Studies of the Synthetic Inorganic Ion Exchanger. IV.[1] *The Separation of the Fission Product and Uranium by Means of a Stannic Phosphate Cation Exchanger*

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(Received May 6, 1964)

The separation of uranium and fission products is one of the main parts of the reprocessing of irradiated nuclear fuels. In such a process it is better to use the unit processes which can be applied to the remote handling operations and which are not interfered with by the irradiation of the high dose of ionized radiation. In this respect, the ion exchange method employing the stannic phosphate cation exchanger which has been developed in this laboratory is considered to be one of the most promising methods.

Stannic phosphate, besides its resistivity against ionized radiation, has various other excellent characteristics and was applied to the separation of fission products in the preceding study of this series.[2] Using various concentrations of nitric acid and ammonium chloride

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[1] Y. Inoue, This Bulletin, 36, 1324 (1963).

[2] Y. Inoue, ibid., 36, 1316 (1963).

solutions as the eluants, the separation was achieved on small columns in a relatively simple operation. It had, however, a shortcoming in that some of the rare earths was eluted with cesium.

The purpose of this study is to modify the method for the mutual separation of fission products in order to prevent the contamination of cesium and to establish a method for the separation of uranium from the fission products.

Experiment

Reagents.—*Ion Exchanger.*—The stannic phosphate used was prepared by the method described previously.[2]

Radioactive Isotopes.—They were the same as those of the last paper of this series.[1]

All the other reagents, such as uranyl nitrate, nitric acid, phosphoric acid, acetic acid, sodium carbonate and ammonium chloride, were of the highest grade of purity.

Apparatus.—All the absorption measurements were made with a Hitachi spectrophotometer, model EPU-2, with 1 cm. silica transmission cells. The pH meter, radiation measurement instruments and fraction collector were those described in the foregoing report.

Procedure.—*The Determination of Uranium.*—In the presence of phosphate, the thiocyanate-spectrophotometric method[3] cannot be used because of the strong interference from phosphate. In this case, the sodium carbonate - hydrogen peroxide - sodium hydroxide method[4] was employed. The calibration curves were made in the presence of the same amount of phosphoric acid as in the sample solution in order to eliminate the interference from phosphate. The procedure was as follows: After less than 10 ml. of the sample solution had been placed in a 100 ml. beaker, the volume was brought to about 10 ml. with distilled water. The pH of the solution was adjusted with sodium hydroxide, and then it was transfered into a 25 ml. volumetric flask. Five milliliters of 5% sodium carbonate, 1 ml. of 10% sodium hydroxide and 2 ml. of 3% hydrogen peroxide solutions were added succesively. After this new solution had been diluted to the 25 ml. mark, the absorbance of the solution was measured against a corresponding blank at the wavelength of 370 or 400 mμ. The concentration of uranium was calculated from the relationship between the absorbance and the concentration represented in Table I.

TABLE I. RELATIONSHIP BETWEEN ABSORBANCE AND CONCENTRATION OF URANIUM IN THE PRESENCE OF PHOSPHORIC ACID

Concn. of H_3PO_4, M	(μg./ml.)/unit absorbance	
	370 mμ	400 mμ
0.0	159.8	238.0
10^{-3}	160.9	239.3
10^{-2}	164.2	238.1
10^{-1}	185.2	238.6
2×10^{-1}	196.5	244.8
4×10^{-1}	232.5	276.6
1.0	281.8	333.2

The Determination of the Distribution Coefficients.—The distribution coefficients were determined by equilibrating 500 mg. of the ion exchanger in a thermostat at 25°C with 50 ml. of suitable solutions for two or three days. This was followed by the filtration of the mixture and by the analysis of the filtrate. If necessary, the pH of the filtrate was measured. The metallic ion content of the exchanger after equilibrium was estimated from the difference between the total initial and final concentrations of metal present in the solution.

