

# THE SEPARATION OF PLUTONIUM FROM URANIUM AND FISSION PRODUCTS ON ZIRCONIUM PHOSPHATE COLUMNS

IVAN GAL AND ALEKSANDAR RUVARAC

*Boris Kidrich Institute of Nuclear Sciences,  
Belgrade (Yugoslavia)*

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In recent years special attention has been given to the ion-exchange properties of zirconium phosphate and similar compounds in aqueous solutions<sup>1-12</sup>. These inorganic cation-exchangers are stable in oxidizing media and at elevated temperatures. Their resistance to ionizing radiation<sup>5</sup> makes them particularly suitable for work with radioactive solutions.

On account of this we considered it worthwhile to investigate the separation of plutonium from uranium and fission products on zirconium phosphate columns. We were interested in nitric acid solutions containing macro-amounts of uranium (a few grams per litre), and micro-amounts of plutonium and long-lived fission products.

To obtain a better insight into the ion-exchange behaviour of the different ionic species towards zirconium phosphate, we first determined the dependence of the distribution coefficients of uranium, plutonium and fission product cations on the aqueous nitric acid concentration. Then, taking the distribution data as a guide, we separated plutonium on small glass columns filled with zirconium phosphate and calculated the decontamination factors.

## EXPERIMENTAL

### *The exchanger characteristics*

The term "zirconium phosphate" refers to the product whose stoichiometric composition is given in Table I. The exchanger was prepared by precipitating zirconyl chloride in 1 M HCl with an excess of phosphoric acid. After standing for 24 h, the precipitate was filtered and washed with distilled water until chloride ions disappeared in the filtrate, then dried at about 100°, crushed and ground. The granular product was conditioned by converting it to the Na<sup>+</sup> form with a NaCl solution, and then changing it back to the H<sup>+</sup> form with a HCl solution. Finally, it was washed with distilled water and dried at room temperature to a constant weight. The main properties of the exchanger are given in Table I.

The capacity of the exchanger was determined by the column method. A neutral salt solution (NaCl, CaCl<sub>2</sub>) was percolated through a small exchanger bed (in H<sup>+</sup> form) until the effluent reached pH 5. The collected effluent was then titrated with a standard alkali solution and the capacity calculated. The anion-exchange capacity of zirconium phosphate seems to be negligible; the upper limit of Cl<sup>-</sup> uptake at pH 1.65 is below 0.05 mequiv./g. No significant swelling of particles was observed in acidic and neutral solutions.

TABLE I  
DATA FOR THE ZIRCONIUM PHOSPHATE CATION-EXCHANGER

Particle size	100-150 mesh
Capacity for Na <sup>+</sup>	2.12 mequiv./g
Capacity for Ca <sup>2+</sup>	2.30 mequiv./g
"Free H <sub>2</sub> O" (by weight loss at 105°)	1.92%
Stoichiometric composition (by quantitative analysis)	(ZrO <sub>2</sub> ) <sub>1.15</sub> P <sub>2</sub> O <sub>5</sub> ·2.7H <sub>2</sub> O

#### *Tracers and solutions used*

The following radioactive tracers were used: <sup>90</sup>Sr, <sup>144</sup>Ce, <sup>95</sup>Zr + Nb, <sup>106</sup>Ru, <sup>137</sup>Cs and <sup>59</sup>Fe. Except for <sup>59</sup>Fe, they all belong to the important long-lived fission products. The isotopes were practically "carrier free" as nitrate salts in nitric acid solutions. In addition, solutions of <sup>239</sup>Pu (0.1-0.5 mg/l) were prepared. The plutonium ions were held at the desired valency by means of the following oxidizing and reducing agents: hydrazine for Pu<sup>3+</sup>, sodium nitrite for Pu<sup>4+</sup> and potassium bromate for PuO<sub>2</sub><sup>2+</sup>. In the nitrate solutions uranium was always in the form of uranyl ion.

#### *Procedure*

The distribution coefficients (*q*) were determined by equilibrating 25 ml of tracer solution with 1 g of the airdried exchanger. This was performed by shaking the mixtures in small flasks on a simple laboratory shaker for 17 h at 20°. The distribution coefficient (expressed as: amount or c.p.m. per 1 g exchanger divided by the amount or c.p.m. per 1 ml solution) was calculated from the difference between the concentration of the adsorbate before and after equilibrium.

