Studies of the Synthetic Inorganic Ion Exchanger. III. The Separation of the Fission Product by Means of a Stannic Phosphate Cation Exchanger

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(Received June 8, 1963)

Previously, stannic phosphate, one of the synthetic inorganic ion exchangers which would be expected to have radiation and thermal stability, has been prepared and its fundamental properties investigated, as has been described in preceding reports.[1,2]

Stannic phosphate is one of the polybasic acids which have several dissociable hydrogen atoms. However, the functional group, with the pK_a value of approximately three, is most important in a weakly acidic solution, and in such a solution this exchanger is useful; therefore, it may be assumed that, from the practical point of view, stannic phosphate is a weakly acidic cation exchanger with only one functional group. The ion exchange equilibrium can be elucidated from the mass action law; the ion exchange properties of stannic phosphate are also affected by heat treatment in air. For instance, the separation of alkali metals does not proceed well when the exchanger is dried at 110°C because of the slow rate of exchange. On the other hand, stannic phosphate is fairly stable against heat treatment in water; that is, it changes for the worse only in a slight decrease in exchange capacity even when it is treated in water at 250°C. It is so stable against radiation that is not affected at all by gamma ray irradiation up to 10^9 r. Thus, the stannic phosphate has been shown to be, for the most part, a good cation exchanger except for a few shortcomings such as unstability against alkaline solutions and against heat treatment in air; as an example of practical applications, the mutual separation of various nuclides in a fission product cooled for one or two years has been carried out using ammonium chloride and nitric acid as eluants. The results will be described below.

Experimental

Reagents and Apparatus. — *Reagents.* — *Ion Exchanger:* Stannic phosphate prepared by the method described previously was used.[2]

Radioactive Isotopes: The kinds of radioactive isotopes, their suppliers, commercial forms and the methods of pretreatment are shown in Table I. Their radiochemical purity was certified by gamma ray spectrometry or by analyses of their beta ray absorption curves before use.

Other chemicals, such as nitric acid and ammonium chloride, were of the highest purity grade.

Apparatus.—All pH measurements were performed with a Toa Dempa pH meter, model HM-5, calibrated with the appropriate buffer solutions prior to the experiments. Measurements of beta rays and gamma rays were made by a Hitachi Model RT-1 G. M. counter and a Hitachi well-type scintillation counter respectively. A Hitachi Model RDA-2 single-channel gamma-ray spectrometer or TMC-400 channel pulse-height-analyzer Model 406-6 were used for the measurement of the gamma-ray spectra.

Procedures.—The column was prepared as follows. To 2 g. of a dried exchanger in hydrogen form (100~200 mesh) sufficient distilled water was added to allow thorough enough mixing to expell any adhering air bubbles. After 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 the height of 40 mm.. When the ammonium form exchanger was used, the column was conditioned by the passage of 50 ml. of a 3 M ammonium chloride solution, followed by that of 50 ml. of distilled water, at the flow rate of 0.5~0.6 ml./min.

The flow rate of the influent was kept nearly constant, 10~12 drops per min. corresponding to 0.5~0.6 ml./min., throughout this experiment.

For making elution curves, effluents were received in polyethylene test tubes every 2 g. by means of a Toyo Kagaku Sangyo Model SF-200A fraction collector unless otherwise noted; their radioactivity was measured with the well-type scintillation counter. When beta rays were used for the measurement of radioactivity, one drop of effluent was received on aluminum dishes every 2 g. and their radioactivity was measured with the G. M. counter in the usual manner. The identification of the nuclides present in the effluent and the determination of their radiochemicl purity were made by gamma ray spectrometry and by analyses of beta-ray absorption curves at several important points on the elution curves.

The content of rare earth in the cesium fraction was determined in the following way: To the sample solution, 5 mg. of cesium and 20 mg. of lanthanum

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1) Y. Inoue, *J. Inorg. Nucl. Chem.*, in press.
2) Y. Inoue, This Bulletin, **36**, 1316 (1963).

