

BEHAVIOUR OF TRACE IMPURITIES DURING CHEMICAL DISSOLUTION OF A METAL: PLATINUM ELEMENTS IN ALUMINIUM AND NICKEL

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Summary—In order to study the behaviour of trace impurities during aqueous dissolution of a sample, aluminium and nickel-based alloys containing 10^{-4} – 10^{-1} % Ir, Os or Ru were used. Yields of chemical separations such as distillation and ion-exchange were chosen as dissolution criteria. Dissolution of aluminium samples leads to precipitation of the three impurities. The Os and Ru precipitates can afterwards be dissolved by an oxidation procedure, in contrast to commercial powders of these elements. This behaviour may be explained in terms of the small grain-size of the precipitates. The iridium precipitates cannot be dissolved, which prevents quantitative separation of this element from an aluminium matrix. In the case of nickel alloys, these three impurities are dissolved and can be quantitatively separated.

In many analytical methods samples must be dissolved in aqueous media. In activation analysis, use of solutions of samples and standards is actually the easiest way to achieve identical and reproducible counting geometry. Dissolution is also needed when a chemical separation is included in the analytical procedure.

A proper dissolution method should result in a particular component being dissolved either completely (in which case it should also be brought to a definite oxidation state), or not at all. Depending on the chemical properties of the elements, this is not always easy to achieve. It may be a difficulty in the determination of Ru, Os and Ir when present as the metals in more electropositive matrices such as aluminium and nickel. These impurities should be deposited in the metallic state during the dissolution of the sample in either acidic or basic medium, and because of the difficulty of dissolving them it is not easy to see how to bring them to the oxidation state necessary for determination.

We wanted to study this problem with experimental conditions as close as possible to those encountered with an actual sample. For the purpose, we made alloys containing a very small but known quantity of each of these elements in aluminium or nickel¹ and irradiated them in a thermal neutron flux. Thus, we had aluminium or nickel samples doped with radioactive tracer of Ru, Os or Ir. In order to state whether the tracer dissolves or not, we thought that the best way was to submit the dissolved sample to a chemical separation. We assumed that the extent of dissolution of the tracer would be defined by the yield of the chemical separation, calculated from radioactivity measurements.

From the possible chemical separations we chose distillation for Ru and Os, which have volatile oxides,

and ion-exchange for all three elements. Anion-exchange was performed in hydrochloric,^{2,3} hydrobromic⁴ or nitrite media,⁵ and cation-exchange in hydrochloric acid-ethanol medium.⁶

EXPERIMENTAL

Experiments were performed on Al or Ni containing from 0.5 to 20,000 μg of Os, Ru or Ir per g of matrix and on commercial Os and Ru powders. Samples (2–100 mg) were irradiated for periods ranging from 30 min to 2 days, according to the concentrations, in a thermal-neutron flux of $3 \times 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ in the EL₃ reactor at Saclay. After application of the experimental procedures, the yield of the chemical separation was calculated from radioactivity measurements of the various chemical fractions, on a Ge(Li) detector coupled to a pulse-height analyser.

Distillation procedures

These were studied only with aluminium samples. We used a distillation apparatus consisting of a 250-ml flask wherein the samples were dissolved, a 10-cm distillation column, a condenser, and two receivers containing 20 ml of 9M sodium hydroxide.⁷ The apparatus was flushed with air at a flow-rate of 200 ml/min. Various techniques were tried, as follows. The samples were dissolved in 10–15 ml of the acids and bases mentioned.

Procedure D₁ (Os, Ru). The sample was dissolved in 10 ml of sodium hydroxide 6M. The solution was then adjusted to be 6–8M in hydrochloric acid and the distillation performed according to Payne.⁸ After addition of 10 ml of 20% perchloric acid, and then 15 ml of 20% sodium bromate solution, the distillation was continued for 30 min longer, and then for a further 40 min after dropwise addition of 15 ml of 20% sodium bromate solution. The radioactivities of the receiver solutions and of the residue were compared.

Procedure D₂ (Os, Ru). The sample was dissolved in 6M hydrochloric acid. The acidity was adjusted to be 8M and the solution treated as in procedure D₁.