Column separations were performed at constant temperature in small Pyrex columns jacketed with a heating mantle. The exchanger bed in the columns was usually 0.4 cm ø × 15 cm. Constant flow-rates in the range 0.5-1 ml cm<sup>-2</sup> min<sup>-1</sup> were maintained. The free volume of the columns was about 55% of the geometrical volume of the bed. Usually, in a run 5 ml of the active solution was introduced on to the column and then eluted with 10 and 15 ml portions of nitric acid of appropriate concentration. Fractions of effluent were collected continuously. For each fission product separate runs were performed at 20 and 50°. The amount of uranium introduced on to the columns was the same in all runs.

#### *Analysis*

The uranium in the solutions was determined spectrophotometrically by the thioglycollate method<sup>13</sup>. The plutonium, on stainless steel disks, was counted with a ZnS alpha scintillation counter (Tracerlab, type P-12). In most cases the self-absorption could be neglected as thin samples (less than 0.1 mg/cm<sup>2</sup>) were used. However, in some plutonium samples uranium and sodium nitrite were present, so that a correction for self-absorption had to be made. Counts due to uranium were then subtracted (these were determined by counting specially prepared uranium samples) from the total corrected alpha counts and the net alpha activity of plutonium in the sample was obtained. To check the correctness of the counting, a balance of the total counts between the input and the output in every run was made; this balance was always within 100 ± 2%. The activity of the fission products in the solutions was measured

by commercial GM tubes and gamma activity was determined in well type scintillation counters in the usual way. Since discrimination between the gamma rays of  $^{95}\text{Zr}$  and  $^{95}\text{Nb}$  is not possible, the sum of the activities of both isotopes in the effluent was recorded, and then the Zr was separated from Nb by extraction with TTA (thenoyltrifluoroacetone)<sup>16</sup>.

## RESULTS AND DISCUSSION

The dependence of the distribution coefficient of the uranyl ion on the exchanger load for different  $\text{HNO}_3$  concentrations is shown in Fig. 1. The initial concentration of nitric acid is given for each curve in the figure, but for a low exchanger load this concentration is practically equal to the equilibrium concentration.

Fig. 2 shows the distribution coefficients of  $\text{UO}_2^{2+}$ ,  $\text{Pu}^{3+}$ ,  $\text{Pu}^{4+}$ ,  $\text{PuO}_2^{2+}$ ,  $\text{Fe}^{3+}$  and fission product cations as functions of the equilibrium  $\text{HNO}_3$  concentration. For  $\text{UO}_2^{2+}$ , the extrapolated values from Fig. 1 were used. The valence state of each cation, except for ruthenium whose actual state was rather uncertain, is given.

The position of some of the curves in Fig. 2 is noteworthy. For instance,  $\text{Cs}^+$  is adsorbed more strongly than many multivalent cations. Also, the  $\text{PuO}_2^{2+}$  curve does not coincide with the  $\text{UO}_2^{2+}$  curve; this can be attributed to the presence of  $\text{KBrO}_3$  in the solutions of hexavalent plutonium. Finally, the position of the  $\text{Ce}^{3+}$  and  $\text{Pu}^{3+}$  curves relative to the  $\text{UO}_2^{2+}$  curve is unexpected if the charges of these cations are