TABLE I. RADIOACTIVE ISOTOPES USED IN THIS WORK

Nuclide	Supplier	Commercial form	Pre-treatment
F. P.	Oak Ridge National Laboratory, U. S. A.	Nitrate	Treated with HNO_3: Cooled for about 1.5 years
^{89}Sr	Oak Ridge National Laboratory, U. S. A.	Chloride	^{90}Y removal by ion exchange: Converted into HNO_3 form
^{106}Ru-^{106}Rh	Radiochemical Center, England	Trichloride	Converted to HNO_3 form
^{95}Zr-^{95}Nb	Oak Ridge National Laboratory, U, S. A.	Oxalate	Each nuclide is separated by means of TTA extraction: Converted to HNO_3 form
^{137}Cs	Oak Ridge National Laboratory, U. S. A.	Chloride	Converted to HNO_3 form
^{144}Ce(III)	Radiochemical Center, England	Trichloride	H_2O_2 reduction
^{144}Ce(IV)	Radiochemical Center, England	Trichloride	$KBrO_3$ oxidation-ether extraction-back extracted into dil. HNO_3
^{90}Sr-^{90}Y	N. V. Philips-Roxane Pharmaceutish-Chemishe Industrie "Duphar", Holland	Chloride	Converted to HNO_3 form

were added as carriers, and a slight excess of ammonium hydroxide solution was also added to precipitate lanthanum hydroxide. The precipitate thus formed was filtered, washed, and dissolved into a possibly small amount of hydrochloric acid. Precipitation was repeated until the activity of the lanthanum hydroxide became free from that of the cesium. Then the precipitate was put into a polyethylene sample tube and its activity was measured by the well type scintillation counter.

Results

Distribution Coefficients.—To contribute to the establishment of the method of separation, the distribution coefficients of various nuclides contained in the fission product were determined in a nitric acid medium, as shown in Table II.

^{95}Zr and ^{95}Nb show high distribution coefficients of about 3×10^3 ml./g. extending over a wide range of acidity. This is perhaps attributable to the formation of insoluble phosphates. On the contrary, although there is a slight tendency for ruthenium to adsorb from concentrated nitric acid on the exchanger bed, the distribution coefficients for ruthenium are nearly zero throughout the wide range of acidity. For ^{137}Cs, ^{89}Sr, ^{90}Y, ^{144}Ce(III) and ^{144}Ce(IV), the distribution coefficients decrease with increasing acidity in accordance with the usual relationship observed in ion exchange resins. It is noticeable that cesium has exceedingly high distribution coefficients. It is assumed that a zirconium-niobium equilibrium mixture and ruthenium may be easily separated from the remaining nuclides because of their peculiar behavior toward the exchanger. Therefore, at first the conditions for the mutual separation of ^{137}Cs, ^{89}Sr and ^{144}Ce, and of ^{90}Sr and ^{90}Y were determined; then the behavior of zirconium-niobium and ruthenium towards the column operation was investigated.

The Separation of ^{137}Cs and ^{89}Sr.—As Table II indicates, the separation of ^{137}Cs and ^{89}Sr by the hydrogen-form exchanger was intended using nitric acid as the eluant. In this case, strontium shows a gently sloping elution curve when acidity is low; the peak of the elution curve cannot become sharp until the acidity of the eluant is increased to more than 5 N. Cesium is in part eluted with nitric acid of a high concentration such as 5 N, but the major part of it remains on the top of the column.

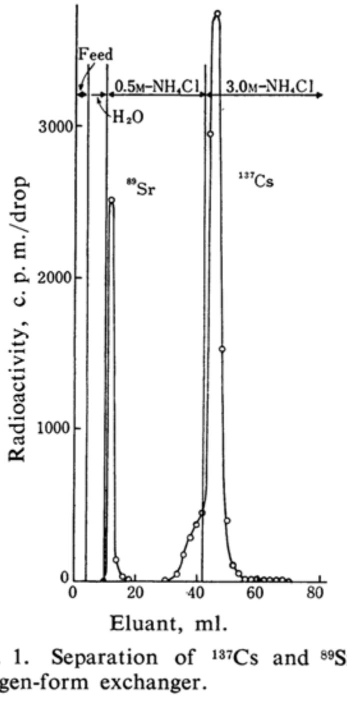

Fig. 1. Separation of ^{137}Cs and ^{89}Sr by hydrogen-form exchanger.

