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Extractive Separation of Osmium and Ruthenium from Thiocyanate Media

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The sequential separation of osmium and ruthenium as thiocyanate complexes by extraction into mesityl oxide and cyclohexanone is described. The conditions for their re-extraction prior to determination from the respective organic layers have been established. Alternatively, the amounts of osmium and ruthenium were established spectrophotometrically from the coloured mesityl oxide and cyclohexanone layers respectively. The developed procedure has been applied to the separation of these metals present in synthetic samples of various minerals.

The reaction of thiocyanate with osmium and ruthenium has been extensively investigated for the spectrophotometric determination of these elements after extraction into diethyl ether, 2-octanone or isobutyl methyl ketone.[1–3] Though the extraction of osmium into diethyl ether or 2-octanone has been reported to be selective, the extraction behaviour of ruthenium has not been described.[1] In the extraction of ruthenium as tetraoxide into carbon tetrachloride,[2] osmium interferes demanding a separation prior to determination. Recently a method[3] has been described for the sequential separation of osmium and ruthenium when present together. This procedure is based on the extraction of the thiocyanate complex of osmium into peroxide containing ether and subsequently ruthenium into isobutyl methyl ketone. The extraction efficiency of osmium and ruthenium however are critically dependent on various experimental parameters such as acidity and duration of heating for complex formation in addition to peroxide content of ether. In the course of our study on the extraction behaviour of the thiocyanate complexes of osmium and ruthenium, it was found that osmium forms such complex at very low concentrations of thiocyanate and low acidities at room temperature itself while the formation of such extractable complex of ruthenium requires heating besides higher acidity and thiocyanate concentration. This formed the basis of the sequential solvent extractive separation procedure described here.

Experimental

Reagents. *Osmium(VIII) Solution*: Prepare by dissolving 1 g of osmium tetraoxide in 250 cm^3 of water as described elsewhere.[4] A working solution containing 100 μg cm^{-3} of osmium is prepared by suitably diluting the stock solution with water.

Ruthenium(III) Solution: Dissolve 0.513 g of ruthenium trichloride (LOBA-CHEMIE-PURISS) in 25 cm^3 of concentrated hydrochloric acid and dilute with water to 250 cm^3 to get a solution 1000 ppm in ruthenium.

Potassium Thiocyanate Solutions (0.05 mol dm^{-3} and 4 mol dm^{-3}) Sulfuric Acid (3 and 10 mol dm^{-3}).

Solvents: Mesityl oxide, cyclohexanone and cyclohexane.

Apparatus: A carl Zeiss PMQ-II spectrophotometer with 10 mm quartz cells.

Recommended Procedure. *Separation*: Transfer a suitable aliquot of sample solution (upto 8 cm^3) into a 60 cm^3 separatory funnel, add 1 cm^3 each of 0.05 mol dm^{-3} potassium thiocyanate and 3.0 mol dm^{-3} sulfuric acid and dilute to 10 cm^3. Equilibrate the solution with 5 cm^3 of mesityl oxide for 5 min. Separate the organic layer and equilibrate the aqueous layer with 10 cm^3 of cyclohexanone to remov the traces of dissolved mesityl oxide. Drain the aqueous layer into a 25 cm^3 beaker. Add 1.5 cm^3 of 10 mol dm^{-3} sulfuric acid and 3 cm^3 of 4 mol dm^{-3} potassium thiocyanate and dilute to 15 cm^3. Heat the solution at 75 °C for 20 min. Transfer the cooled solution after diluting to 15 cm^3 with water into a 60 cm^3 separatory funnel and equilibrate with 5 cm^3 of cyclohexanone for 1 min.

Equilibrate the mesityl oxide layer with 10 cm^3 of 0.1 mol dm^{-3} sodium hydroxide for 5 min to re-extract osmium. Add 15 cm^3 of cyclohexane to cyclohexanone layer and equilibrate with 10 cm^3 of water for 5 min. Use suitable aliquots of the stripped layers, if necessary, after diluting to a known volume and proceed with the determination as follows:

Determination: Add with mixing 5% potassium thiocyanate solution (2.5 cm^3 for osmium[5] and 1 cm^3 for ruthenium[6]) and 2.5 cm^3 of 1 mol dm^{-3} sodium acetate. Adjust the pH to 3, dilute to about 15 cm^3 with water and heat on a boiling water bath for 20 min. Cool and transfer into 25 cm^3 volumetric flasks. Add 5 cm^3 of 0.005% Rhodamine 6G solution and 1 cm^3 of 1% gelatin. Make up the solutions to mark and measure the absorbance at 565 nm in 10 mm cells against the respective reagent blanks. Establish the concentration by reference to corresponding calibration graphs prepared by using 0 to 40 μg of osmium and 0 to 8 μg of ruthenium.