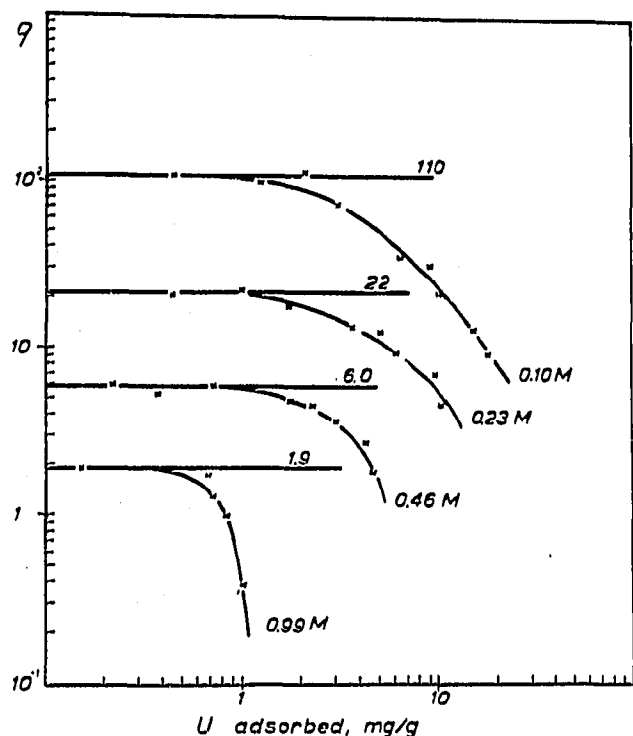


Fig. 1. The distribution coefficient of  $\text{UO}_2^{2+}$  plotted against the exchanger load. Initial aqueous  $\text{HNO}_3$  molarity given on each curve.

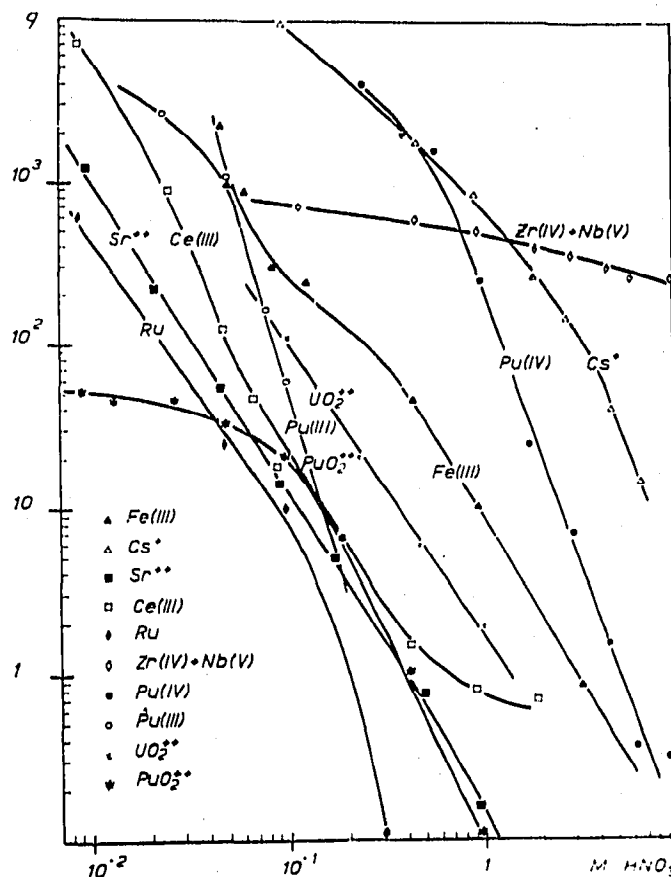


Fig. 2. The dependence of the distribution coefficients on the equilibrium  $\text{HNO}_3$  concentration. All adsorbates present in tracer amounts. Pu (III) solutions 0.02 M in hydrazine, Pu (IV) 0.02 M in  $\text{NaNO}_2$ , and Pu (VI) 0.02 M in  $\text{KBrO}_3$ .

taken into account. However, the uranyl ion is not a true bivalent cation such as  $\text{Sr}^{2+}$ , for instance; its chemical behaviour is rather like that of a cation of higher charge. Similar behaviour was noted on silica gel<sup>14</sup>, where  $\text{UO}_2^{2+}$  was adsorbed more strongly than  $\text{Gd}^{3+}$ .

The sorption of the cations is strongly influenced by the acidity of the aqueous solution; this would be expected for a true ion-exchange process. The only notable exception is the pair Zr–Nb, as is seen from Fig. 2. In this case, the sorption is apparently not much affected by the aqueous acidity, so that merely ion-exchange cannot be accepted.

In an earlier paper<sup>12</sup> we showed that the mass action law can be applied to the exchange of uni-univalent and uni-divalent ions on zirconium phosphate. This was also demonstrated by LARSEN AND VISSERS<sup>10</sup>, and by BAETSLÉ AND HUYS<sup>11</sup>. In this respect, the very strong affinity of  $\text{Cs}^+$  towards zirconium phosphate is noteworthy. We have found, for instance, that the standard free energy change for the substitution  $\text{Cs}^+ - \text{H}^+$  is  $\Delta F^\circ_{293} = -3.7$  kcal/mol., compared to  $\Delta F^\circ_{293} = +1.2$  kcal/mol. for  $\frac{1}{2} \text{Sr}^{2+} - \text{H}^+$ . For more details about the equilibrium and kinetics of adsorption, the reader should refer to our earlier paper<sup>12</sup>.