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

Acidity (N)	Nuclide							
	^{95}Zr	^{95}Nb	^{137}Cs	^{89}Sr	^{90}Y	^{144}Ce(III)	^{144}Ce(IV)	^{106}Ru*
0.1	2.7×10^3	2.2×10^3	3.8×10^3	6.7×10	1.4×10^3	9.3×10^2	6.5×10^2	~0
0.5	3.5×10^3	2.6×10^3	1.3×10^3	~7	1.6×10	1.2×10	1.1×10	~0
1.0	3.5×10^3	2.7×10^3	1.8×10^2	~2	~3.6	~4	~1	~0
3.0	3.6×10^3	2.5×10^3	1.0×10^2	~2	~2	~2	~1	~3
10.0	3.7×10^3	4.0×10^3	~3.7	~0	~0	~0	~0	~8

* The species of ^{106}Ru is not identified.

Therefore, cesium and strontium cannot be separated with the hydrogen-form exchanger using nitric acid as the eluant. When ammonium chloride is used, the sharp peaks of ^{89}Sr and ^{137}Cs appeared in the 0.5 M and 3.0 M fractions respectively, as Fig. 1 shows. The amount of cesium remaining on the column after the elution is only 0.1% or less of the total cesium present; therefore, it is concluded that the separation is complete. When the ammonium-form exchanger is used instead of the hydrogen-form, the elution of strontium by 0.5 M ammonium chloride solution is not sharp, as Fig. 4 shows. To get a sharp elution curve, it is necessary to add a little hydrogen ion to the eluant, as shown in Fig. 5. According to this principle, strontium and cesium can be separated on the ammonium-form exchanger by a step elution technique using 0.1 N nitric acid-0.2 M ammonium chloride and 3 M ammonium chloride as the eluants respectively.

The Separation of ^{89}Sr and ^{144}Ce and of ^{90}Sr and ^{90}Y.—The separation of ^{89}Sr and ^{144}Ce was carried out using a hydrogen-form exchanger, as Fig. 2 shows. As to strontium, the elution was performed in a manner similar to that in Fig. 1. Because cerium is eluted only in a small part when ammonium chloride is used alone, whatever concentrated solution may be used, it is necessary to add hydrogen ions to some extent for the complete elution of cerium. In this case, however, the addition of ammonium chloride is not always necessary and cerium can be completely eluted by nitric acid above 1 N alone, as Fig. 10 shows.

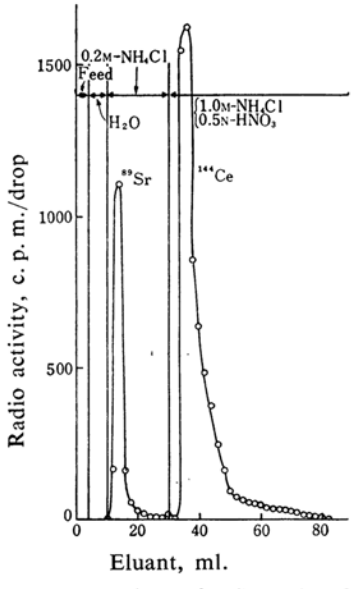

Fig. 2. Separation of ^{89}Sr and ^{144}Ce by hydrogen-form exchanger.

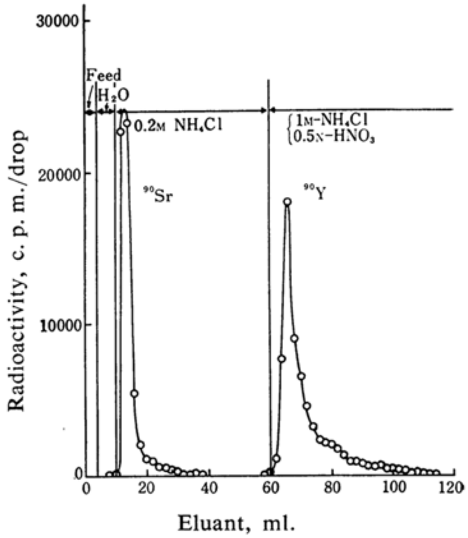

Fig. 3. Separation of ^{90}Sr and ^{90}Y by hydrogen-form exchanger.

