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The Ion Exchange Properties of Silica Gel

II. Separation of Plutonium and Fission Products from Irradiated Uranium

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A procedure, based on selective sorption on silica gel, has been worked out for the separation of plutonium and fission products from uranium which has been irradiated with thermal neutrons

In part I of this investigation [1], it has been shown that metal ion sorption on silica gel can be described by an ion exchange mechanism, with silica gel acting as an ion exchanger of the weakly acid type.

The distribution coefficient between gel and solution for the different metal ions accordingly increases strongly with increasing pH. The distribution coefficient is also larger for high-valent ions than for low-valent ones at a given acidity of the solution. A graphical comparison of the metal ions investigated is given in Ref.[1], Fig. 6. It can be seen that the affinity for the ion exchanger is given by the order

$$\mathrm{Zr(IV)} > \mathrm{U(IV)} \approx \mathrm{Pu(IV)} > \mathrm{U(VI)} > \mathrm{Gd} > \mathrm{Ca} \approx \mathrm{Ba} \approx \mathrm{Na}$$

In the same investigation it was also found that some species are sorbed very fast and other more slowly. UO_2^{2+}, Gd^{3+}, Ca^{2+}, Ba^{2+} and Na^+ belong to the first group while the second contains Zr(IV), U(IV) and Pu(IV). The ions of the second group are all strongly hydrolysed in the actual solutions and occur mainly as polynuclear aggregates. For Pu(IV) it was found that at higher pH the sorption rate is dependent on the age of the solution.

From these results it is clear that it should be possible to separate Zr(IV), U(VI) and Pu(IV) both from one another and from Gd^{3+}, Ca^{2+}, Ba^{2+} and Na^+ by suitably varying the pH of the solution.

The aim of this investigation has been to use this selective sorption on silica gel for a separation of uranium, plutonium and fission products from a nitric acid solution of neutron irradiated uranium.

After a cooling period of 100 days rather few elements contribute appreciably to the activity still remaining with the irradiated uranium. Apart from plutonium these are, in order of decreasing activity, zirconium + niobium, yttrium and several lanthanides, ruthenium + rhodium, strontium, barium and cesium (see *e.g.* the compilation of Rydberg[2]). A cooling period shorter than 100 days is not used as a rule because most reprocessing methods presuppose that ^{239}Np, ^{237}U, ^{133}Xe and ^{131}I have decayed before the treatment is started [3].

On the dissolution of uranium metal in nitric acid, uranium is oxidized to U(VI), while most of the plutonium is present as Pu(IV). The standard potentials for the different redox steps between Pu(III), Pu(IV), Pu(V) and Pu(VI) are so close to each other [4] that there is always a certain disproportionation in a solution of the mean oxidation state + 4. There are always finite concentrations of at least Pu(III) and Pu(VI) and at lower acidities also Pu(V). Zirconium is found as Zr(IV) and niobium probably as Nb(V), both more or less hydrolysed. Ruthenium occurs mainly as various nitrosylnitrato complexes of Ru(III) [5]. The actual state is highly dependent on the conditions at dissolution [6]. The other fission products have a less complicated chemistry and occur as hydrated metal ion. These of higher charge especially exist to a considerable part as nitrate complexes in the solution.

The ions to be found in a solution of neutron irradiated uranium metal are thus the same or in any case analogous to those ions, the sorption properties of which have been investigated in I. The behaviour of ruthenium, which cannot be anticipated from the experiments already performed, remains obscure. Another serious difficulty is that the separation of uranium and plutonium requires that they are in the oxidation states + 6 and + 4, respectively. Pu(VI), as plutonyl ion, has the same sorption properties as the analogous uranyl ion, while tervalent plutonium as Pu^{3+} shows a close resemblance to the lanthanide group. By a suitable choise of pH and total concentration of plutonium, C_{Pu}, the disproportionation can however be greatly suppressed [7-9]. At low pH, the position of the equilibrium which is independent of C_{Pu} strongly favours Pu(IV). As the pH is raised, a considerable disproportionation will exist in equilibrium, but the rate of the disproportionation reaction is quite slow at low values of C_{Pu}. Thus at pH = 1 in perchlorate medium the rate is less than 1 % an hour for $C_{Pu} < 10^{-4}$ M. The rather strong complex formation between Pu^{4+} and NO_3^- [10,11] also stabilises Pu^{4+} relative to Pu^{3+} and PuO_2^{2+} if a nitrate medium is used.