Results and Discussion

Extraction of Osmium: Preliminary studies were carried out by extracting 100 μg each of osmium or ruthenium into 5 cm^3 of mesityloxide from 10 cm^3 of weakly acidic and acidic solutions containing 0.05 mol dm^{-3} potassium thiocyanate. The per cent extraction was established by estimating the amounts of osmium and ruthenium left out in the aqueous phase using the procedures described under 'Determination.'

The effect of varying the potassium thiocyanate concentration on the extraction of osmium (curve A) and ruthenium (curve B) are shown in Fig. 1. It is evident that though a concentration of as low as 5×10^{-4} mol dm^{-3} potassium thiocyanate is sufficient for the quantitative extraction of osmium, higher concentrations upto 0.9 mol dm^{-3} do not affect the extraction. There is no extraction of ruthenium until the potassium thiocyanate concentration is raised to 0.4 mol dm^{-3}.

Curve A in Fig. 2 shows the effect of acidity on the extraction of osmium from which it is clear that the extraction of osmium is quantitative from 0.1 to 0.6 mol dm^{-3} sulfuric acid. Over the whole range of acidity studied, ruthenium is found to be not at all extracted

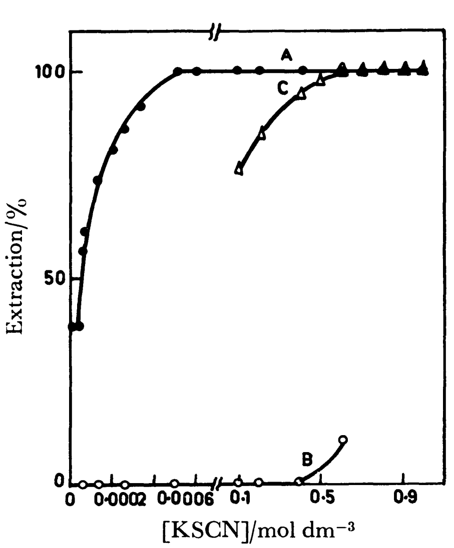

Fig. 1. Effect of potassium thiocyanate (0.30 mol dm^{-3} in H_2SO_4; 5 cm^3 mesityl oxide).
A: Osmium, B: ruthenium, C: ruthenium (1 mol dm^{-3} in H_2SO_4; 5 cm^3 cyclohexanone).

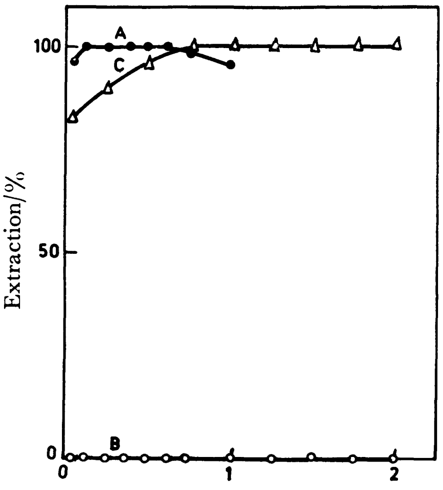

Fig. 2. Effect of acidity -H_2SO_4 (0.005 mol dm^{-3} in KSCN; 5 cm^3 mesityl oxide).
A: Osmium, B: ruthenium, C: ruthenium (0.8 mol dm^{-3} in KSCN; 5 cm^3 cyclohexanone).

(*cf.* curve B Fig. 2).

The extractability of osmium and ruthenium into a variety of solvents has been studied from a medium 0.005 mol dm^{-3} in potassium thiocyanate and 0.3 mol dm^{-3} in sulfuric acid. The results are summarised in Table 1 from which it is clear that only mesityl oxide extracted osmium quantitatively while none of the solvents extracted ruthenium under similar conditions. It is also established that a minimum of 3 min of equilibration is essential for the quantitative extraction of osmium into mesityl oxide and a ten-fold increase of the aqueous phase volume to that of the organic phase did not affect the extraction.

Extraction of Ruthenium. As ruthenium forms the extractable thiocyanate complex only on heating, extraction studies on ruthenium are carried out by heating 100 μg of ruthenium in a media which is 0.8 mol dm^{-3} in thiocyanate and 1 mol dm^{-3} in sulfuric acid to 70 °C in a water bath and equilibrating with 5 ml each of various solvents. As clear from Table 2, cyclohexanone alone extracts ruthenium quantitatively while mesityl oxide and cyclohexanol extract only partially. Other solvents like diethyl ether, benzene, cyclohexane, and pentyl acetate do not at all extract ruthenium. Cyclohexanone is preferred in further studies.