The distribution coefficients were calculated by means of the usual relationship:

$$K_d=\frac{\left(\begin{array}{c}\text{Amount of cation in exchanger/}\\ \text{Wt. of exchanger in g.}\end{array}\right)}{\left(\begin{array}{c}\text{Amount of cation in solution/}\\ \text{Vol. of solution in ml.}\end{array}\right)}$$

Cerium was carrier-free ^{144}Ce, and the concentration of uranium was 10^{-3} M. They were determined radiochemically and spectrophotometrically respectively.

Column Operation.—The column was prepared as follows. To 2 g. of a dried exchanger in the hydrogen form (100~200 mesh), sufficient distilled water was added to allow a mixing thorough enough to expel any adhering air bubbles. After this mixing, the slurry was poured into a glass column, 7 mm. in internal diameter, using glass wool as a column support. The column thus prepared had a height of 40 mm. The flow·rate of the influent was controlled according to the rate of exchange for each experiment and is described in figures of the elution curve. For making elution curves, effluents were received in polyethylene test tubes in suitable amounts; their radioactivities were measured with a well-type scintillation counter, and their uranium contents were determined by the method described above. When beta-rays were used for the measurement of the radioactivity, one drop of solution from every 2 g. of the effluents was placed on an aluminum dish, and their radioactivities were measured by a G. M. counter in the usual manner.

Results

The Modification of the Separation Method of a Fission Product Solution.—In the mutual separation of fission products, cesium was not obtained in a radiochemically pure state when it was eluted by a 3 M ammonium chloride solution as has been described previously. When this eluant was applied to the fission product solution containing uranium, rare earths and also uranium were eluted by this eluant, as will be shown later. This is perhaps

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[3] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York (1959), p. 916.

[4] Ibid., p. 915.

because of the partial elution of rare earths and uranium by the hydrogen ions which are replaced from the column by the action of concentrated ammonium ions. This is supported by the fact that this objectionable phenomenon is less pronounced when the exchanger is treated with a sufficient amount of 3 M ammonium chloride beforehand. Even with this pretreatment, however, the exchanger was not completely converted to the ammonium form. (This was clearly indicated by the fact that when an ammonium carbonate solution came in contact with the exchanger, bubbles of carbon dioxide were generated.) Moreover, even if the exchanger were completely converted to the ammonium form, the contamination of cesium would not be eliminated, as the presence of some acid in the eluant is needed for the complete elution of strontium, which is completed before the elution of cesium. Therefore, at all events, it is essential to devise a procedure by which cesium can be eluted in a radiochemically pure state.

It is conceivable that the interfering effect of the remaining hydrogen ions can be eliminated by the treatment of the column with a neutral solution before the elution of cesium. As one such reagent, ammonium acetate was chosen, and, as is shown in Fig. 1, a clear-cut elution curve was obtained. It was confirmed by the radiochemical analyses of several representative aliquots of the effluents that no contamination of cerium occurred in the cesium fraction.

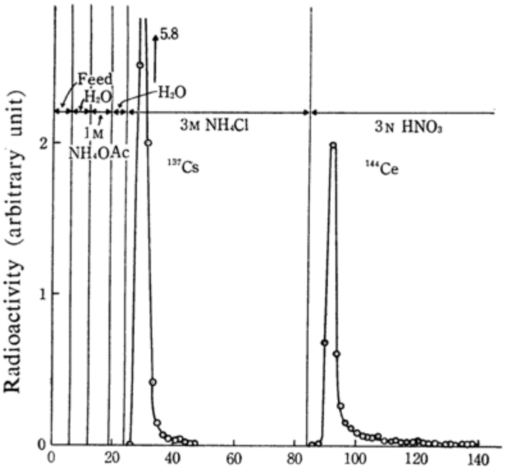

Fig. 1. Separation of ^{144}Ce and ^{137}Cs. Flow rate: 0.5~0.6 ml./min.