Procedure D₃ (Os). The sample was dissolved in 6M sodium hydroxide. The solution was adjusted to be 12M in sulphuric acid and the distillation performed according

to Chung and Beamish⁹ after addition of 30 ml of 30% hydrogen peroxide.

Procedure D₄ (Os). The sample was dissolved in 6M hydrochloric acid and the distillation performed as in procedure D₃.

Procedure D₅ (Os). The sample was dissolved in 6M hydrochloric acid and the distillation performed from *aqua regia*.

Procedure D₆ (Os, Ru). The sample was dissolved in 6M hydrobromic acid. After evaporation the residue was treated with a solution of 6M hydrobromic acid containing 2% of bromine. The solution was evaporated (during the evaporations only 0.01% Ru and 0.67% Os were lost) and submitted to distillation procedure D₃ for Os and D₁ for Ru.

Procedure D₇ (Os). The sample was dissolved in 8M sulphuric acid and then treated as in procedure D₃.

Procedures using ion-exchange for aluminium samples

Procedure E₁ (Os, Ru). The sample was dissolved in a 6M hydrobromic acid–2% bromine solution. The resulting solution was adjusted to be 0.5M in hydrobromic acid and 0.0035M in bromine and passed through a column (height 12 cm, diameter 1 cm) of Dowex 1 × 4 resin, Br⁻ form, at a flow-rate of 1.5 ml/min. The column was washed with 20 ml of a solution having the same concentrations of the acid and bromine as the test solution. The radioactivities of the primary solution, of the resin and of the eluate were measured.

Procedure E₂ (Os, Ru). The sample was dissolved as in procedure E₂ and the solution was evaporated almost to dryness. The residue was dissolved in 1M sodium nitrite and adjusted to be 0.1M in nitrite at pH 6 in a volume of 30 ml. This solution was passed through a column (height 10 cm, diameter 1 cm) of Dowex 1 × 8 resin, NO₂⁻ form, at a flow-rate of 1 ml/min. The column was washed with 30 ml of 0.1M sodium nitrite at pH 6. The radioactivities were measured as in procedure E₁.

Procedure E₃ (Ir). The sample was dissolved in 6M hydrochloric acid. The solution was evaporated almost to dryness, treated with 0.5 ml of 0.5% ceric sulphate solution in 4M sulphuric acid and adjusted to be 1M in hydrochloric acid in a volume of 30 ml. The solution was passed through a column (height 15 cm, diameter 1 cm) of Dowex 1 × 8 resin, Cl⁻ form, at a flow-rate of 2 ml/min. The column was washed with 30 ml of 1M hydrochloric acid containing 0.05% ceric sulphate. The radioactivity measurements were performed as in procedure E₁.

Procedure E₄ (Ir). The sample was dissolved in 6M hydrochloric acid. Concentrated nitric acid was added in order to produce *aqua regia*, which was then evaporated almost to dryness. The residue was dissolved in 2M hydrochloric acid and oxidized with a cerium (IV) solution. The solution obtained (20 ml) was passed through a column (height 10 cm, diameter 0.6 cm) of Dowex 1 × 8 resin, Cl⁻ form, at a flow-rate of 2 ml/min. The column was washed with 20 ml of 2M hydrochloric acid containing 0.05% ceric sulphate. The measurements were performed as in procedure E₁.

Procedure E₅ (Ir). The sample (5-μg/g alloy only), and 30 mg of non-irradiated 0.4% alloy used as carrier, were dissolved in 5M sodium hydroxide. The solution was then treated with sulphuric acid and cerium (IV) and boiled for 30 min. This solution (20 ml), 1M in sulphuric acid, was passed through a column (height 10 cm, diameter 6 cm) of Dowex 1 × 8 resin, initially in the Cl⁻ form and previously treated with 0.05% ceric sulphate solution. The column was washed with 20 ml of 1M sulphuric acid containing 0.05% ceric sulphate. The radioactivity measurements were performed as in procedure E₁.