From the distribution data given in Fig. 2, it can be concluded that: (1) the separation of  $\text{Pu}^{4+}$  from  $\text{UO}_2^{2+}$  can be achieved by merely changing the  $\text{HNO}_3$  concentration, (2) among the long-lived fission products,  $^{90}\text{Sr}$ ,  $^{144}\text{Ce}$  and  $^{106}\text{Ru}$  should follow the uranium fraction, while  $^{137}\text{Cs}$  and  $^{95}\text{Zr} + \text{Nb}$  will probably contaminate the plutonium fraction.

After some preliminary experiments, we chose the following procedure for practical separations: a 0.5 M  $\text{HNO}_3$  + 0.02 M  $\text{NaNO}_2$  solution containing uranium, plutonium and fission products is percolated through the column; uranium passes through practically unadsorbed, while  $\text{Pu}^{4+}$  remains firmly fixed. After washing the column with a 0.5 M  $\text{HNO}_3$  solution, plutonium is removed with 8 M  $\text{HNO}_3$ . To check this separation quantitatively, some experiments with solutions containing only  $\text{UO}_2^{2+}$  and  $\text{Pu}^{4+}$  (without fission products) were made at 20 and 50°. Two typical results are shown in Table II.

TABLE II

SEPARATION OF  $\text{UO}_2^{2+}$  AND  $\text{Pu}^{4+}$ 

Column 0.4 cm  $\sigma \times 15$  cm, flow-rate 0.73 ml  $\text{cm}^{-2} \text{min}^{-1}$ . Input: 5 ml 0.5 M  $\text{HNO}_3$  + 0.02 M  $\text{NaNO}_2$  with U and Pu, followed by 10 ml 0.5 M  $\text{HNO}_3$  and  $2 \times 15$  ml 8 M  $\text{HNO}_3$ . Effluent collected in 4 fractions: 5 + 10 + 15 + 15 ml.

Effluent fraction	Uranium found		Plutonium found	
	mg	% of input	c.p.m.	% of input
<i>Temp. 20°. Input: 9.50 mg U, 48050 c.p.m. Pu</i>				
(1) 5 ml (0.5 M)	7.85	82.7	685	1.4
(2) 10 ml (0.5 M)	1.64	17.2	310	0.6
(3) 15 ml (8.0 M)	—	—	46375	96.7
(4) 15 ml (8.0 M)	—	—	368	0.8
<i>Temp. 50°. Input: 9.45 mg U, 38700 c.p.m. Pu</i>				
(1) 5 ml (0.5 M)	7.30	77.2	660	1.7
(2) 10 ml (0.5 M)	2.00	21.0	225	0.6
(3) 15 ml (8.0 M)	—	—	37325	96.3
(4) 15 ml (8.0 M)	—	—	291	0.7

It can be seen from Table II, that no significant difference exists between the two runs at 20 and 50°. The recovery of plutonium (the last two fractions) is 97–98%; the rest is lost in the uranium fraction, probably as  $\text{Pu}^{3+}$  or colloidal plutonium. The recovered plutonium is essentially free from uranium. For instance, in the third fraction the uranium content (by the ferrocyanide spot test) is below 0.01 mg (less than 0.1% of the input), so that plutonium is decontaminated with respect to uranium by at least a factor of 1000. The clear-cut separation of  $\text{Pu}^{4+}$  from  $\text{UO}_2^{2+}$  was also confirmed by an elution curve which is reproduced in Fig. 3. This curve was obtained by collecting fractions of 0.3 ml on stainless steel disks, which were later dried and checked for total alpha counts.