In the case of the ammonium-form exchanger, in contrast to the hydrogen-form, strontium is completely eluted with dilute ammonium chloride as 0.5 M only with the aid of nitric acid, as shown in Figs. 4 and 5. Figure 6 shows that cerium is not eluted at all with a 0.1 N nitric acid-0.2 M ammonium chloride solution. Therefore, these nuclides can be separated according to this principle (Fig. 7). The separation of a ^{90}Sr–^{90}Y equilibrium mixture is possible in an analogous manner, as Figs. 3 and 8 show.

The Separation of ^{137}Cs and ^{144}Ce.—Applying the fact that cerium can not be eluted by

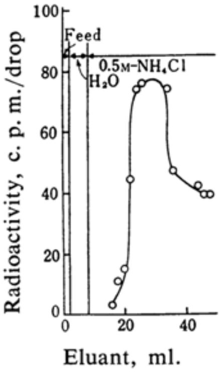

Fig. 4. Elution of strontium by 0.5 M ammonium chloride (ammonium-form exchanger).

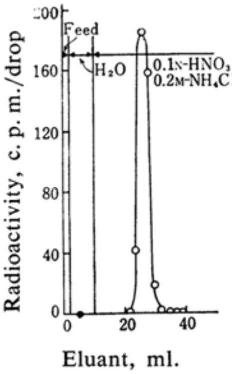

Fig. 5. Elution of strontium by 0.1 N nitric acid−0.2 M ammonium chloride (ammonium-form exchanger).

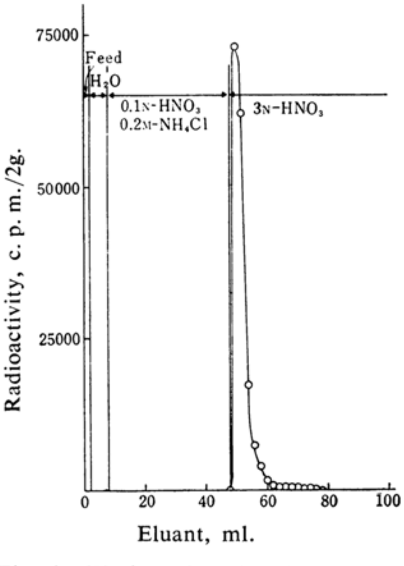

Fig. 6. Elution of cerium by hydrogen-form exchanger.

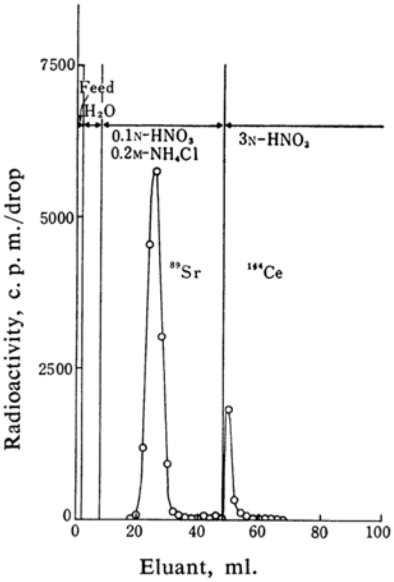

Fig. 7. Separation of ^{89}Sr and ^{144}Ce by ammonium-form exchanger.