Furthermore, this procedure did not affect at all the elution processes after that of 3 M ammonium chloride.

The Distribution Coefficients of Uranium in a Nitric Acid Solution.—To contribute to the establishment of the method of separation, the distribution coefficients of uranium were determined in a nitric acid medium, as is shown in Table II. For the purpose of comparison, the values for nuclides present in fission products are cited in the table quoted from the preceding report. The distribution coefficients of uranium decrease with an increase in the acidity and resemble those of rare earths. From these results, it is expected that the separation of uranium from rare earths by nitric acid is very difficult, while that from other nuclides is easy. First the conditions for the mutual separation of uranium and individual nuclides in fission products were determined; then the separation of uranium and gross fission products was carried out.

TABLE II. DISTRIBUTION COEFFICIFNTS IN NITRIC ACID SOLUTION (ml./g.)

Acidity N	Nuclides				
	UO_2(II)	^{95}Zr	^{95}Nb	^{137}Cs	^{89}Sr
0.0	2.9×10^3	—	—	—	—
0.1	3.5×10^2	2.7×10^3	2.2×10^3	3.8×10^3	6.7×10
0.5	4.1×10	3.5×10^3	2.6×10^3	1.3×10^3	~7
1.0	2.0×10	3.5×10^3	2.7×10^3	1.8×10^2	~2
3.0	6.1	3.6×10^3	2.5×10^3	1.0×10^2	~2
10.0	1.2	3.7×10^3	4.0×10^3	~3.7	~0

Acidity N	Nuclides			
	^{90}Y	^{144}Ce(III)	^{144}Ce(IV)	^{106}Ru
0.0	—	—	—	—
0.1	1.4×10^3	9.3×10^2	6.5×10^2	~0
0.5	1.6×10	1.2×10	1.1×10	~0
1.0	~3.6	~4	~1	~0
3.0	~2	~2	~1	~3
10.0	~0	~0	~0	~8

The Separation of ^{89}Sr and Uranium.—The separation of ^{89}Sr and uranium was carried

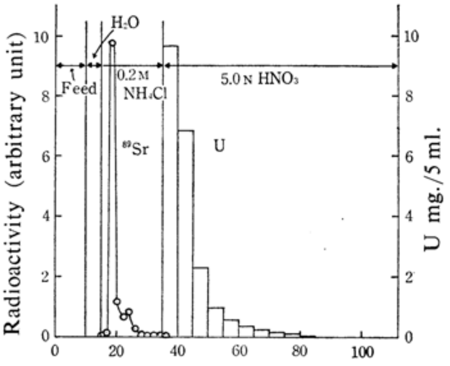

Fig. 2. Separation of ^{89}Sr and uranium. Flow rate: 0.5~0.6 ml./min.

out by the hydrogen-form exchanger. Ten milliliters of a sample solution containing a 10^{-2} M uranyl nitrate and carrier-free ^{89}Sr were passed through the column, and then 0.2~0.5 M ammonium chloride and 5 N nitric acid solutions were passed through in order to elute strontium and uranium successively. The separation went well, as is shown in Fig. 2. When an ammonium-form exchanger was used, it was necessary to use an eluant containing some acid in order to make a complete elution of strontium. A part of the uranium was also eluted by this reagent; therefore, an ammonium-form exchanger cannot be used in the separation of these elements.

The Separation of ^{137}Cs and Uranium.—When the hydrogen-form exchanger was used, uranium was eluted partly in 3 M ammonium chloride, as in the case of rare earths, as is shown in Fig. 3. The treatment of the column with a 1 M ammonium acetate solution before the elution of cesium made it possible to prevent the contamination of uranium, and separation was satisfactory, as is shown in Fig. 4.