By treating a disproportionated solution of plutonium with nitrite it is possible to transfer all the plutonium to the oxidation state +4. The reaction is complicated and is certainly not yet fully understood [12].

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The preparations of neodymium, cerium, gadolinium and ytterbium salts were the same as used by Sonesson [13].

Neodymium and ytterbium were analyzed spectrophotometrically using aurinetricarboxylic acid [14]. Cerium(III) was oxidized to Ce(IV) by persulfate and then determined by reduction with Fe(II). The gadolinium solutions contained the isotope ^{153}Gd and were analyzed radiometrically.

The other chemicals were the same as used in I, and were analyzed in the same way as described there.

RESULTS

The investigation consists of the following three parts:

1. Investigation of the sorption properties of separate ions using chromatographic methods.
2. Sorption at continuous passage of solution through the column followed by a determination of the sorption capacity for the metal ions in question.
3. Test separations of solutions of known composition.

Chromatographic experiments. Two different columns have been used, one of 100 cm length and 1.0 cm inner diameter and one of 43 cm length and 1.1 cm diameter. The longer column takes a solution volume of 50 ml, the shorter one a volume of 25 ml. By varying the length of the column and the flow rate, the contact time between solution and gel can be widely varied.

When used, the column is first saturated with nitric acid of desired concentration. Then a given volume of metal ion solution is placed on top of the column. This volume is small compared with the total volume of solution in the column. By means of an acid flow from a vessel on higher level the sample is transported down the column. Fractions of the outflowing solution are collected with a fraction collector and analyzed.

The sorption of *U(VI)* from solutions containing 0.1 and 0.5 M nitric acid was investigated. In both cases, U(VI) passed the column in the solution front. No sorption thus occurred at these acidities, a result consistent with the equilibrium experiments reported in Ref.[1], Fig. 6.

In the *Pu* experiments, the contact time is a variable of about the same importance as the acidity. The following experiments, performed at $C_H = 0.5$ and 0.1 M using different flow rates and column lengths are typical for the influence of each of these variables. For $C_H = 0.5$ M, the results are in Figs. 1 and 2 where C_{Pu} of each fraction, expressed in disintegrations$\cdot$min$^{-1}\cdot$ml^{-1}, is given as a function of the volume of solution which has passed down the column. The position of U(VI) for each column, as determined by the experiments mentioned above, is also indicated. Obviously, the plutonium is separated into two peaks. The first of these is found in the same position on the volume axis as U(VI). It contains about 2 % of the total amount of plutonium, *i.e.*

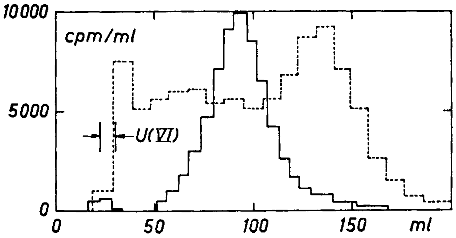

Fig. 1. Sorption of plutonium from 0.5 M nitric acid. Column length 43 cm. Flow rates:
30 ml · h^{-1} · cm^{-2} ————
60 » » » – – – – –
Silica gel: Kebo 100—200 mesh.

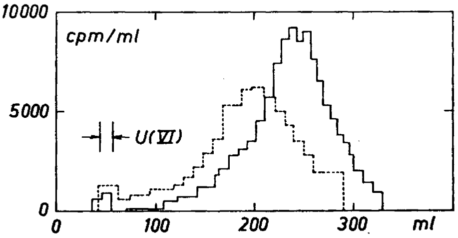

Fig. 2. Sorption of plutonium from 0.5 M nitric acid. Column length 100 cm. Flow rates:
10 ml · h^{-1} · cm^{-2} ————
50 » » » – – – – –
Silica gel: Kebo 50—100 mesh.

Table 1. Plutonium sorption on silica gel from 0.1 M nitric acid, with subsequent elution of Pu(IV) by 4.5 M nitric acid. In the first series, the fractionation was started immediately, in the second after that the plutonium had been sorbed on the column for four days. Flow rate 76 ml · hour^{-1} · cm^{-2}.

Immediate fractionation		Fractionation after 4 days	
0.1 M acid ml	% Pu/fraction	0.1 M acid ml	% Pu/fraction
17.2	0	12.5	0
34.6	0	26.5	0
51.5	3.4	39.9	0
68.5	1.3	52.9	2.9
85.5	0.8	65.9	0.2
438.2	15.4	—	—
4.5 M acid ml		4.5 M acid ml	
25.0	1.2	18.7	0
39.0	0.7	28.8	0
52.5	0.5	39.7	0
66.5	1.1	50.2	0.2
79.5	19.2	60.5	59.6
93.3	55.6	71.0	36.1
106.5	0.8	81.7	0.9
120.3	0	92.2	0.2
133.3	0	103.1	0

just the fraction found by analysis to exist as Pu(III) and Pu(VI). In the second peak the remaining plutonium is found as Pu(IV).

