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Studies of the Synthetic Inorganic Ion Exchanger. V.[1] The Separation of Zirconium-95 and Niobium-95 by Means of a Stannic Phosphate Cation Exchanger

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With the aim of developing a method for the separation of ^{95}Zr and ^{95}Nb, various eluants were investigated, a sulfuric acid solution was found to be most suitable for this purpose. After the stannic phosphate exchanger column had been conditioned with 1 N nitric acid, the sample solution was passed through it to adsorb ^{95}Zr and ^{95}Nb. By using a 2 N sulfuric acid solution and a 3 N sulfuric acid - 0.01 N hydrofluoric acid solution as eluants, ^{95}Zr and ^{95}Nb could be eluted respectively. The separation was not quantitative, however, because of the unfavorable tailing of the elution curves. On the basis of the above results, the posibility of the total radiochemical separation of a long-lived fission product and the mechanism of the adsorption of these ions were discussed.

As one of the inorganic ion exchangers which may be expected to have radiation and thermal stability, stannic phosphate has previously been prepared[2,3] and its fundamental properties, such as its composition, its ion exchange capacity, its chemical stability,[2] its radiation and thermal stability, the nature of its ion exchange equilibrium, its exchange rate and its structure, were investigated.[3] Furthermore, this exchanger has been used for the separation of alkali metals,[2] the separation of individual nuclide contained in the fission products,[4] and the separation of uranium

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[1] Y. Inoue, S. Suzuki and H. Gotô, This Bulletin, **37**, 1547 (1964).

[2] Y. Inoue, *J. Inorg. Nucl. Chem.*, **26**. 2241 (1964).

[3] Y. Inoue, This Bulletin, **36**, 1316 (1963).

[4] Y. Inoue, ibid., **36**, 1324 (1963).

and fission products,[1] the results have been so successful that it was found to be an excellent material for the cation exchange separation.

In a nitric acid solution, this exchanger shows high distribution coefficients of zirconium and niobium, 2—4×10^3 ml./g., over a wide range of acidity. Therefore, in the process of the separation of fission products, these ions once adsorbed on the exchanger bed are not eluted at all with such eluants as ammonium chloride and nitric acid.[4]

With the aim of developing a method for the separation of ^{95}Zr and ^{95}Nb, various eluants, such as hydrochloric acid, hydrofluoric acid, sulfuric acid, oxalic acid, a mixture of hydrochloric acid and hydrofluoric acid and one of sulfuric acid and hydrofluoric acid, were investigated. Of those, oxalic acid, concentrated hydrochloric acid and hydrofluoric acid in a high acidity were not applicable because stannic phosphate could not resist these media. Sulfuric acid solution was found to be the most suitable for this purpose. Then the separation of zirconium and niobium with sulfuric acid eluants was investigated in detail. The results are described below.

Experiments

Reagents.—*Ion Exchanger.*—Stannic phosphate prepared by a method described previously was used.[2]

^{95}Zr-^{95}Nb Equilibrium Mixture.—This was obtained from the Oak Ridge National Laboratories (U. S. A.) and from the N. H. Philips-Roxane-Pharmaceutisch-Chemische Industries "Duphar" (Holland) as an about 1% oxalate solution. Prior to use, concentrated nitric acid was added to this solution and it was evaporated almost to dryness. This process was repeated several times in order to convert the nuclides into their nitrate forms completely. When either ^{95}Zr or ^{95}Nb was in need individually, they were separated from one another by the acetylacetone-benzene extraction method[5] immediately before use.

The other chemicals, such as sulfuric acid, hydrofluoric acid and acetyl acetone, were of the highest purity grade.

Apparatus.—The measurements of the β and γ activities were made by a Hitachi G. M. counter and Kobe Kogyo well-type scintillation counter respectively. For making elution curves in the column operation, a fraction collector, Toyo Kagaku Sangyo Model SF-200A, was used.

Procedures.—The experimental procedures were as follows, except otherwise noted.

The Determination of the Distribution Coefficients.—The batch distribution coefficients were determined after equilibrating 500 mg. of the ion exchanger (100—200 mesh or 200—350 mesh) in hydrogen form with 50 ml. of a suitable solution for about 100 hr. in a thermostat kept at 25°C. An aliquot of the supernatant liquid was then taken out in order to measure the radioactivity. The radioactivity on the exchanger was estimated from the difference between the total activity initially taken and that found finally in the solution.