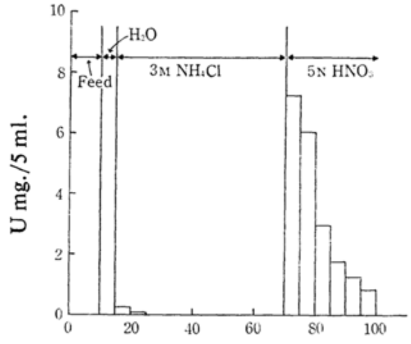

Fig. 3. Elution of uranium from hydrogen form exchanger.
Flow rate: 0.5~0.6 ml./min.

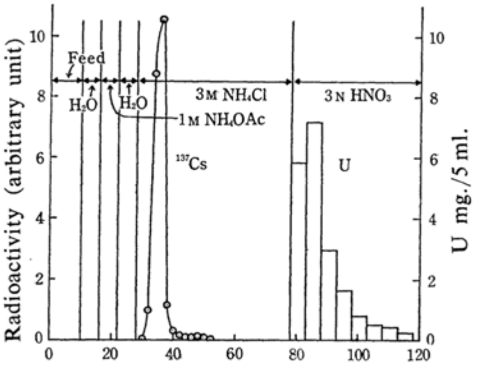

Fig. 4. Separation of ^{137}Cs and uranium.
Flow rate: 0.5~0.6 ml./min.

The Separation of ^{144}Ce and Uranium.—These two elements cannot be eluted by ammonium chloride, and separation by nitric acid seems to be very difficult, as is indicated by the results of Table II. This was also confirmed experimentally by the detailed investigation of the elution curves of uranium using various concentrations of nitric acid as eluants. Therefore, it is necessary to search for the other eluants. For this purpose, various concentrations of ammonium carbonate, ammonium carbonate-ammonium acetate, ammonium carbonate-ammonium chloride, ammonium carbonate-acetic acid-ammonium acetate, sulfuric acid, potassium sulfate, acetic acid-sodium acetate and phosphoric acid were investigated. Among these, ammonium carbonate-ammonium chloride and phosphoric acid looked promising and were investigated in detail.

The Ammonium Carbonate-Ammonium Chloride System.—The distribution coefficients of uranium and cerium measured in this system are presented in Table III. The distribution coefficients of uranium decreased with a decreasing pH, while those of cerium increased. As was described in the foregoing report, this exchanger is unstable at high pH values, so that possibly a low pH is preferable. With 5×10^{-2} M ammonium carbonate-3 M ammonium chloride, the differences between their distribution coefficients were very large, and the pH of the solution was low enough. Consequently, this condition seems to be quite suitable for the separation of these elements. According to this principle, the elution of uranium and cerium was conducted by using 5×10^{-2} M ammonium carbonate-3 M ammonium chloride and 1 N nitric acid as the eluants respectively. Uranium exhibited a sharp elution peak, but it showed considerable tailing and the yield was only 40% with an initial 150 ml. of eluants (Figs. 5 a and b). In other words, although it was possible to remove cerium from uranium

TABLE III. DISTRIBUTION COEFFICIENTS OF URANIUM AND CERIUM IN AMMONIUM CARBONATE-AMMONIUM CHLORIDE SYSTEM

Concn. of $(NH_4)_2CO_3$ M	Concn. of NH_4Cl M	pH	K_d (ml./g.) U	Ce
10^{-1}	10^{-1}	8.9	1.65×10^2	4.20×10
10^{-1}	5×10^{-1}	8.6	8.88×10	9.12×10
10^{-1}	1	8.4	6.18×10	4.20×10^2
10^{-1}	3	8.0	2.70×10	8.09×10^2
5×10^{-2}	10^{-1}	8.6	4.13×10	1.62×10^2
5×10^{-2}	5×10^{-1}	8.2	3.61×10	3.00×10^2
5×10^{-2}	1	8.0	3.02×10	5.42×10^2
5×10^{-2}	3	7.5	1.88×10	8.80×10^2