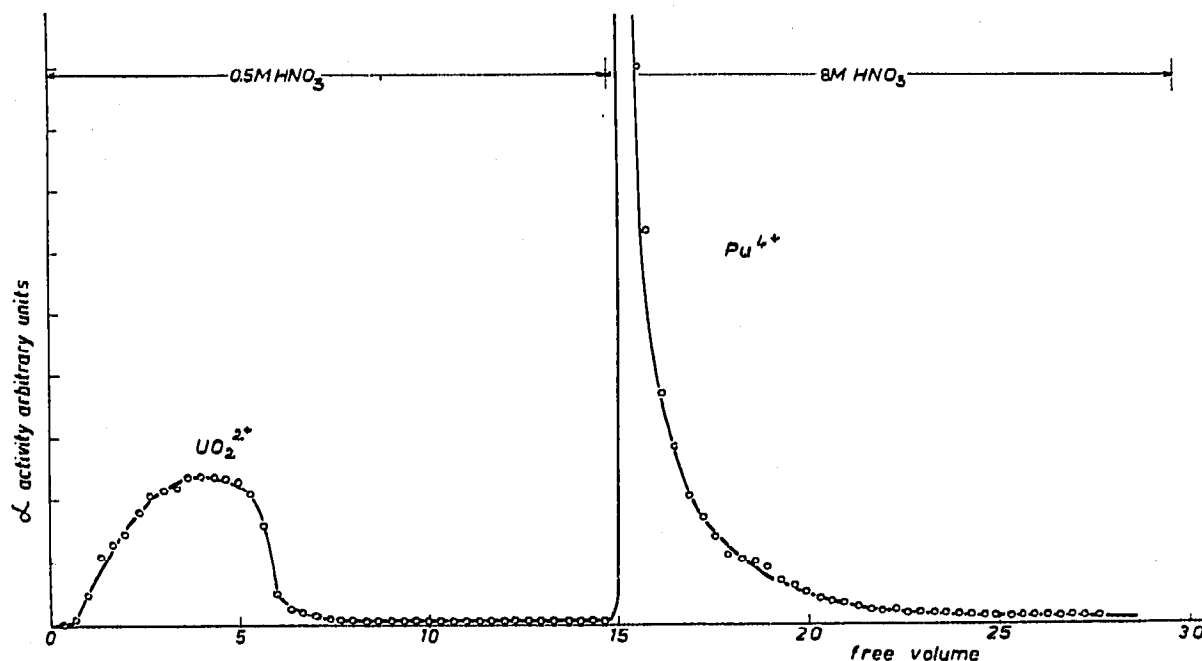


Fig. 3. Separation of  $\text{Pu}^{4+}$ - $\text{UO}_2^{2+}$ . Column 0.6 cm  $\phi$   $\times$  11 cm, temp. 20°, flow-rate 0.5 ml  $\text{min}^{-1}$   $\text{cm}^{-2}$ . Loading and elution as in Table II.

To determine how the fission products are distributed between the uranium and plutonium fractions of the effluent, a number of runs identical to those in Table II were made. In each run, one fission product was added to the 5 ml feed solution and the effluent was collected in two fractions of exactly 15 ml each. The first fraction contained the whole amount of uranium, the second 96–97% of plutonium (see Table II). Both fractions were analyzed, and the individual fission product decontamination factors of the plutonium product were thus easily calculated. The results are summarized in Table III.

The isotopes  $^{95}\text{Zr}$  and  $^{95}\text{Nb}$  were added together, in a known proportion, but in the effluent they were separated by TTA extraction, as mentioned above. This enabled us to follow the distribution of both isotopes individually in the effluent.

Table III shows that for Ru, Ce and Sr the sum of activities in both fractions is within  $100 \pm 2\%$  of the input. However, this is not true for Cs, Zr and Nb which remain to a great extent fixed on the column. Zirconium, for instance, is not eluted at all. This is not surprising if we bear in mind the affinity of zirconium towards phosphate

TABLE III  
DISTRIBUTION OF FISSION PRODUCTS IN THE EFFLUENT  
For experimental conditions see Table II