The above conclusions are further strengthened by the fact that the plutonium of the first peak is not extracted at pH = 0 by a 0.1 M solution of thenoyltrifluoroacetone (TTA) in benzene, while the plutonium in the second peak is completely extracted into the organic phase under the same conditions [15].

At the low flow rates a complete separation into two peaks is achieved. If the flowrate is increased, the separation is not so good (as was expected), but the existence of two peaks is nevertheless quite clear.

At $C_H = 0.1$ M, the distribution coefficient for plutonium is much larger than at $C_H = 0.5$ M. An experiment with the long column and a flow rate of 76 ml·hour^{-1}·cm^{-2} is reproduced in Table 1. From this table it can be seen that Pu(IV) is very strongly sorbed and that there is only a small plutonium leakage, less than 1 % of the total amount per fraction of 17 ml, during the continued passage of 0.1 M nitric acid. Pu(III) and Pu(VI) are found as before in the solution front.

By passing 4.5 M nitric acid through the column the plutonium is quantitatively eluted in the strong acid front, as its distribution coefficient at this acidity is very low. In Table 1 another experiment analogous to the previous one is also to be found. The only difference is that in the latter case the plutonium solution has remained for four days on the column before washing with 0.1 M nitric acid. Pu(III) and Pu(VI) are found as before in the solution front but no Pu(IV) leakage could be detected. On elution with 4.5 M nitric acid, all the Pu(IV) came out as before in the strong acid front.

These column experiments confirm that the plutonium sorption is a fairly slow process. This is also evident from a determination of the *plutonium distribution on the column.* Sorption and subsequent washing with 0.1 M HNO_3 were made in the same way as in earlier experiments. The solution phase was then removed by blowing compressed air through the column. After drying, the silica gel column was removed in sections of fixed length. These were eluted with 4.5 M nitric acid and the amount of plutonium was determined. The resulting distribution curve is reproduced in Fig. 3 and shows that the plutonium penetrates rather deeply into the column before the sorption is complete.

The plutonium(IV) sorption is not entirely reproducible. A large number of experiments have been performed which show a leakage varying between zero and an upper limit given by the first of the experiments reproduced in Table 1. Furthermore the Pu(IV) leakage always decreases with decreasing flow rate.

As is evident from earlier equilibrium experiments [1] the sorption behaviour of *zirconium* is very complicated. The variation in sorption rate with pH is more pronounced than for plutonium(IV). The results from the equilibrium

Table 2. Zirconium sorption on silica gel from nitric acid of different concentrations, with subsequent elution by 0.1 M oxalic acid. Flow rate 38 ml · hour^{-1} · cm^{-2}.

0.1 M acid ml	% Zr/fraction	1.5 M acid ml	% Zr/fraction	5 M acid ml	% Zr/fraction
17.6	0	10.0	0	12.1	0
36.6	6.0	29.0	0.2	35.4	0
53.4	39.2	41.7	2.5	49.0	0.9
72.0	1.2	54.2	0.9	64.5	0.1
89.8	0.5	65.1	0.1	80.8	0
109.2	0.3	76.1	0	94.8	0
126.7	0.1	—	—	—	—
144.5	0.2	—	—	—	—
161.5	1.1	—	—	—	—
179.3	0.6	—	—	—	—
195.8	0.3	—	—	—	—
213.3	0.4	—	—	—	—
226.8	0.3	—	—	—	—
0.1 M oxalic acid ml		0.1 M oxalic acid ml		0.1 M oxalic acid ml	
17.0	0.4	12.5	0	14.8	0
34.7	0.3	28.6	0	28.9	0
51.7	44.7	44.2	9.8	42.0	0
70.3	3.4	60.3	86.0	56.1	90.7
86.7	0.6	71.8	0.4	69.4	7.6
104.0	0.4	—	—	83.7	0.6