In each case, the distribution coefficient was calculated by the following equation:

$$K_d=\frac{\text{Radioactivity on exchanger/g. of exchanger}}{\text{Radioactivity in solution/ml. of solution}}$$

Column Operation.—Into 2 g. of an air-dried exchanger in hydrogen form (100—200 mesh) a sufficient amount of distilled water was well stirred in order to expel any adhering air bubbles. After mixing, the slurry was poured into a glass column tube 7 mm. in internal diameter, in which glass wool had been put as a column support. The column thus prepared was 40 mm. high. Then the exchanger bed was conditioned by 1 N nitric acid, the sample solution was loaded on the bed to adsorb zirconium and niobium, and an elution was started. The flow rate of the influent was kept nearly constant, at 0.2—0.3 ml./min., throughout this experiment.

Results and Discussion

Distribution Coefficients. — In order to contribute to the establishment of the method of separation, the distribution coefficients of ^{95}Zr and ^{95}Nb were determined in sulfuric acid media; the results are shown in Table I. In contrast with the case of a nitric acid solution,[4] the distribution coefficients of these ions decrease with the increase in the acidity and a remarkable difference between zirconium and niobium is observed; that is to say, zirconium shows a distribution coefficient lower than niobium by one order. This indicates the possibility of separating zirconium from niobium. However, the distribution coefficients of these ions vary with the particle size of the exchanger used. This phenomenon offers one reason for the ill-defined elution peak; it may also be considered to depend on the nature of the ion exchange reaction. This will be discussed in detail later.

TABLE I. DISTRIBUTION COEFFICIENT OF ZIRCONIUM AND NIOBIUM IN SULFURIC ACID SOLUTION

Concn. of H_2SO_4 N	Particle size Mesh	Distribution coefficient	
		Zr	Nb
0.5	100—200	1.18×10^2	10.9×10^2
1.0	100—200	0.37×10^2	4.65×10^2
1.5	200—350	7.48×10^2	16.6×10^2
2.0	200—350	4.61×10^2	14.4×10^2
2.5	200—350	3.59×10^2	12.6×10^2
3.0	100—200	0.10×10^2	1.10×10^2
6.0	100—200	0.02×10^2	0.17×10^2

The Separation of ^{95}Zr and ^{95}Nb.—In order to seek some good conditions for the selective elution of ^{95}Zr, the elution of zirconium and niobium by sulfuric acid solutions of various concentrations was carried out. The results are shown in Fig. 1. Although the elution curves of zirconium show remarkable tailing under any of the conditions

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[5] T. Shigematsu, M. Tabushi and M. Matsui, *Bull. Inst. Chem. Res., Kyoto Univ.*, **41**, 212 (1963).

examined, the higher the acidity, the sharper the elution curve. Corresponding to the shape of the elution curve, the yield of zirconium increases with the increase in the acidity of eluant. When the acidity is 1 N, the yield is only 20% with 100 ml. of the eluant; when the acidity is 2 N, the yield is about 80% with 110 ml.; when the acidity is 2.5 N, the yield is about 90% with 100 ml. Niobium, however, is eluted a little with 2.5 N sulfuric acid solution, so this acid concentration is not desirable for the separation of zirconium from niobium, although the yield of zirconium is indeed high. From the above fact, a 2 N sulfuric acid solution seems to be most adequate for the selective elution of zirconium. In order to confirm this, the zirconium solution obtained after the elution was submitted to the drawing of a β-ray absorption curve by aluminum absorbers; it was confirmed that this solution contained a monoenergetic nuclide with a maximum energy of 0.40 MeV. This fact establishes the complete separation of zirconium from niobium.

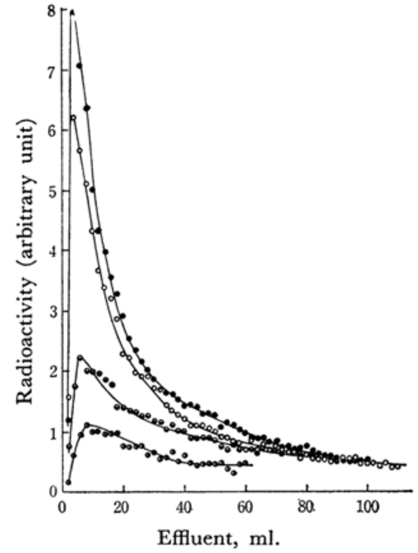

Fig. 1. The elution curves of zirconium and niobium.