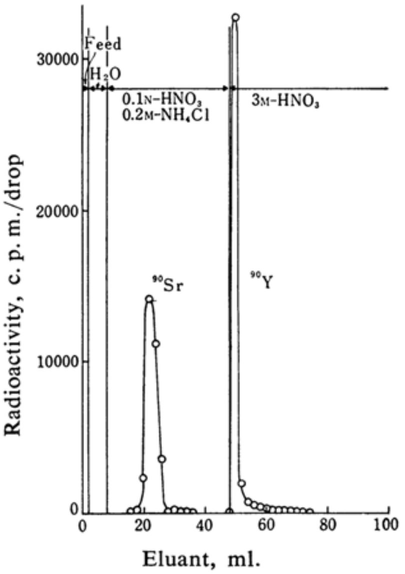

Fig. 8. Separation of ^{90}Sr and ^{90}Y by ammonium-form exchanger.

ammonium chloride alone, the separation of cesium and cerium has been carried out with the hydrogen-form exchanger, as shown in Fig. 9. It is necessary to note that the small peak appears in the beginnig of the 3 M ammonium chloride fraction. The analytical results show that this is mainly due to cerium. This is attributable to the elution of cerium with the hydrogen ions which are liberated from the hydrogen-form exchanger when the concentrated ammonium chloride solution is passed through it. Therefore, the complete separation of cesium and cerium on the hydrogen-form exchanger is impossible. However, as represented in Fig. 10, cerium is seldom eluted by 3 M ammonium chloride from the ammonium-form exchanger. On the basis of the above results, it is assumed that cesium and cerium can be separated by the step elution technique using 3 M ammonium chloride and 3 N nitric acid as the respective eluants. It is apparent from Fig. 11 that well-defined curves are obtained and that the separation is complete.

The Adsorption of Zirconium and Niobium.—The behavior of the zirconium-niobium equilibrium mixture was investigated in detail with the column operation in order to determine whether or not the results of the batch experiments could be applied to the column separation experiment. Ten milliliters of a 0.1 N nitric acid solution containing a zirconium-niobium equilibrium mixture were applied to the top of the column, and the column was then washed with 50 ml. of 5 N nitric acid. The leakage of $^{95}Zr-^{95}Nb$ from the column bed amounts to about 4.5 per cent, and the uptake is not complete. However, from the shape of

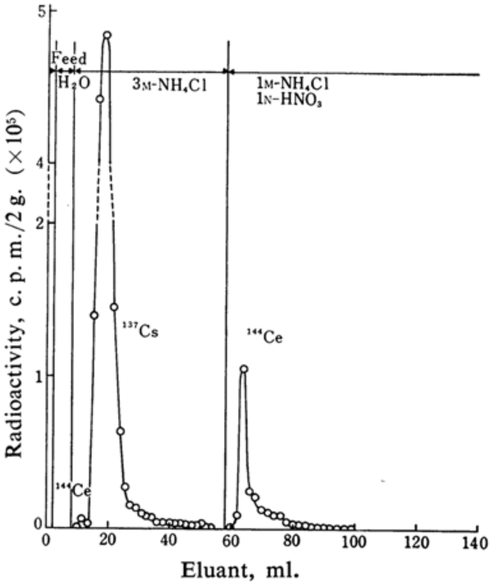

Fig. 9. Separation of ^{137}Cs and ^{144}Ce by hydrogen-form exchanger.

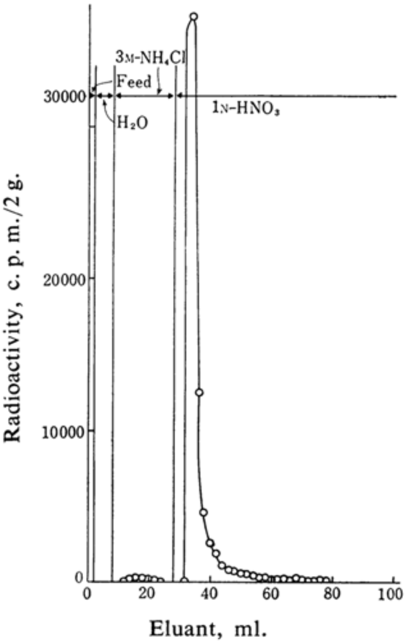

Fig. 10. Elution curve of cerium by ammonium-form exchanger.

