002
66.2	0.40	66.2	0.0021
68.1	0.40	68.0	0.0037
63.8	0.60	63.8	0.0050

TABLE 10

Separation of Ruthenium from Tin

Element taken, mg		Element in final solution, mg	
Ru	Sn	Ru	Sn
65.0	5.1	65.0	0.0031
65.8	5.1	65.7	0.0022
67.1	5.1	67.1	0.0047
68.6	5.1	68.6	0.0013
70.1	5.1	70.0	0.0013

TABLE 11

Trace Elements in Samples of Ruthenium

	Sample									
	A		B		C		D		E	
	1[a]	2	1	2	1	2	1	2	1	2
Pt	<10	n.d.	<10	n.d.	<10	n.d.	<10	n.d.	<10	n.d.
Pd	28	<10	24	<10	14	<10	12	<10	10	<10
Rh	94	<10	52	<10	25	<10	48	<10	41	<10
Os	1215	⩽50	1230	⩽50	348	⩽50	492	⩽50	427	⩽50
Au	<10	n.d.	14	n.d.	<10	n.d.	<10	n.d.	<10	n.d.
Fe	131	29	122	44	15	12	22	15	20	8
Sn	4	<1	5	<1	4	n.d.	3	n.d.	16	n.d.
Sb	45	<10	43	<10	12	<10	14	<10	15	<10

[a] The first and second results give the content in ppm before and after purification, respectively.

and that a considerable proportion of the latter can be readily recovered from the organic extract by equilibration with aqueous 3 *M* sodium hydroxide solution. The separation of ruthenium from the other elements studied is excellent.

The procedure has been applied to the purification of some commercial samples of ruthenium and the results of emission spectrographic analyses are presented in Table 11.

DISCUSSION

Although it should be emphasized that the present study has been carried out only on a laboratory scale, the results suggest that

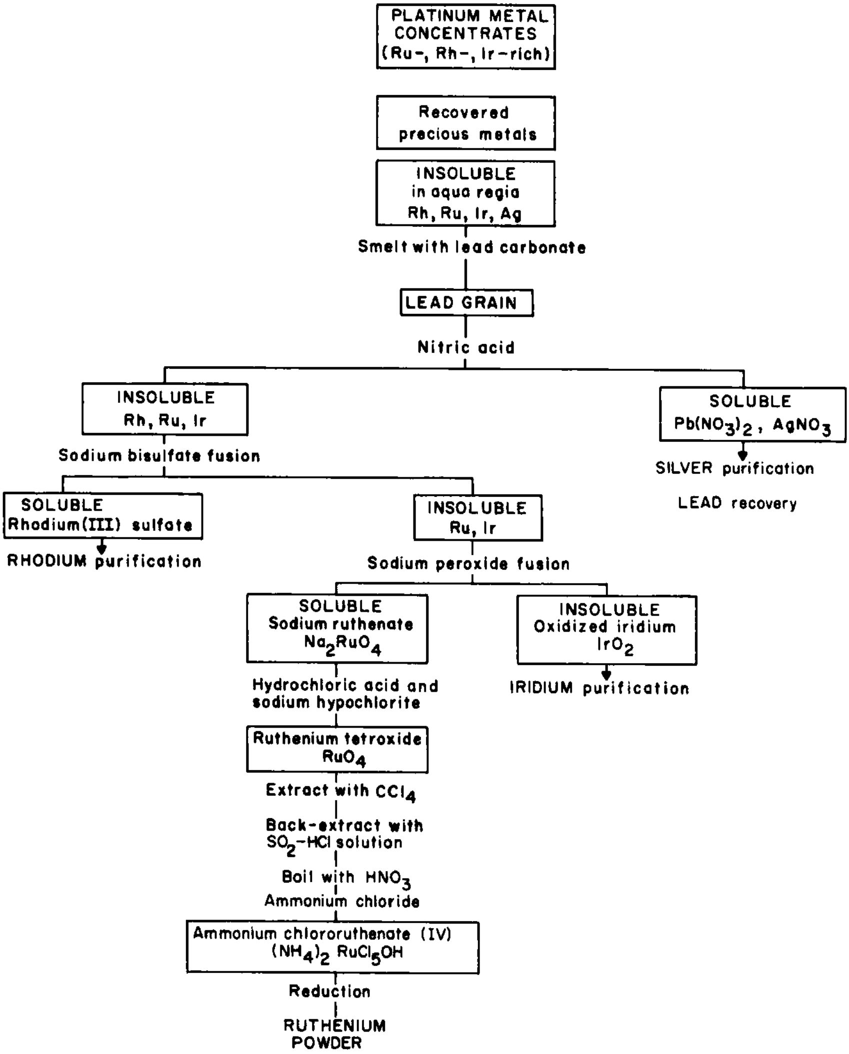

FIG. 1. Suggested outline flow sheet for refining of ruthenium.

it could be advantageous to substitute a scaled-up version of the method in place of the distillation procedure currently employed in the refining of ruthenium from concentrates of precious metals. A suggested new outline flow sheet is presented in Fig. 1. The boiling of the solution resulting from the solvent extraction stage with nitric acid should remove final traces of osmium. In any case these are likely to be very small, as the concentrates from which ruthenium is extracted have a low content of osmium.