—◒—: Zr, 1 N H_2SO_4;
—●—: Zr, 2.5 N H_2SO_4;
—○—: Zr, 2 N H_2SO_4;
—◑—: Nb, 2.5 N H_2SO_4.

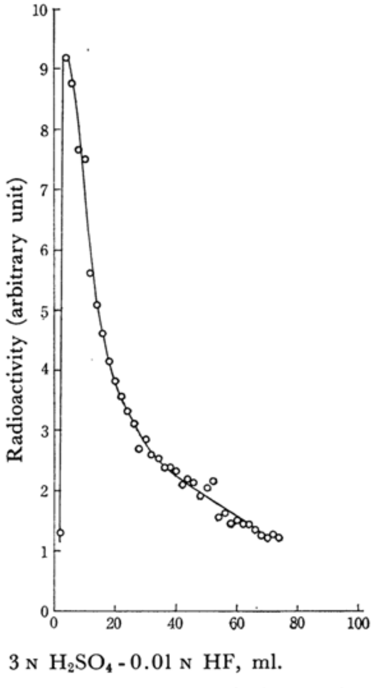

Fig. 2. The elution curve of niobium by 3 N sulfuric acid - 0.01 N hydrofluoric acid.

From the values of the distribution coefficients, the sulfuric acid solution seems to be ineffective in the elution of niobium. Therefore, its elution was performed with a sulfuric acid solution containing a small amount of hydrofluoric acid. In this case the hydrofluoric acid concentration should be kept as low as possible because too many fluoride ions may dissolve the exchanger. As is shown in Fig. 2, the 3 N sulfuric acid - 0.01 N hydrofluoric acid mixture was effective in the elution of niobium. Tailing was observed in this curve as in the case of zirconium, but the shape of elution curve is comparatively sharp and the yield is about 80% with 75 ml. of the eluant.

As has been mentioned above, the separation of zirconium and niobium can be achieved by using a 2 N sulfuric acid solution at first for zirconium, and then a 3 N sulfuric acid - 0.01 N hydrofluoric acid solution for niobium. The niobium fraction, however, is partially contaminated with

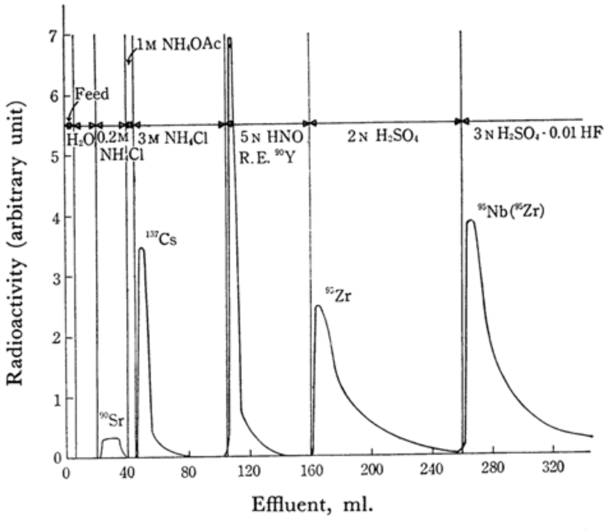

Fig. 3. Schematic representation of the separation of fission products.

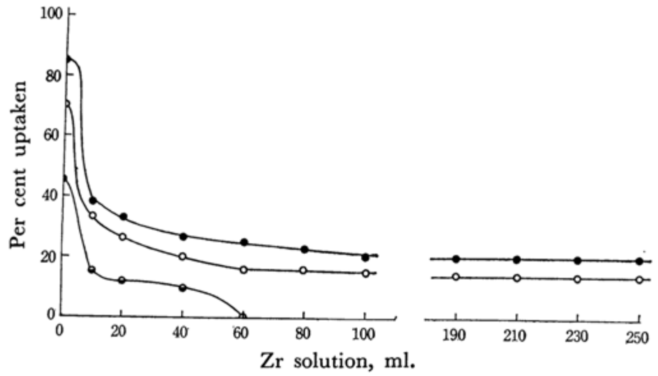

Fig. 4. Adsorption of zirconium from 1 N nitric acid solution.
Concn. of Zr: 0.01 M; —◒—: −100 mesh; —○—: 100—200 mesh; —●—: 200—350 mesh

zirconium because of the incomplete elution of the latter.