Procedure E₆ (Ir). The sample was dissolved in 6M hydrobromic acid–2% bromine solution. After evaporation almost to dryness, the residue was dissolved in more of

the solvent mixture, again evaporated almost to dryness, and redissolved in 20 ml of 0.5M hydrobromic acid. This solution was filtered through a porosity 4 sintered-glass filter covered with an Ederol No. 4/M filter paper. The filtrate was adjusted to be 0.05M in hydrobromic acid–0.0035M bromine in 20 ml. The radioactivities of the filtrate and of the filter were measured. The filtrate was passed through a column (height 15 cm, diameter 1.2 cm) of Dowex 1 × 4 resin, Br⁻ form, at a flow-rate of 1 ml/min. The column was washed with 20 ml of 0.05M hydrobromic acid–0.0035M bromine. The radioactivities of the resin and of the eluate were measured.

Procedure E₇ (Ir). The sample was dissolved in 6M hydrochloric acid. Concentrated nitric acid was added in order to produce *aqua regia*, which was then evaporated almost to dryness. The residue was dissolved in 4M hydrochloric acid and oxidized with hydrogen peroxide. The solution was evaporated and adjusted to be 0.1M in hydrochloric acid and to contain 90% ethanol. This solution (40 ml) was passed through a column (height 10 cm, diameter 1 cm) of Dowex 50 × 8 resin, H⁺ form, at a flow-rate of 2 ml/min. The column was washed with 40 ml of 0.1M hydrochloric acid–90% ethanol.

The eluate was adjusted to be 0.2M in sodium nitrite and passed through a Dowex 1 × 8 column as in procedure E₂. The yields of sorption on both columns were determined by radioactivity measurements.

Procedure E₈ (Ir). The sample was dissolved in 5 ml of the bath used for chemical polishing of aluminium¹¹ (70% phosphoric acid, 25% sulphuric acid, 5% nitric acid) at 90°. The solution was diluted to 60 ml and passed through Dowex 50 × 8 resin as in procedure E₇.

Procedure E₉ (Ir). The sample was dissolved in a 1:1 v/v nitric acid–hydrofluoric acid mixture.¹² The solution was evaporated in order to eliminate the acids and then made 0.1M in hydrochloric acid and to contain 90% ethanol. It was then treated as in procedure E₇.

Procedure using ion-exchange for nickel samples

Procedure E₁₀ (Ir). The nickel sample was dissolved in 6M nitric acid. The solution was evaporated twice in presence of concentrated hydrochloric acid, in order to eliminate the nitric acid. The solution was then adjusted to be 0.1M in hydrochloric acid and to contain 90% ethanol, and passed through Dowex 50 × 8 and Dowex 1 × 8 resins as in procedure E₇.

RESULTS AND DISCUSSION

Separation yield with a nickel matrix

We did not observe a precipitate during the dissolution of a nickel sample. The separation yields of platinum elements were always very good. It seems that the electropositivity of the matrix has no effect

Table 1. Chemical separation yield of Ru in Al by various procedures (%)

Sample	Procedure				
	D ₁	D ₂	D ₆	E ₁	E ₂
Al–Ru 0.34%	96.2	—	—	—	—
Al–Ru 0.30%	—	95.1	98.2	84.5	99.8
Al–Ru 50 μg/g	95.3	97.1	97.8	—	—
Ru commercial powder	≤0.5	≤0.7	≤0.7	—	—

Table 2. Chemical separation yield of Os in Al by various procedures (%)

Sample	Procedure								
	D_1	D_2	D_3	D_4	D_5	D_6	D_7	E_1	E_2
Al-Os 2%	70	—	99.8	99.2	—	—	99.2	68.3	—
Al-Os 0.68%	—	79	99.7	—	99.9	99.9	—	—	98.6
Al-Os 50 $\mu\text{g/g}$	—	—	99.8	—	—	—	99.1	—	—
Al-Os 5 $\mu\text{g/g}$	—	—	99.5	—	—	≥ 99.9	—	—	—
Os commercial powder	≤ 0.2	—	≤ 0.8	≤ 0.7	1	≤ 0.5	≤ 0.1	—	—

when nitric acid is used for the dissolution. Platinum elements are probably dissolved as soon as they appear at the sample surface.

Separation yield with an aluminium matrix

In the case of aluminium we observed black precipitates during the dissolution of the less dilute alloys. The behaviour of these precipitates depends on the element concerned and on the further treatment.