The effect of temperature on the formation of thiocyanate complex is established by heating the solution 0.8 mol dm^{-3} in potassium thiocyanate and 1 mol dm^{-3} in sulfuric acid for 20 min in a thermostat maintained at various temperatures and extracting into 5 cm^3 of cyclohexanone after cooling. The results indicate that for quantitative extraction the complex should be formed over the temperature range 70 to 85 °C. Higher temperatures are found to cause lower recoveries of ruthenium possibly due to the decomposition of the extractable species. It is also found that a minimum of 15 min of heating at 75 °C is essential for the complete formation of the complex while heating upto even one hour did not affect the extraction.

The effect of varying the concentration of thiocyanate (curve C, Fig. 1) indicates that a minimum of 0.6 mol dm^{-3} potassium thiocyanate is essential for the quantitative extraction of ruthenium. The effect of acidity on the extraction of ruthenium is studied using varying amounts of sulfuric acid in a medium 0.8 mol dm^{-3} in potassium thiocyanate. The results are indicated in

TABLE 1. CHOICE OF SOLVENT–OSMIUM STAGE

Solvent	Distribution ratio	
	D_{Os}	D_{Ru}
Carbon tetrachloride	6.9	<0.01
Chloroform	7.5	<0.01
Benzene	<0.01	<0.01
Cyclohexane	6.4	<0.01
Isobutyl methyl ketone	18.0	<0.01
Cyclohexanone	98.0	<0.01
1-Butanol	10.3	<0.01
Cyclohexanol	14.0	<0.01
Pentyl acetate	7.2	<0.01
Diethyl ether	5.3	<0.01
Mesityl oxide	$\gg 100$	<0.01

TABLE 2. CHOICE OF SOLVENT–RUTHENIUM STAGE

Solvent	Distribution ratio D_{Ru}
Carbon tetrachlride	0.286
Chloroform	0.174
Benzene	<0.01
Cyclohexane	<0.01
Isobutyl methyl ketone	0.667
Cyclohexanone	$\gg 100$
1-Butanol	1.704
Cyclohexanol	26.220
Pentyl acetate	<0.01
Diethyl ether	<0.01
Mesityl oxide	18.000

curve C, Fig. 2, from which it is clear that over the range of 0.75 to 2 mol dm^{-3} sulfuric acid, the extraction is quantitative. The extraction is found to be quantitative with equilibration times as low as 10 seconds and an aqueous to organic phase volume ratio of 3.5 : 1 does not affect the extraction.

Sequential Separation of Osmium and Ruthenium. From the studies on the individual extraction of osmium and ruthenium it is found that osmium forms a quantitatively extractable complex at concentrations of thiocyanate as low as 5×10^{-4} mol dm^{-3} from weakly acidic media at room temperature itself. Further, it is found that, under these conditions, increasing the thiocyanate concentration or acidity does not increase the extraction of ruthenium considerably. It has also been observed that ruthenium can form such extractable complex only on heating and the various parameters have been optimized for the quantitative extraction of ruthenium.

TABLE 3. RECOVERY STUDIES

Sample No.	Composition of the mixture (μg)		Amount recovered (μg)		Recovery (%)	
	Os	Ru	Os	Ru	Os	Ru
1	10	10	10	9.8	100	98
2	50	50	49.5	50	99	100
3	100	100	100	100	100	100
4	1000	1000	1000	1000	100	100
5	1000	10	1000	9.8	100	98
6	500	20	495	19.8	99	99
7	50	1000	49	1000	98	100
8	50	200	50	200	100	100
9	10	100	9.9	100	99	100
10	20	1000	20	1000	100	100