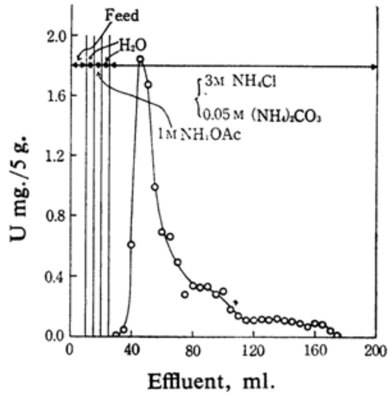

Fig. 5a. Elution of uranium by carbonate solution.
Flow rate: 0.3~0.4 ml./min.

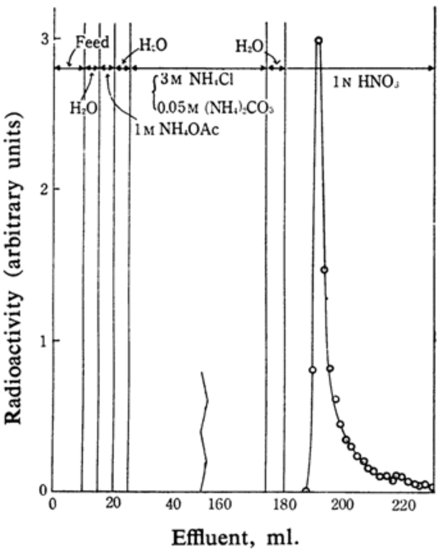

Fig. 5b. Elution of cerium.
Flow rate: 0.3~0.4 ml./min.

completely, the yield was very low, so this method of separation was by no means suitable.

TABLE IV. DISTRIBUTION COEFFICIENTS OF URANIUM AND ^{144}Ce(III) IN PHOSPHORIC ACID SOLUTION

Concn. of H_3PO_4 M	K_d (ml./g.) Ce	K_d (ml./g.) U
0.021	—	447
0.050	2.73×10^3	159
0.100	6.62×10^3	73.1
0.205	—	39.2
0.500	6.62×10^3	5.05
1.000	3.56×10^3	0.79
5.000	5.84×10	0.00

The Phosphoric Acid System.—The distribution coefficients of uranium and cerium in various concentrations of phosphoric acid solutions are shown in Table IV. The distribution coefficients of uranium decreased monotonously with an increase in the acid concentration, and scarcely any uranium was adsorbed from phosphoric acid solutions above 1 M. On the contrary, although the distribution coefficients of cerium showed a maximum value between 0.1 and 0.5 M acidity and then rather decreased with an increase in the acidity, still it showed a fairly high value of about 3600 in 1 M phosphoric acid; it thus differed considerably from the uranium, and so it may be presumed that the condition is suitable for use. Ten milliliters of a sample solution containing 10^{-3} M uranium and carrier-free ^{144}Ce were poured into a hydrogen-form exchanger bed; when the level of the solution reached the top of the exchanger bed, 5 ml. of water, 60 ml. of 1 M phosphoric acid, 6 ml. of water and 50 ml. of 3 N nitric acid were passed through the column succesively. One of the examples is shown in Fig. 6. The elution curve showed tailing to some extent, and the yield of uranium was about 92%. The use of a larger volume of phosphoric acid improves the yield, but it is not practical, as can be predicted from the shape of the elution curve. In any case, it is easy to recover over 90% of uranium without any contamination of cerium. The unfavorable tailing results from the slow rate of exchange.