In Tables 1 and 2 are presented the separation yields for Ru and Os. We did not apply procedures D_3 , D_4 , D_5 and D_7 to Ru, as these methods do not give quantitative distillation of this element, even if a soluble salt is used.⁹ Such methods could not be used to test the dissolution of ruthenium.

Tables 1 and 2 show that the alloys and commercial powders exhibit completely opposite behaviour. The commercial powders could never be dissolved, whereas Os and Ru resulting from alloy dissolution were separated in 95–100% yield by methods D_3 , D_4 , D_5 , D_6 , D_7 , E_2 and D_1 , D_2 , D_6 , E_2 respectively.

Distillation of osmium after oxidation by bromate (methods D_1 and D_2) and sorption of Os and Ru on an anion-exchange resin in hydrobromic acid medium did not give quantitative separations. Low yields were obtained even when soluble salts (ammonium hexachloro-osmate and hexachlororuthenate) were used. The results showed that methods D_1 , D_2 and E_1 could not be used to test the dissolution.

Table 3. Fixation of Ir from Al samples, on anion-exchange resin by various procedures (%)

Ir in alloy, w/w	Procedure		
	E_3	E_4	E_5
10^{-2}	—	92.6	—
4×10^{-3}	—	97.1	—
2.9×10^{-3}	—	87.8	—
5×10^{-5}	86.7	95	—
3.2×10^{-5}	—	90.5	—
5×10^{-5}	—	88.7	88.5
5×10^{-6}	—	93.6	—

In the case of iridium neither of the ion-exchange methods leads generally to a quantitative separation (Table 3). The separation yield could not be correlated to the alloy concentration. Experiments performed with a soluble salt of iridium (tetrachloride obtained by electrolytic dissolution of Ir^{10}) showed the same result, which could mean that the precipitate is dissolved during the oxidation process. However the presence of a black precipitate even after oxidation in the case of the 1% alloy, suggested that the ion-exchange resin might act as a filter. In order to check this hypothesis, we applied procedure E_6 in which the solution was filtered before passage through the resin. The results presented in Table 4 show that an appreciable fraction of the iridium was retained on the filter. This fraction was not very

Table 4. Separation of Ir from Al samples by procedure E_6 . Ratio of fixation on filter to total quantity (F/T) and of fixation on resin to quantity introduced onto the resin after filtration [$R/(R + E)$]

Ir in alloy, w/w	Experiment 1		Experiment 2	
	F/T , %	$R/(R + E)$, %	F/T , %	$R/(R + E)$, %
10^{-2}	33.6	94.9	26.2	97.6
2.9×10^{-3}	40.6	93.9	38.3	95.7
5×10^{-5}	6.4	97.5	32.5	91.7
5×10^{-6}	28.6	85.4	38.9	88.5
5×10^{-7}	9.6	88.4	3.8	88.2

Table 5. Fixation of iridium on Dowex 50 X8 and Dowex 1 X8 resins from Al and Ni samples after various dissolution procedures

Alloy Matrix	Ir $\mu\text{g/g}$	Procedure	Retained on Dowex 50, %	Retained on Dowex 1, %
Al	5	E_7	94.1	100
Al	50	E_7	96.6	100
Al	2900	E_7	97.8	100
Al	2900	E_8	84.1	100
Al	2900	E_9	94.4	100
Ni	744	E_{10}	4.8	
			3.0	100
			2.2	

reproducible, however, and could not be correlated to the alloy concentration. When the filtrate was passed through the ion-exchange column, the sorption yield was more reproducible and varied as the alloy concentration.

In order to check the possibility of fixing iridium on a resin by a filtration mechanism we applied procedure E_7 , which is analogous to procedure E_{10} applied to nickel (Table 5). In the case of the aluminium alloys, iridium is fixed on the cation-exchange resin, even at very low concentration, but this is not the case with the nickel matrix nor, more generally, with soluble iridium salts. It can be explained by the filtration effect, which probably occurs for all fixations of iridium on Dowex 1 resin without previous passage through a Dowex 50 column.

The direct dissolution of iridium from a nickel sample can be attributed to the oxidizing character of the nitric acid used for dissolution. We tried to use oxidizing dissolution baths with aluminium also (procedures E_8 and E_9), but they did not lead to a better dissolution of iridium.