Fission product	Input c.p.m.	Found in U-fraction		Found in Pu-fraction	
		c.p.m.	% of input	c.p.m.	% of input
<i>Temperature 20°</i>					
<sup>106</sup> Ru	4.40 · 10 <sup>6</sup>	4.31 · 10 <sup>6</sup>	98.0	6.42 · 10 <sup>3</sup>	1.5
<sup>144</sup> Ce (III)	2.51 · 10 <sup>6</sup>	2.45 · 10 <sup>6</sup>	97.5	1.42 · 10 <sup>3</sup>	0.57
<sup>90</sup> Sr	1.45 · 10 <sup>6</sup>	1.47 · 10 <sup>6</sup>	101.3	n.d.*	—
<sup>137</sup> Cs	4.74 · 10 <sup>6</sup>	3.15 · 10 <sup>3</sup>	0.7	3.11 · 10 <sup>6</sup>	65.6
<sup>96</sup> Zr	1.95 · 10 <sup>6</sup>	n.d.	—	n.d.	—
<sup>96</sup> Nb	4.25 · 10 <sup>6</sup>	1.45 · 10 <sup>4</sup>	3.4	1.77 · 10 <sup>4</sup>	4.17
<i>Temperature 50°</i>					
<sup>106</sup> Ru	5.38 · 10 <sup>6</sup>	5.31 · 10 <sup>6</sup>	98.6	7.07 · 10 <sup>3</sup>	1.3
<sup>144</sup> Ce (III)	2.51 · 10 <sup>6</sup>	2.43 · 10 <sup>6</sup>	97.0	1.46 · 10 <sup>3</sup>	0.58
<sup>90</sup> Sr	6.28 · 10 <sup>4</sup>	6.39 · 10 <sup>4</sup>	101.5	n.d.	—
<sup>137</sup> Cs	4.91 · 10 <sup>6</sup>	2.40 · 10 <sup>4</sup>	4.9	4.58 · 10 <sup>6</sup>	93.1
<sup>96</sup> Zr	2.01 · 10 <sup>6</sup>	n.d.	—	n.d.	—
<sup>96</sup> Nb	4.39 · 10 <sup>6</sup>	1.01 · 10 <sup>4</sup>	2.3	2.83 · 10 <sup>4</sup>	6.5

\* n.d. = not detected.

ions. The effect of temperature upon the elution is significant only for Cs and Nb.

The behaviour of niobium depends, unfortunately, on many unpredictable factors. For example, the results for Nb in Table III were obtained with a feed solution (0.5 M HNO<sub>3</sub>) to which a few drops of a Zr-Nb stock solution (3 M HNO<sub>3</sub>) had previously been added. The solution thus prepared was aged for 2 days before use. When the same solution was allowed to age for 15 days, we found 20 and 46% of niobium in the uranium and plutonium fraction, respectively. It seems that slow processes such as hydrolysis, colloid formation, etc., which alter the niobium species in aqueous solution, interfere in the adsorption. This is probably the reason why the amount of niobium eluted depends so much on the mode of preparation of the feed solution.

In contrast to the peculiar behaviour of niobium, we found that zirconium is in all circumstances firmly fixed on the exchanger.

The decontamination factors (DF) for the plutonium product were obtained from the data in Table III and are shown in Table IV.

The DF values in Table IV can be compared favorably with the values obtained on synthetic organic cation-exchangers<sup>15</sup>, except perhaps those for caesium. However, plutonium solutions obtained by a solvent-extraction process usually do not contain

TABLE IV  
PLUTONIUM PRODUCT DECONTAMINATION FACTORS

	UO <sub>2</sub> <sup>3+</sup>	<sup>90</sup> Sr	<sup>144</sup> Ce(III)	<sup>106</sup> Ru	<sup>96</sup> Zr	<sup>96</sup> Nb	<sup>137</sup> Cs
DF(20°)	~ 10 <sup>3</sup>	~ 10 <sup>3</sup>	178	68	> 10 <sup>3</sup>	24*	1.5
DF(50°)	~ 10 <sup>3</sup>	~ 10 <sup>3</sup>	172	76	> 10 <sup>3</sup>	15*	1.1

\* Feed solution aged for 2 days.

caesium, and therefore the low DF value is not a serious drawback. However, the DF value of Zr is very high, and the fact that zirconium remains fixed on the column may be inconvenient. (It can be accumulated up to a high radiation level.)

On the whole, zirconium phosphate columns have been found to be useful in the separation and isolation of plutonium, especially if a high radiation stability of the exchanger is essential. However, for a strict comparison between zirconium phosphate and other ion-exchangers regarding plutonium recovery, further experiments with high plutonium loading-rates are required.

#### SUMMARY

A procedure for the separation of plutonium from uranium and long-lived fission products on zirconium phosphate columns is described. Traces of plutonium are separated from nitric acid solutions containing a few grams per litre uranium. Data such as the distribution coefficients, plutonium recovery and decontamination factors are presented.

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