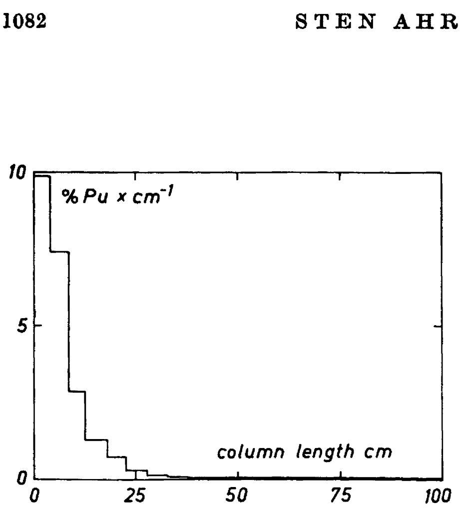

Fig. 3. The distribution of plutonium on the silica gel column when sorbed from 0.1 M nitric acid at a flow rate of 60 ml · h^{-1} · cm^{-2}.

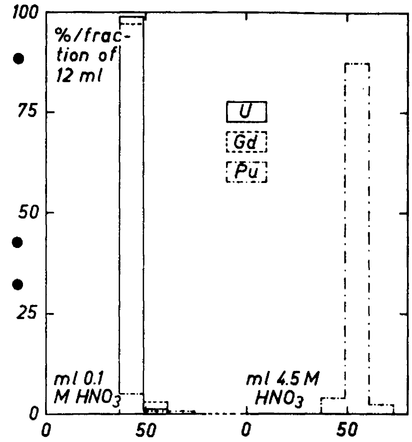

Fig. 4. Separation of Pu(IV) from U(VI), Pu(VI), Pu(III) and Gd(III) by sorption on silica gel from 0.1 M nitric acid, with subsequent elution of Pu(IV) by means of 4.5 M nitric acid. Column length 100 cm, flow rate 60 ml · h^{-1} · cm^{-2}.

measurements have been confirmed qualitatively by column experiments. The long column has been used for all the experiments and the amount of zirconium added has always been 1 ml of 11 mM zirconium(IV) solution.

The results from three runs at $C_{\mathrm{H}} = 0.1$, 1.5 and 5 M nitric acid and a constant flow rate of about 38 ml·hour^{-1}·cm^{-1}, are given in Table 2. The Zr(IV) leakage is very large at the lowest acidity, but rather slight at the higher ones. This behaviour is expected as a result of the very low sorption rate at higher pH-values (*cf.* part I). If the flow rate is increased the leakage also increases rapidly. Thus a doubling of the flow rate at $C_{\mathrm{H}} = 1.5$ M gives a leakage of the same magnitude as found for $C_{\mathrm{H}} = 0.1$ M at the lower flow rate.

After a nitric acid wash, the column was eluted with 0.1 M oxalic acid. Because of the high distribution coefficient for Zr(IV) a strong complexing agent is needed for the elution. 1 M sulfuric acid and 0.1 M oxalic acid were both tried, but 0.1 M oxalic acid was the better of the two.

The above is in qualitative accordance with results obtained by Rydberg [2] for sorption of tracer amounts of zirconium on silica gel. According to Rydberg, the leakage is very large even at $C_{\mathrm{H}} = 1.5$ M. The reason for this difference might be differences in flow rate (not specified in Rydberg's work) or zirconium concentration.

As representatives of yttrium and the lanthanides, neodymium, gadolinium and ytterbium have been studied. The experiments have been performed separately for each ion, using the long column. The result was that no sorption could be proved in 0.1 M nitric acid. Like U(VI), all the lanthanides passed down the column in the solution front.

The results of the chromatographic experiments indicate that Pu(IV) and Zr(IV) might be separated from one another and from U(VI) + lanthanides by a suitable variation of pH. In order to get a good separation the flow rate must not be too high.

The following experiment was performed to confirm this. A solution of U(VI) (0.1 ml 285 mM uranyl perchlorate solution), Pu(IV) (0.1 ml 0.51 mM nitrate solution containing 94.5 % Pu(IV)) and Gd(III) (0.1 ml 4.4 mM perchlorate solution) was chromatographed on the long column at a nitric acid concentration of 0.1 M.

The result, given in Fig. 4 is in complete accord with the previous experiments. U(VI), Gd(III), Pu(III) and Pu(VI) travel down the column in the solution front. Pu(IV) is nearly quantitatively sorbed, the leakage is less than 0.2 % of the total amount of plutonium per fraction of 12 ml. By passing 4.5 M nitric acid, all plutonium sorbed can be quantitatively eluted. The total yield of plutonium is 93.5 %, compared with the initial amount of 94.5 % Pu(IV).