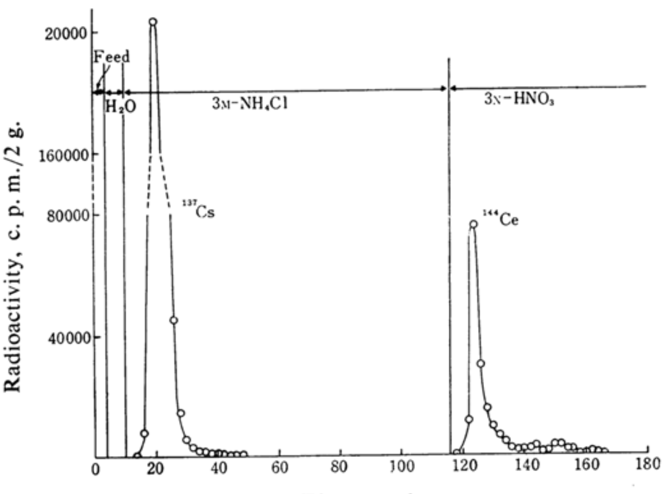

Fig. 11. Separation of ^{137}Cs and ^{144}Ce by ammonium-form exchanger.

the breakthrough curve it seems that the leakage from the exchanger bed does not occur by the elution of ions once retained on exchanger, but takes place during the adsorption step (Fig. 12a). Such peculiar behavior can probably be attributed to the presence of a radiocolloidal form of zirconium. This seems quite possible, since the stock solution was only 0.1 N in free acid. On the basis of the above considerations, a zirconium solution which had been treated with hot concentrated nitric acid for a few hours was used immediately after being diluted to the desired acidity, but no decrease in the leaked activity was observed. When the effluent is passed through the exchanger bed three times, zirconium can be adsorbed almost completely, but this method cannot be used in the practical separation of the fission product because the separation of cesium and strontium is interfered with by this operation. The unadsorbed zirconium is almost completely washed out with 10 ml. of distilled water, as Fig. 12(b) shows. In order to make sure, the distribution coefficients of zirconium and niobium in a 1 N nitric acid solution were determined as a function of the ammonium nitrate concentration; it was found that these elements can be completely retained on the column, even in the concentrated salt solution. Putting these findings together, it is apparent that the total zirconium and niobium activity can be precisely estimated from the sum of the activity remaining on the column after the elution is finished and the sum of the leaked activity during the adsorption step.

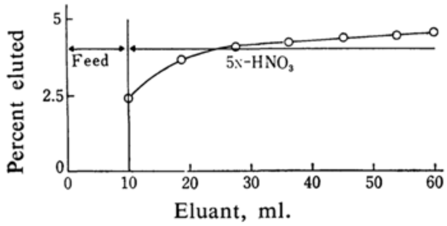

Fig. 12 (a). Breakthrough curve of zirconium by 5 N nitric acid.

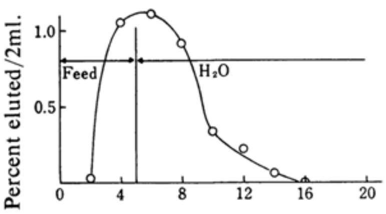

Fig. 12 (b). Breakthrough curve of zirconium by water.

The Adsorption of Ruthenium.—The behavior of ruthenium was investigated in detail with the column operation in order to determine whether or not the results of batch experiments could be applied to the column operation.

Ten milliliters of a 0.1 N or 0.2 N nitric acid solution containing ruthenium activity was passed through the exchanger bed. When the level of the solution reached the top of the exchanger bed, nitric acid of the same concentration was percolated through and the effluent was collected every 10 ml. The results are presented in Fig. 13. The curves represent the accumulated percentage value of the eluted activity as a function of the effluent volume. When the ruthenium solution which has been treated with concentrated nitric acid is used, only about 40% of ruthenium activity is eluted. When the ruthenium treated enough with fuming nitric acid is used, more ruthenium is eluted, but the percentage still does not reach 80%. When the concentration of the eluant is 0.2 N nitric acid, the 90% mark of the ruthenium is broken through. However, strontium is also completely eluted under these conditions, so this concentration is unfavorable for the elution of ruthenium in the separation of the fission product. The reason for the discrepancy between this and the batch experiment is not clear; at any rate, it is impossible to separate ruthenium from the other nuclides with the column operation. Consequently, the complete separation of fission product cannot be effected without the separation of ruthenium in advance by a method other than the ion exchange.