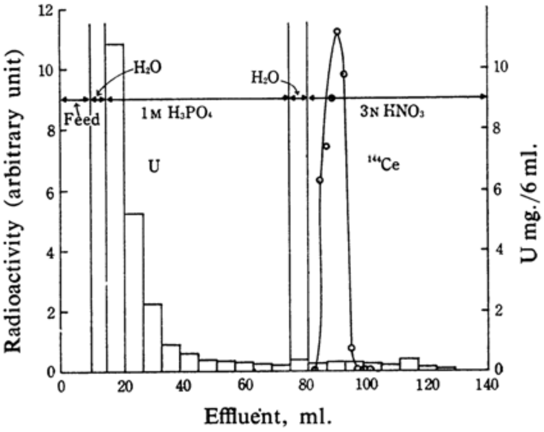

Fig. 6. Separation of uranium and ^{144}Ce.
Flow rate: 1 M H_3PO_4, 0.2 ml./min.; 3 N HNO_3 0.5~0.6 ml./min.

The Behavior of Zirconium and Niobium.—The behavior of ^{95}Zr and ^{95}Nb in equilibrium was also investigated. As these nuclides were eluted partly by 1 M phosphoric acid, there was fear of contaminating uranium. As has been described previously, uranium was quantitatively eluted by nitric acid above 1 N but

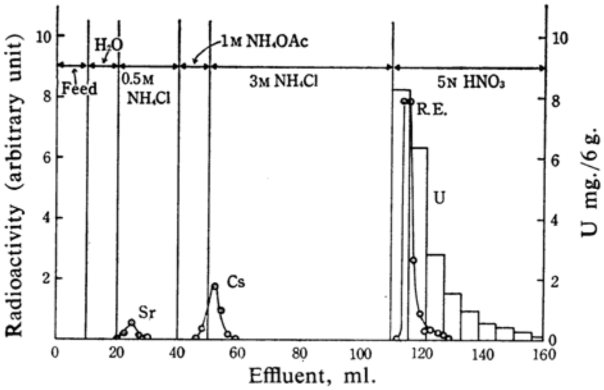

Fig. 7a. Separation of uranium and fission product.
Flow rate: 0.5~0.6 ml./min.

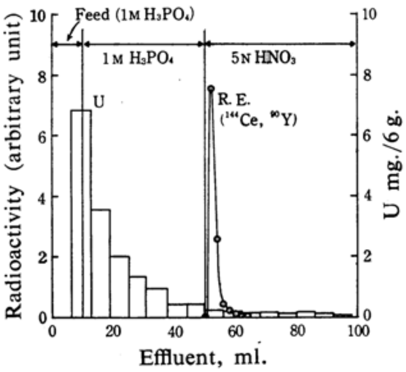

Fig. 7b. Separation of uranium and rare earths.
Flow rate: 1 M H_3PO_4, 0.2 ml./min.; 5 N HNO_3; 0.5~0.6 ml./min.

zirconium and niobium were not eluted at all. Therefore, the separation of uranium and a zirconium-niobium mixture was achieved by means of 3 N nitric acid.

The Separation of Uranium and the Fission Product.—Putting the above results together, the best conditions for the separation of uranium and the fission product were decided upon. To the sample solution, 5 ml. of concentrated perchloric acid were added; this was boiled until a yellow color had appeared once and then diminished. (It is advisable to lead the distillate into water in order to prevent any health hazard.) Then the residual solution was evaporated almost to dryness on a hot plate. After it had cooled, 1 ml. of 1 N nitric acid was added; the mixture was heated to dissolve the residue and then diluted to 10 ml. with water. This was poured into an exchanger bed; when the level of the solution reached the top of the exchanger bed, 10 ml. of water (by which no adsorbable form of zirconium and niobium could be washed out), 20 ml. of 0.5 M ammonium chloride (the elution of strontium), 10 ml. of 1 M ammonium acetate, 100 ml. of 3 M ammonium chloride (the elution of cesium), and 100 ml. of 5 N nitric acid (the elution of uranium and rare earths) were passed through the column successively. The 5 N nitric acid effluent was heated on a hot plate until the metastannic acid had coagulated completely. After the effluent had been cooled and diluted enough to prevent any destruction of filter paper, it was filtered to remove the metastannic acid (no uranium is lost by this procedure), and then the filtrate was evaporated almost to dryness. After it had cooled again, 10 ml. of 1 M phosphoric acid was added, and heated to dissolve the residue. This was poured into another exchanger bed, and, after the level of the solution had reached the top of the exchanger bed, 1 M phosphoric acid was percolated in until the yellow color of the column faded. A 5 N nitric acid solution was also passed through to elute rare earths. The elution curves are shown in Figs. 7a and b. The yields of uranium and beta and gamma decontamination factors are summarized in Table V. It goes without saying that if the fission product is cooled long enough to provide the decay of zirconium-95, radiochemically pure uranium can be collected in the 1 M phosphoric acid effluant which is inserted between 3 M ammonium chloride and 5 N nitric acid in the above procedure. This is shown in Fig. 8.