Discussion.—As has been stated in a preceding report,4) in the separation of long-lived fission products, ^{95}Zr and ^{95}Nb in the nitric acid solution were not quantitatively adsorbed on the exchanger, but they could not be eluted at all by any eluants when they were once adsorbed. From the results of the present investigation, it may be considered that they can be separated from other fission products by eluting them with the eluants mentioned above after rare earths have been eluted according to the procedure described in the third part of this series.4) This process is shown schematically in Fig. 3. It should be borne in mind that zirconium contaminates niobium to some extent because of the unfavorable tailing of its elution curve.

Many peculiar aspects of the behavior of zirconium and niobium in response to this ion exchanger have been observed. One of these aspects is the independency of the distribution coefficients on the concentration of nitric acid solution, as has been stated earlier.4) It is clear from this observation that the adsorption of zirconium cannot be explained by the simple cation exchange reaction for which the mass action law holds. The other aspects are the intense tailing of the elution curve and the difference in the distribution coefficients obtained with the ion exchanger as its particle size varies. This behavior has not been observed in the case of the other ions, so it seems to characterize zirconium and niobium. In order to clarify this point, the adsorption of zirconium from 1 N nitric acid was examined by the column operation of the above-mentioned experimental procedure with the exchanger having various particle sizes, as is shown in Fig. 4. These curves do not show a S-shape, as is usually observed in an ion-exchange resin; rather, they composed of two parts, one of which represents rapid adsorption, while the other is a part of the long tailing. The effect of the particle size is remarkable; namely, when it is greater than 100 mesh, the exchanger is saturated with the passage of only 60 ml. of a 0.01 M zirconium solution. On the other hand, when the particle size is smaller than this, the exchange is not saturated with even more than 250 ml. of a 0.01 M solution. If we assume that one molecule of zirconium corresponds to four equivalents, the break-through capacity of the exchanger coarser than 100 mesh is calculated to be 0.096 meq./g. When the exchanger is 100—200 mesh, the amounts of zirconium adsorbed after the passage of 250 ml. of a 0.01 M solution is 0.44 meq./g. These values are extremely low compared with the hydrogen absorption capacity and the hydrogen liberation capacity of 1.3—1.4 meq./g. as defined in the first part of this series.2) The tailing encountered in the elution step and the incomplete uptake of zirconium seem to be attributable to the slow rate of the adsorption-desorption reaction. This can also be reasonably explained by the fact that when adsorption is continued after an interruption of 10 hr. or more, the adsorption curve comes to be as if it were obtained with a new exchanger. From the above results it may reasonably be postulated that there are two kinds of adsorption sites. One is on the surface of the exchanger particle, while the other is in the inner part. On the surface, zirconium is adsorbed rapidly and reversibly, whereas in the inner part of the particle the adsorption is slow and irreversible. The adsorption in the inner part of the particle may proceed by one of the following two mechanisms. One is the formation of stable zirconium compounds with the phosphate because the presence of a lot of free phosphate groups close to each other in the inner part of the particle, unlike such a grouping on the surface of the materials, may facilitate the reaction. This argument is consistent with the property of zirconium, which easily forms sparingly-soluble compounds with phosphate, even in a strong acid solution. Another possibility is the exchange of tin, one of the elements constructing the exchanger net work, for the zirconium ion. At present it cannot be decided conclusively which is the correct mechanism. Therefore, further investigations must be carried out.

Summary

The separation of zirconium and niobium has been carried out by means of a stannic phosphate cation exchanger. By using a 2 N sulfuric acid solution and a 3 N sulfuric acid-0.01 N hydrofluoric acid solution as eluants, zirconium and niobium could be eluted respectively. However, the separation was not quantitative because of the unfavorable tailing of the elution curves. From the above results, the possibility of the total radiochemical separation of long-lived fission products and the mechanism of the adsorption of these ions have been discussed.

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