Some Notes on the Chemistry of the Separation Method

The fusion of ruthenium with sodium peroxide gives a green mass containing perruthenate, RuO_4^-. On dissolving the cake in water, the deep orange ruthenate(VI) ion RuO_4^{2-} is formed and this is quite stable in the alkaline solution (*12*). Watanabe (*13*) has shown that osmium is oxidized by the fusion to OsO_4 and is dissolved in the aqueous leach as $[OsO_4(OH)_2]^{2-}$. On heating with sodium peroxide iridium is changed to a black dioxide and, since this is insoluble in water, a good separation of bulk iridium from ruthenium is achieved by the fusion and dissolution process.

On acidification of the alkaline solution of sodium ruthenate, the following reactions apparently occur (*14*):

$$2RuO_4^{2-} + 3H^+ = RuO_4^- + RuO(OH)_3\downarrow$$

$$3RuO_4^- + 3H^+ = 2RuO_4 + RuO(OH)_3\downarrow$$

The precipitate dissolves in sodium hypochlorite solution and further addition of hydrochloric acid yields RuO_4 as the predominant ruthenium species present (*12,15*).

The distribution of ruthenium tetroxide between carbon tetrachloride and aqueous alkali, acid, and neutral salt solutions has been thoroughly investigated by Martin (*16*). The distribution ratio D = (molarity of tetroxide in the organic phase)/(molarity of tetroxide in the aqueous phase) for zero ionic strength at 20° is ~59. The corresponding value for osmium tetroxide is 12–13 at 25° (*17,18*). The values of D appear to be independent of the concentration of the tetroxides over considerable ranges.

Although quantitative potentials for the reduction of OsO_4 and RuO_4 in acid solution do not seem to be available, it would appear from estimated data (*19*) that both the tetroxides should be reduced by the sulfurous acid solution used for back-extraction of ruthenium. However, it must be borne in mind that oxidation potentials measure energy differences and bear no relation to reaction kinetics. Surasiti (*20*) has shown that RuO_4 is reduced rapidly by iron(II) in acid solution, whereas reduction of OsO_4 is slow.

Acknowledgments

The authors are indebted to International Nickel Limited for generous support of the investigation. Appreciation is extended to Mr. J. H. Bond for his collaboration with the spectrographic analyses. One of the authors (M.A.K.) gratefully acknowledges the grant of leave from The Panjab University, Lahore, West Pakistan.

REFERENCES

1. M. A. Khan and D. F. C. Morris, *J. Less-Common Metals*, **13**, 53 (1967).
2. *The Mond Platinum Metals Refinery*, International Nickel Limited, London, *Publ. 1978* (1959).
3. F. S. Clements, *Ind. Chemist*, **1962**, 345.
4. *5 Platinum Metals*, International Nickel Limited, London, *Publ. 4074* (1967).
5. E. I. Wyatt and R. R. Rickard, *Natl. Acad. Sci., Natl. Res. Council Rept. NAS-NS 3029* (1961).
6. J. W. T. Meadows and G. M. Matlack, *Anal. Chem.*, **34**, 89 (1962).
7. S. S. Dehmlow and I. L. Preiss, *Z. Anal. Chem.*, **194**, 183 (1963).
8. D. F. C. Morris and M. A. Khan, *Radiochim. Acta*, **6**, 110 (1966).
9. G. H. Ayres, and F. Young, *Anal. Chem.*, **22**, 1277 (1950).
10. J. R. DeVoe, *Natl. Acad. Sci., Natl. Res. Council. Publ. NAS-NRC 895* (1961).
11. P. Kruger, *Nucleonics*, **20**(4), 102 (1962).
12. R. E. Connick and C. R. Hurley, *J. Am. Chem. Soc.*, **74**, 5012 (1952).
13. K. Watanabe, *J. Chem. Soc. Japan*, **78**, 983 (1957).
14. G. Nowogroki and G. Tridot, *Bull. Soc. Chim. France*, **1965**, 688.
15. M. Koyama, *J. Chem. Soc. Japan*, **82**, 1182 (1961).
16. F. S. Martin, *J. Chem. Soc.*, **1954**, 2564.
17. R. D. Sauerbrunn and E. B. Sandell, *J. Am. Chem. Soc.*, **75**, 4170 (1953).
18. G. Goldstein, *Inorg. Chem.*, **2**, 425 (1963).
19. W. M. Latimer, *The Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd ed., Prentice-Hall, Englewood Cliffs, N.J., 1959.
20. C. Surasiti, Ph.D. thesis, University of Minnesota, Minneapolis, 1957.

Received by editor August 10, 1967
Submitted for publication August 30, 1967