Structure of the precipitates

The oxidation treatments did not lead to complete and reproducible dissolution of iridium precipitates resulting from aluminium alloys. These results are more in agreement with those expected from the metallic properties of Ir, than those for Os and Ru.

The difference between the behaviour of Os and Ru precipitates from the aluminium alloy and that of the commercial powders may be explained either by a difference in chemical composition, for instance the presence of oxides, or by a difference in the crystallite sizes. In order to choose between these postulates we took X-ray diffraction patterns of the available commercial powders (Os and Ru) and of the precipitates. In all cases we observed the characteristic peaks of metallic Ru, Os and Ir; we did not detect any other peak. We concluded that the precipitates were mainly composed of pure metal crystallites. A

more detailed analysis allowed an estimate of the crystallite size from the formula^{13,14}

$$D = \frac{0.9 \lambda}{2 \cos \theta \sqrt{\Delta^2 - \Delta_0^2}}$$

where D is the particle diameter, λ the wavelength of the incident X-ray (the K_α X-ray of cobalt in our case, $\lambda = 1.78 \text{ \AA}$), θ the Bragg angle, Δ the half-height width of the observed peak and Δ_0 the half-height width of a standard peak close to the one observed and given by a product with large well-crystallized grains (sodium chloride in this case).

The grain size of the precipitates was within the range 35–100 \AA . For the commercial powders of Ru and Os the peak widths were close to those which result from the spectral width of the incident X-rays. We could only calculate a lower limit of 1000 \AA for the grain size of the commercial powders.¹⁵

In order to confirm these results we made light- and electron-microscopy observations. The light-microscopy measurements gave a mean size of 0.01 mm for the commercial powders.

The precipitates obtained during alloy dissolution were deposited, after washing and centrifuging, on collodion-covered grids and observed with a Philips EM 300 electron microscope. At high magnification (about 200,000 \times) we saw individual grains and formations which seemed to be grain clusters. We could not establish a correlation between the grain or cluster size and the nature or concentration of the alloys. The diameter of individual grains varied from 20 to 50 \AA , that of the clusters from 150 to 400 \AA .

All these results seem to show that the precipitates are in the metallic state. Both methods lead to the same range of grain size for the precipitates: 20–100 \AA . The grain size of the commercial powders was found to be at least 1000 times larger. This value could explain the difference in the dissolution behaviour of the powders and precipitates.

CONCLUSION

Using dilute alloys of Os, Ru and Ir we have shown the decisive influence of the method of sample dissolution on the chemical separations and consequently on the analytical results. As might be foreseen from the chemical properties, Os, Ru and Ir are not dissolved during the dissolution of the aluminium-based alloy either in acid or in basic aqueous solutions. Further treatment could not completely dissolve iridium and allow a quantitative separation of this element.

The Os and Ru precipitates obtained can be dissolved by using a suitable oxidation treatment and quantitatively separated for instance by distillation. On the contrary, commercial powders of the same two elements cannot be dissolved. This difference of behaviour seems to arise from grain size differences, and probably explains why alloying platinum elements with an acid-soluble metal facilitates their dis-

solution.¹⁶ When the alloy is attacked with acids, the platinum elements form finely divided precipitates which are more easily dissolved than the initial samples. Osmium and ruthenium impurities can thus be brought into aqueous solution. Although iridium as impurity gives precipitates of the same grain size as Os and Ru, it cannot be directly brought into aqueous solution and other means of dissolution have to be used, for instance alkaline fusion. Sodium peroxide attack was successfully used by some authors for the determination of iridium in rocks and meteorites.^{3,17,18} Unfortunately this procedure is not suitable for aluminium. For the determination of iridium in this metal we recommend dissolving the sample in hydrochloric acid, evaporating to dryness and attacking the residue with sodium peroxide.

We observed that Os, Ru and Ir are dissolved from a nickel-based alloy during the dissolution of the sample in nitric acid. The difference in behaviour of aluminium and nickel alloys may be explained by a difference either in the alloy structure or in the dissolution mechanism. It is difficult to discuss the influence of alloy structure as the phase diagrams and solubilities of platinum elements in aluminium and nickel are not well known. For the dissolution mechanisms there is a real difference: nickel is dissolved by oxidation with nitric acid, whereas aluminium is dissolved by oxidation with protons, yielding hydrogen.

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