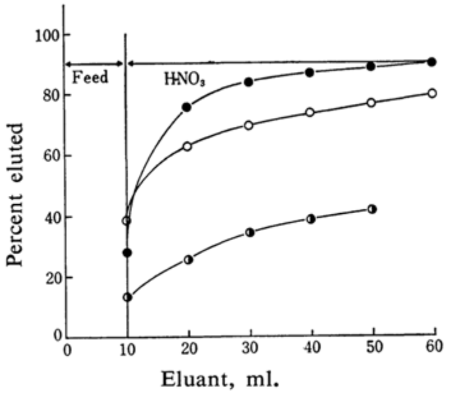

Fig. 13. Elution of ruthenium.

-◑- Eluant : $0.1\ \text{N-HNO}_3$
-○- Eluant : $0.1\ \text{N-HNO}_3$, treated with fuming nitric acid
-●- Eluant : $0.2\ \text{N-HNO}_3$, treated with fuming nitric acid

The Volatilization of Ruthenium.—It is advisable to remove ruthenium without the introduction of foreign salts. It was found in detailed

TABLE III. SEPARATION OF SYNTHETIC SAMPLES

Experimental No.	^{137}Cs Yield, %	^{137}Cs Yield, % corrected	^{144}Ce-^{144}Pr Yield, %	^{144}Ce-^{144}Pr Yield, % corrected	^{95}Zr-^{95}Nb Yield, %	^{89}Sr Yield, %
1	114.2	104.9	73.3	98.7	110.2	98.9
2	111.5	102.2	81.6	107.0	98.9	98.7
3	112.9	103.6	78.4	103.7	90.7	103.6
Mean		103.5		103.1	99.9	100.4

TABLE IV. ANALYSIS OF FISSION PRODUCT
(measured by well type scintillation counter)

	E. P. used	Analytical result Sr	Cs*	R. E.*	Zr-Nb	Ru	Total
c. p. m.	771675	7463	103083	483242	10288	163308	767384
%	100	1.0	13.4	62.6	1.3	21.2	99.5

* Contamination of Cs with R. E. is corrected.

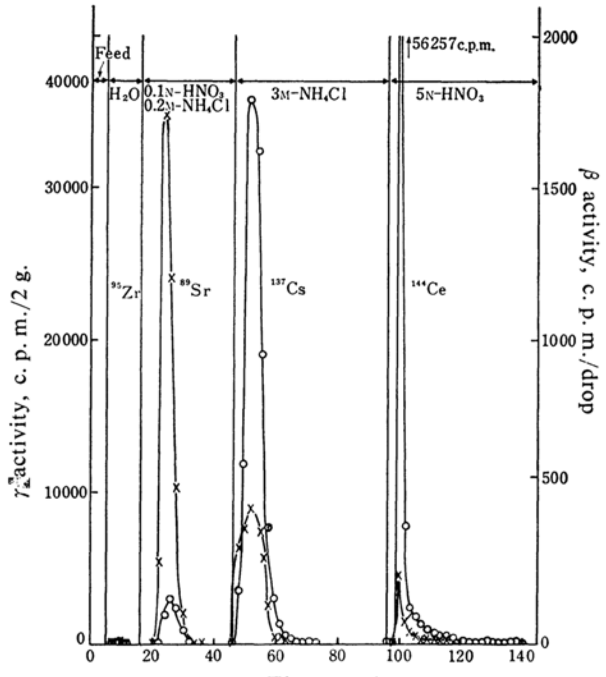

Fig. 14. Separation of synthetic sample.

examinations that the best method for removing ruthenium was the volatilization from boiling concentrated perchloric acid. Not less than 99% of ruthenium is removed by the boiling of concentrated perchloric acid solution, and this procedure does not affect the following ion exchange separation. It is necessary, however, to boil off ruthenium violently instead of fuming it gently.