TABLE V. YIELD AND DECONTAMINATION FACTOR OF URANIUM
(uranium added; 23.81 mg.)

Uranium recovery		Decontamination factor	
Found (mg.)	%	β	γ
22.22	93.3	2.4×10^3	2.0×10^3
22.22	93.3	1.1×10^3	7.0×10^2
21.46	90.0	2.3×10^3	1.7×10^3

The Enhancement of the Yield of Uranium.—As can be seen from Table V, the yield of uranium was 90% or so; for the improvement of the recovery of uranium it is necessary to use a larger volume of eluant; the large volume of the eluant and the time needed make it impractical in all respects. If the saturation of a column by uranium does not affect the adsorption of rare earths, the column can be used for the uptake of rare earths until the break-through capacity for them is saturated. If a uranium solution contains only a low concentration of rare earths, such as a

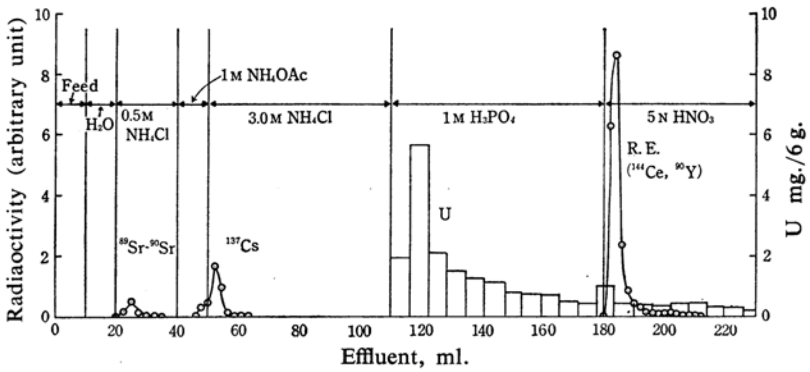

Fig. 8 Separation of uranium and fission product (in the absence of ^{95}Zr-^{95}Nb).
Flow rate: 0.5∼0.6 ml./min. except with 1 M H_3PO_4 (0.2 ml./min.)

carrier-free concentration, the perfect recovery of rare earth-free uranium can be accomplished by such a simple method as passing the solution through a column previously treated with a uranium solution, and this column could be used to an almost unlimited extent. When a 1 M phosphoric acid solution saturated with cerium ions was used, the column quantitatively adsorbed cerium from 26 ml. of the solution and then started to break through. This corresponded to about 0.2 meq. of cerium(III).

Summary

The separation of fission products and uranium has been carried out by means of a stannic phosphate cation exchanger. By using various concentrations of nitric acid and ammonium chloride solutions as eluants, the separation of uranium-strontium and uranium-cesium has been easily performed, but that of uranium-rare earths is very difficult. Among the various reagents investigated, a 1 M phosphoric acid solution is most suitable for the separation of uranium from rare earths. In view of the above results, the separation of uranium and gross fission products has been carried out; the resultant yield of uranium is more than 90%, and the decontamination factor is $(2\sim3)\times10^3$.

Part of the expenses for this investigation have been defrayed by a grant-in-aid by the ministry of education.

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