Sorption behaviour on continuous passage of solution. For work with larger amounts of material it is desirable to be able to use a continuous sorption process. In this case it is of interest to know the sorption capacity $S \equiv C_{\mathrm{MG}}$ for the column. By applying the law of mass action to the exchange reaction (Ref.[1], eqn. (4)) the following expression is obtained

$$S \equiv [\mathrm{MG}_n] = K \frac{[\mathrm{M}^{n+}]\,[\mathrm{HG}]^n}{[\mathrm{H}^+]^n}$$

where K is the concentration constant of the exchange equilibrium. From this expression it can be seen that S increases with increasing $[\mathrm{M}^{n+}]$, *i.e.* with increasing C_{MS} and decreasing $[\mathrm{H}^+]$. For very high C_{MS}, S will of course finally reach an upper limit when practically all sorption places are occupied by M^{n+} instead of the original H^+. For the sorption of Pu(IV) or fission products where C_{MS} is fairly low as a rule, this saturation value will not, however, be approached in practice.

The sorption capacity, S, has been determined as a function of C_{MS} and pH for a number of metal ions. A solution of fixed metal ion concentration, C_{M}, and pH is passed down the column and the effluent solution analyzed on the ion in question. The column capacity for a solution of the value of C_{M} used has been reached when the solutions entering and leaving the column have the same concentration $= C_{\mathrm{M}}$ which is then identical with C_{MS} as defined above. From the break-through curve the sorption capacity is then easily calculated. The value thus obtained was then checked in the following way: The column was rinsed free from mechanically adherent solution by washing with pure solvent of the same pH as was used at the sorption. In order not to disturb the equilibrium in the column appreciably, the volume of the washing liquid was only one to two column volumes. After washing the column was eluted with strong acid and the eluate analyzed. The sorption capacity has been determined in this way as a function of pH for Zr, U(IV), U(VI), Ce(III), Gd, Ca and Ba.

Table 3. The sorption capacities for U(IV) and U(VI) as functions of pH and the total concentration of metal ion, C_M.

U(VI)						U(IV)		
C_M mM	pH	S mequiv/g	C_M mM	pH	S mequiv/g	C_M mM	C_H mM	S mequiv/g
11.4	2.00	0.005	22.8	2.70	0.041	10	25	0.18
11.4	2.30	0.011	22.8	2.86	0.070	10	50	0.12
11.4	2.50	0.016	22.8	3.44	0.296	10	100	0.10
11.4	2.70	0.023	22.8	3.75	0.473	10	500	0.008
11.4	3.10	0.106	22.8	4.21	1.595	25	50	0.13
11.4	3.40	0.176	45.6	2.40	0.023	25	100	0.16
11.4	3.60	0.240	45.6	3.31	0.320	25	500	0.011
11.4	3.80	0.336	45.6	3.58	0.493	50	50	0.25
						50	100	0.16

Table 4. The sorption capacities for Gd(III), Ce(III) and Zr(IV) as functions of pH.

Gd(III) C_M = 2.8 mM		Ce(III) C_M = 25 mM		Zr(IV) C_M = 9.2 mM	
pH	S mequiv/g	pH	S mequiv/g	C_H M	S mequiv/g
1.0	0.000	3.2	0.001	1.5	0.56
2.0	0.003	4.2	0.003	5.0	0.40
3.0	0.006	5.2	0.007		
4.0	0.009				

Table 5. The sorption capacities of Ca^{2+} and Ba^{2+} as functions of pH.

Ca C_M = 25 mM		Ba C_M = 25 mM	
pH	S mequiv/g	pH	S mequiv/g
9.25	0.093	10.30	0.92
9.66	0.378	10.51	1.90
10.25	1.86	10.85	2.52
10.44	2.84	10.94	3.46
10.50	3.97	11.20	3.46
10.61	4.50	11.28	3.76
11.10	4.37		

Because of the very low affinity of the ion exchanger for calcium and barium ion experiments with these ions have been done in ammoniacal solution, all the others in nitric acid solution. The results are given in Tables 3—5.

From these tables it can be seen that the sorption capacities for the trivalent lanthanide ions examined are very small within the pH range investigated.

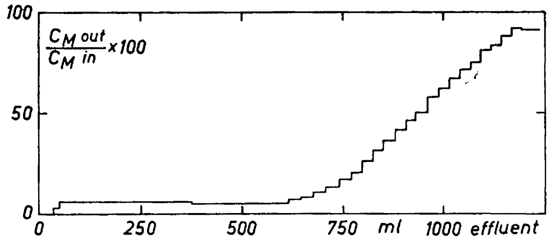

Fig. 5. Break through curve for Zr(IV) on a column filled with 60 g silica gel. Column length 100 cm, corresponding to a solution volume of 50 ml. Flow rate 60 ml · h^{-1} · cm^{-2}. $C_M = 0.92$ mM, $C_H = 5$ M.