The Separation of a Fission Product Solution. —Putting the above results together, the mutual separation of various nuclides contained in a fission product is carried out in the following way: To the sample solution, 5 ml. of concentrated perchloric acid is added, and this is boiled until a yellow color has once appeared and then diminished. (It is advisable to lead the distillate into water in order to prevent any health hazard.) Then the residual solution is evaporated almost to dryness on the hot plate. After cooling, 1 ml. of 1 N nitric acid is added, heated to dissolve the residue, and diluted to 10 ml. with water. This is poured into an ammonium-form exchanger bed;

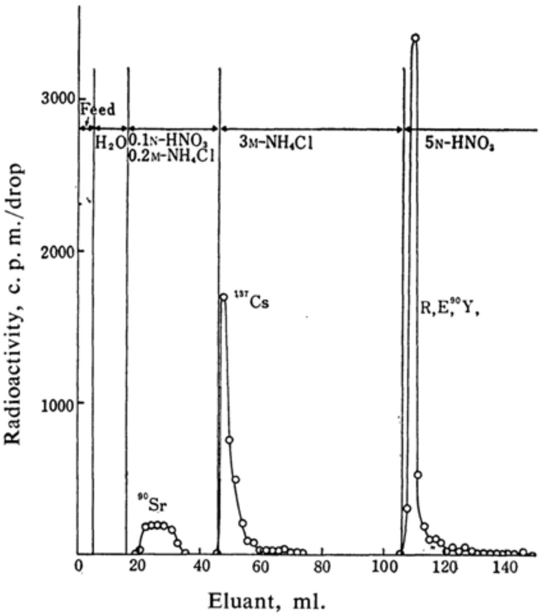

Fig. 15. Separation of fission product.

when the level of the solution reaches the top of the exchanger bed, 10 ml. of water, 30 ml. of 0.1 N nitric acid-0.2 M ammonium chloride, 60 ml. of 3 M ammonium chloride, and 60 ml. of a 5 N nitric acid solution are passed through the column successively.

The separation of a synthetic sample containing nearly equal activities of ^{89}Sr, ^{137}Cs, ^{95}Zr–^{95}Nb, ^{106}Ru and ^{144}Ce is shown in Fig. 14. Although the shape of the elution curve shows that satisfactory separation is achieved, it is observed from the analytical results that there is a contamination by cerium of the cesium fraction. The material balance represented in Table III convinces one of this observation. The corrected values obtained by the analysis of the cesium fraction are also shown in Table III; these values agree quite well within the experimental error.

The results of the separation of the fission product are shown in Fig. 15 and Table IV. The reason for the contamination of the cesium fraction is not clear, although it is assumed that the elution step of strontium may affect the separation.

Summary

The mutual separation of various nuclides contained in fission product has been carried out with a stannic phosphate cation exchanger. Various concentrations of nitric acid and ammonium chloride solutions have been used as eluants, and the separation has been performed on hydrogen- and ammonium-form exchangers.

The separations of ^{89}Sr–^{137}Cs, ^{89}Sr–^{144}Ce, ^{137}Cs–^{144}Ce and ^{90}Sr–^{90}Y were easy and complete except for that of ^{137}Cs–^{144}Ce on a hydrogen-form exchanger. ^{95}Zr and ^{95}Nb were almost completely adsorbed on the exchanger over a wide range of acidity and salt concentration; therefore, they were not eluted at all. As the behavior of ^{106}Ru is complex and its separation from other nuclides is impossible, it is necessary to separate the ruthenium from the fission product in advance by a method other than that of ion exchange.

With reference to the above results, the total analysis of the fission product on an ammonium-form exchanger has been carried out. It is almost complete except for the contamination of rare earth in the cesium fraction.

The author wishes to thank Dr. Hidehiro Goto and Dr. Shin Suzuki of Tohoku University for their guidance, discussion and continuous encouragement.

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

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