TABLE 4. ANALYSIS OF SYNTHETIC MIXTURES AFTER OXIDATIVE FUSION

Sample No.	Sample composition (wt%)	Composition of the synthetic sample (μg)	Amount found (μg)	
			Os	Ru
	Osmiridium or Syserkite			
1	Columbia			
	Ir (57.8), Pd(0.63)	Ir(660), Pd(8)	396.5	70.1
	Ru (6.37), Os(35.1)	Ru(70), Os(400)	393.0	68.8
			400.0	70.7
2	California			
	Ir(53.5), Pd(2.6)	Ir(1000), Pd(50)	812.0	9.7
	Ru(0.5), Os(43.4)	Ru(10), Os(800)	784.8	10.0
			800.0	10.2
3	Urals			
	Pt(0.62), Ir(43.28)	Pt(8), Ir(540)	505.0	100.0
	Pd(5.73), Ru(8.49)	Pd(75), Ru(100)	490.4	98.7
	Os(40.11)	Os(500)	501.2	100.6
4	Australia			
	Ir(58.13), Pd(3.04)	Ir(700), Pd(40)	400.0	65.3
	Ru(5.22), Os(33.46)	Ru(65), Os(400)	405.2	64.8
			398.3	65.0
5	South Africa			
	Pt(0.2), Ir(17)	Pt(1.5), Ir(125)	496.4	65.7
	Ru(0.9), Os(69.9)	Ru(65), Os(500)	500.2	65.3
			505.2	64.8
	Iridioosmium or Nevjanskite			
6	Urals			
	Pt(1.1), Ir(77.2)	Pt(50), Ir(3700)	1012.3	9.8
	Pd(0.5), Ru(0.2),	Pd(25), Ru(10),	990.5	10.0
	Os(21)	Os(1000)	1003.1	10.1
7	South Africa			
	Pt(0.1—3.1),	Pt(120), Ir(4500),	2530	20.0
	Ir(46.8—77.2),	Ru(20), Os(2500)	2500	19.7
	Ru(0—0.5), Os(21—49.3),	Rh(30)	2482	20.3
	Rh(0.5—7.7)			

Hence the two individual extraction steps are combined and applied to the sequential separation of osmium and ruthenium from their mixtures in the following manner.

After the extraction of osmium, the thiocyanate concentration of the aqueous phase is increased to 0.8 mol dm^{-3} and acidity to 1 mol dm^{-3} in sulfuric acid, dilute to 15 cm^3 and heated in a boiling water bath at 75 °C for 20 min. The solution was then cooled, diluted to about 15 cm^3 and when equilibrated with 5 cm^3 of cyclohexanone gave lower recoveries of ruthenium. This can be attributed to the presence of dissolved mesityl oxide in the aqueous phase. Equilibration of the aqueous phase, after extracting off osmium, with 10 cm^3 of cyclohexanone renders it free of any dissolved mesityl oxide and in this instance the recoveries of ruthenium are found to be quantitative. The results of the extraction and re-extraction studies of binary mixtures of osmium and ruthenium over varying ratios are indicated in Table 3. From the table it is clear that the developed procedure works quite satisfactorily for the separation of osmium and ruthenium over a widely varying ratios and concentrations.

Estimation. Of the various stripping agents studied only sodium hydroxide (0.1 mol dm^{-3}) is found to re-extract osmium quantitatively while none of the reagents examined are effective for the quantitative stripping of ruthenium. Since hydrocarbons are found not to extract ruthenium (*cf.* Table 2), addition of such hydrocarbons to the organic phase is attempted to facilitate the quantitative re-extraction of ruthenium. Both benzene and cyclohexane are found to be effective. However, the latter is chosen, as in this instance, the phase separation is clean and rapid. A minimum ratio of 3 : 1 by volume of cyclohexane to cyclohexanone is found to be essential for the quantitative stripping of ruthenium into 10 cm^3 of water. The osmium and ruthenium contents are established by subjecting the respective strippings to 'Determination' as described earlier.

Further, it is observed that the organic extracts are coloured blue in the case of osmium and bluish violet in the case of ruthenium. Hence the amounts of osmium or ruthenium extracted are also determined by measuring the absorbance of these layers at 590 nm and 560 nm respectively after centrifuging. The Beer's law ranges are 0.4 to 24 ppm for osmium and 1 to 12 ppm for ruthenium. The molar absorptivities for the determination of osmium and ruthenium are 9.5×10^3 and 1.4×10^4 dm^{-3} mol^{-1} cm^{-1} respectively.

Analysis of Synthetic Samples. As no standard sample is available, the method developed is applied to synthetic samples of syserkite (osmiridium) and Nevjanskite (iridioosmium) containing both osmium and ruthenium, after oxidative fusion with potassium hydroxide and potassium nitrate.[7] The samples were prepared by mixing the respective metal solutions in proportions reported elsewhere.[8] To each sample 1 cm^3 of 5% hydrazine sulfate was added and heated gently almost to dryness to which about 1 g of 8 : 1 mixture of potassium hydroxide and potassium nitrate were added and heated at 800 °C for 30 min. The fused melt was leached with 5 cm^3 of 1 mol dm^{-3} hydrochloric acid and diluted to 50 cm^3. Aliquots of the made up solution are subjected to the separation and determination and the results are summarized in Table 4. The results show that the procedure developed can be directly applied to the analysis of osmium and ruthenium in these minerals.

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