On the other hand, the capacities for U(VI), U(IV) and Zr(IV) are large even at rather low pH-values. A determination of the sorption capacity for plutonium is not possible because of the small amount of material available. A sorption capacity of the same order of magnitude as for other four-valent ions is a plausible estimate.

Calcium and barium ions are not measurably sorbed at pH-values below 7. At higher pH-values there is a strong increase in sorption, a fact also confirmed by other authors [16-18]. For some reason which is still unknown, saturation capacities much higher than those observed for sodium ions (Ref.[1], Table 2) seem to be reached.

The distribution coefficients $D = C_{MG}/C_{MS}$ which can be calculated from these column experiments as the ratio S/C_M agree fairly well with those obtained in the equilibrium experiments of Ref.[1], even for the four-valent ions.

The slow Zr(IV) sorption gives rise to a leakage of between 5 and 10 % of the total amount Zr on continous passage of solution. A typical break through curve is reproduced in Fig. 5. The rise at about 750 ml is caused by saturation of the column.

Analogous experiments have also been performed on plutonium solutions at concentrations about 10^{-5} M. The flow rate was, however, slower, only 2.3—4.6 ml·$hour^{-1}$·cm^{-2}. The results showed a quantitative sorption of plutonium(IV) and, as before, no retention of plutonium(III) and (VI).

These experiments proved that a selective sorption is possible even with a continuous column process. In the next section some test separations on solutions of known composition are described.

ForU(IV), the found increase of S with C_{MS} is somewhat irregular (*cf.* Table 3) which is certainly due to the fact that solutions of different age were used for the experiments. U(IV) solutions of low C_H alter their properties markedly with time, due to slow hydrolytic reactions [19].

Test separations on solutions of known composition. The first solution had the following composition: $C_{Zr} = 9.17$ mM, $C_{Pu} = 2.39 \times 10^{-3}$ mM, $C_{U(VI)} =$ 199 mM, $C_H = 4$ M and a total volume of 100 ml. The γ-activities of the components were measured separately before mixing. For 5 ml samples the U(VI) solution gave 1 525 cpm and the Zr solution 9 663 cpm. The latter

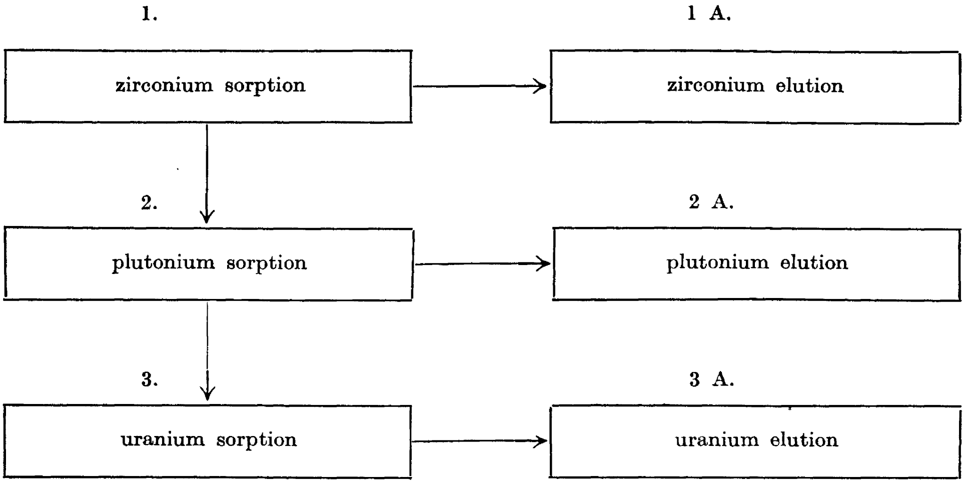

Fig. 6. Block scheme for the separation of uranium, plutonium and zirconium.

solution contained activities from ^{95}Zr, ^{95}Nb and ^{181}Hf, as discussed in Ref.[1] The separation procedure can be illustrated by the block scheme, Fig. 6.

The different steps in the above scheme will now be separately described.

1. The zirconium sorption step is made at $C_H = 4$ M, and a flow rate of about 3.5 ml·hour^{-1}·cm^{-2}.

1 A. After sorption the column is first washed with 4 M nitric acid and then eluted with 0.1 M oxalic acid which quantitatively removes the zirconium.

2. The solution which has passed down the column in step 1 is evaporated to dryness to remove excess nitric acid and is then restored to the initial volume with 100 ml 0.1 M nitric acid. The heating with 4 M nitric acid caused a strong disproportionation and possibly also oxidation of the plutonium. A TTA-extraction proved that only about 12 % of the total amount remained as plutonium (IV). All this amount plus zirconium leakage from step 1 was quantitatively sorbed.

2 A. After washing with 0.1 M HNO_3, plutonium was eluted with 4.5 M HNO_3. Zirconium remained sorbed.

3 and 3 A. After step 2 the solution was partially neutralized with sodium hydroxide, to a pH of about 3. When this solution was passed down the column the uranium was quantitatively sorbed. Sorbed uranium is then removed by a strong acid.

The other solution of known composition which has been separated was a nitric acid solution of neutron irradiated uranium. After irradiation the uranium had cooled for three years. The solution was obtained from A. B. Atomenergi, Stockholm, which gave its composition as: $C_{U(VI)} = 1.075$ M, $C_{Pu} = 1.45 \times 10^{-5}$ M, $C_H = 0.95$ M. The solution also contained long-lived fission products, mainly ^{106}Ru—^{106}Rh, ^{144}Ce—^{144}Pr, ^{90}Sr—^{90}Y and ^{137}Cs—^{137}Ba.

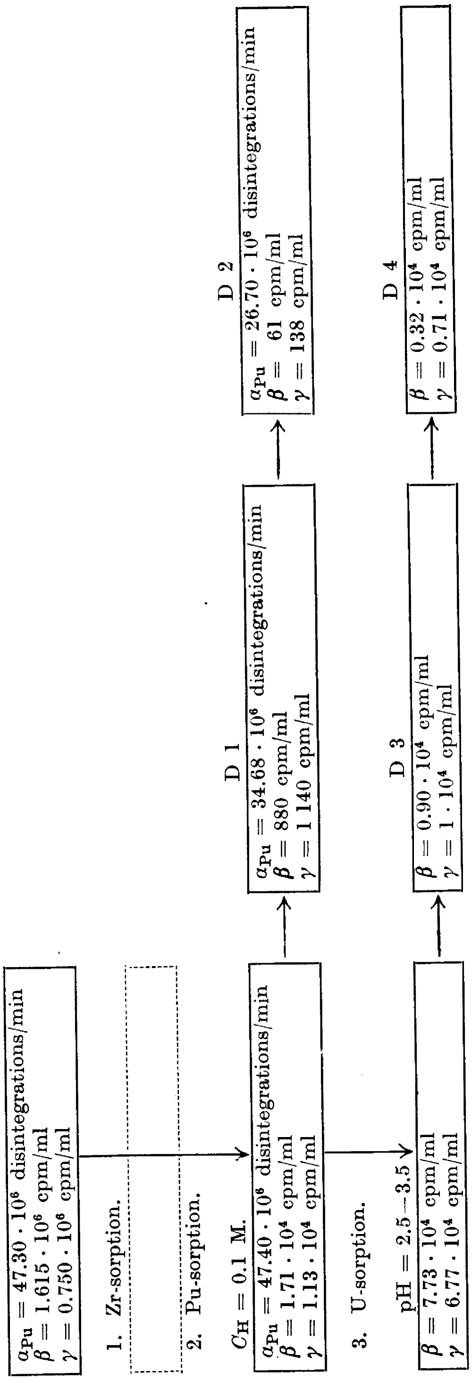

Fig. 7. Block scheme for the separation of the components of a solution of irradiated uranium.

β and γ activities were determined by scintillation counting. The β detector was a Tracerlab P-20 C with a stilbene crystal, the γ detector was the same as used in Ref[1]. The initial activities were $\gamma = 7.500 \times 10^5$ cpm/ml and $\beta = 1.615 \times 10^6$ cpm/ml.

As the amount of plutonium was known (the volume of solution being 100 ml) the total number of plutonium α- decays per minute could be calculated and was $\alpha_{Pu} = 47.30 \times 10^6$. The separation process can be described with the block scheme, Fig. 7, where the different activities at different stages in the separation have also been inserted. The activities are everywhere related to an initial volume of 100 ml and are measured in constant geometry.

1. Because of the short half life ($T_{1/2} = 65$ days) for ^{95}Zr, all ^{95}Zr$-^{95}$Nb has disappeared during the cooling period. The first stage of the process was therefore omitted.

2. The acid excess was removed by evaporationg to dryness and the solid residue dissolved in 100 ml 0.1 M nitric acid. The evaporation also caused in this case a strong plutonium disproportionation but by treating the solution with sodium nitrite the oxidation state was restored to + 4. At a nitrite concentration of 50 mM, this was achieved in a few hours at 80°C. The high concentration of nitrate ions in the rather concentrated uranyl nitrate solution also stabilized the plutonium very much as Pu(IV).

After cooling the solution was passed down the column at a rate of about 3.5 ml·hour^{-1}·cm^{-2}. After washing with 0.1 M nitric acid plutonium was quantitatively eluted with strong nitric acid. The result (Fig. 7) shows that the all plutonium was sorbed and that most of the fission porducts were removed from the plutonium fraction. A further decontamination was obtained by sorbing the plutonium twice more onto the column.

D 1. The eluate from 2 was evaporated to dryness, dissolved in 100 ml 0.1 M nitric acid and treated as before with sodium nitrite. As no uranium was present the nitrate concentration was rather small, 0.1 M compared with 2.3 M at the first reduction. In this solution Pu(IV) disproportionates and in fact only 73.5 % of the plutonium remained fourvalent. On passage down the column a small Pu(IV) leakage, about 0.5 % of the total amount plutonium, was observed. The activity measurements showed a further decontamination from fission products and the plutonium(IV) yield is greater than 99.5 % (Fig. 7).

D 2. The eluate from D 1 is evaporated to dryness and then treated as in the previous decontamination step. About 77 % plutonium was found in the oxidation state + 4. After elution α, β and γ-activities were measured as before (Fig. 7).

The plutonium solution finally obtained was completely separated from uranium and partially decontaminated from fission products. The decontamination factors were for γ-activity 5.4×10^3 and for β-activity 2.65×10^4. On the assumption that plutonium is kept in oxidation state + 4 the separation can be made with a yield larger than 99.5 %. Plutonium missing in D 2 is found as Pu(III) and Pu(VI) leakage from D 1 and D 2. To collect the plutonium in the leakage from D 1, this portion was treated with sodium nitrite. After sorption and elution an amount of plutonium $= 9.6 \times 10^6$ disintegrations · min^{-1} was recovered.

3. From the solution which hade been passed down the column at 2 the uranium was recovered. By adding sodium hydroxide the pH was increased to between 2.5 and 3.5 and from this solution uranium was sorbed on the column. The column was washed with water and eluted with strong acid. The β and γ activities of this fraction were then measured. After subtracting the activies due to daughter products of uranium (determined separately by measuring a pure uranium solution) the activities of the fission products were obtained.

As seen from Fig. 7 (U-sorption), a small decontamination from fission products was achieved. To get a larger total decontamination the above treatment was repeated twice, decontamination steps D 3 and D 4. The uranium yield was always 100 % and the decontamination factors for the final uranium solution were for β activity 505 and for γ activity 106.

In order to trace the behaviour of the different fission products present, γ-spectra have been recorded for the original solution, the plutonium fraction 2 and the uranium fraction 3. The spectrum of the original solution showed that the γ-activity almost completely came from ^{137}Cs. A small peak from ^{144}Ce, only a few percent of the cesium peak, could also be seen. Spectra from fractions 2 and 3 also showed the presence of ^{137}Cs, while ^{144}Ce had disappeared.

The long cooling period is of course the reason why the γ-activity comes almost exclusively from ^{137}Cs and the uranium decay series and the β-activity from ^{90}Sr and the uranium series.

According to Ref.[1], Fig. 6, Cs^+ and Sr^{2+}, which are very similar to Na^+ and Ca^{2+}, Ba^{2+}, ought not to be sorbed at the pH in question and the decontamination factors are consequently unexpectedly small. For a further study of the pH influence a new decontamination was performed on a part of the original solution. Uranium was sorbed as before but the column was washed with 0.1 mM nitric acid instead of water. After elution and measurements of the activities the decontamination factors were calculated as 75 for γ-activity and 20 for β-activity compared with 8.6 and 6.8 for the corresponding factors in D 3. It is evident that the distribution curve for Cs^+ and Sr^{2+} which ought to be the same as the curves in Ref.[1], Fig. 6, for Na^+ and Ca^{2+}, Ba^{2+} have been shifted towards lower pH-values at the low Cs^+, Sr^{2+} concentrations used here.

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