# *Systematic Separation of Fission Products by Solvent Extraction Method*

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Solvent extraction methods have often been employed for the separation of individual fission products. The purpose of the present investigation was to establish a new scheme of systematic separation of fission products having relatively long half-lives by combining and modifying the solvent extraction methods developed previously. The fission products considered in this investigation were limited to the nuclides, the radioactivities of which are higher than one per cent after all the fission products have been aged for one year. The nuclides which fall in this category are zirconium-niobium-95, cerium-praseodymium-144, promethium-147, strontium-yttrium-90, ruthenium-rhodium-106, cesium-137-barium-137$^{m}$, strontium-89, and yttrium-91. Since the chemical behaviors of strontium-89 and yttrium-91 are just the same as those of strontium-90 and yttrium-90, respectively, these were excluded from the scope of the present investigation. All of the other nuclides except promethium-147 are composed of the pairs of parent and daughter. Among these pairs, praseodymium-144, rhodium-106, and barium-137$^{m}$ are relatively short-lived daughters. Therefore, the nuclides considered finally for this study were zirconium-niobium-95, cerium-144, promethium-147, strontium-yttrium-90, ruthenium-106, and cesium-137.

Marinsky, Hume and Ballow(1) reported that zirconium-95 and niobium-95 can be extracted from a hydrochloric acid solution into chloroform with cupferron. Kiba and Kanetani(2) found that rare earth nuclides, cerium-144, promethium-147, and yttrium-90 can be separated from an acetate solution of pH 4 to 5 into chloroform with cupferron. Kiba and Mizukami(3) investigated the separation of strontium-90 and yttrium-90 and found that strontium-90 can be extracted from an acetate solution of pH 8 with TTA dissolved in hexone. Kiba and Hirono(4) reported that ruthenium-106 can be extracted from hydrochloric acid solution into a mixture of TBP and kerosene with diphenyl thiourea. Combining and modifying the methods mentioned above the present authors have presented a new systematic method for the separation of fission products by the liquid-liquid extraction processes.

## Experimental

All of the radioactive nuclides were purchased from the Oak Ridge National Laboratory of the

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1) J. A. Marinsky, D. N. Hume and N. E. Ballow, "Radiochemical Studies; The Fission Products", National Nuclear Energy Series IV-9, (1951), p. 1514.

2) T. Kiba and M. Kanetani, This Bulletin, 31, 1013 (1958).

3) T. Kiba and S. Mizukami, ibid., 31, 1007 (1958).

4) T. Kiba and H. Hirono, presented at the 11th Annual Meeting of the Chemical Society of Japan, Tokyo, April 5, 1958.

United States of America. Stock solutions of these unclides were made as follows. The original solution of zirconium-niobium-95 in 0.03 M oxalic acid was diluted with 0.33 M oxalic acid. The original solution of cerium-144 as cerous nitrate in nitric acid, that of promethium-147 in hydrochloric acid, that of strontium-yttrium-90 in nitric acid, that of ruthenium-106 as nitrosyl ruthenium trinitrate in 8 M nitric acid, and that of cesium-137 in 1 M nitric acid were diluted with 3.75 M hydrochloric acid, respectively. About 0.05 to 0.1 μc of the carrier-free nuclides was used for each experiment.

TBP was purified by distillation. All other chemicals of the guaranteed or the first grade of Japan Industrial Standards were used without further purification. An electric shaker was used for shaking of separatory funnels. Whole or aliquots of both aqueous and organic phases were taken into small porcelain dishes after five to ten minute shaking for each extraction. The content of each dish was evaporated or ignited, and the beta activity was measured with an end-window type GM counter.

## Results and Discussion

The whole scheme of the systematic separation is demonstrated in Table I. The method is composed of four-step extractions. The first

TABLE I. SCHEME OF SYSTEMATIC SEPARATION

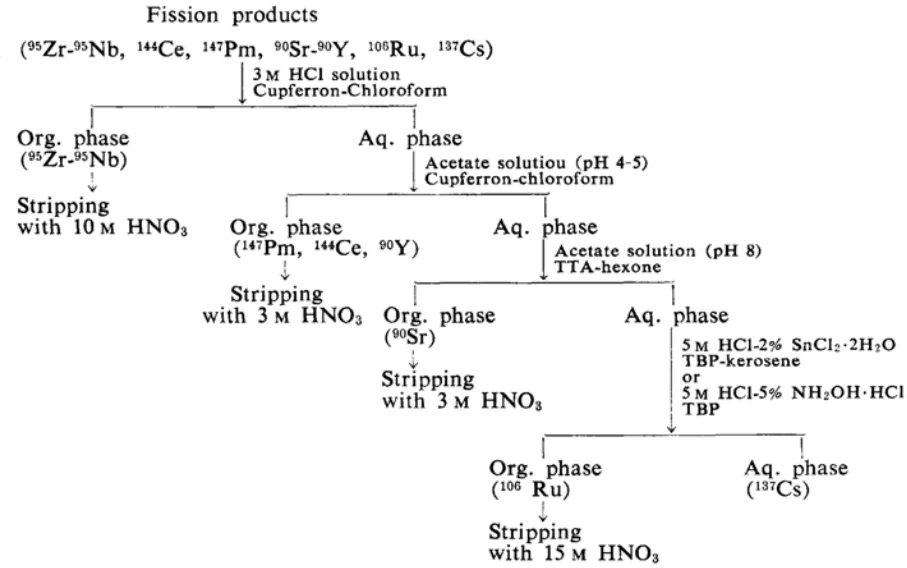

TABLE II. DETAILS OF EXTRACTION CONDITIONS

| Extraction step | Composition of aqueous phase | | Organic phase | |
|---|---|---|---|---|
| 1 | Sample solution<br>3.75 M HCl—0.043 M $H_2C_2O_4$<br>20% $NH_2OH \cdot HCl$<br>5% Cupferron | 0.5 ml.<br>3.5 ml.<br>0.5 ml.<br>0.5 ml. | Chloroform | 5 ml. |
| 2 | Aqueous solution after the first step extraction<br>9 M $NH_3$<br>0.9 M $NH_4AcO$<br>5% Cupferron | 5 ml.<br>1.6 ml.<br>10.4 ml.<br>3 ml. | Chloroform | 5 ml. |
| | 5% Cupferron | 3 ml. | Chloroform | 5 ml. |
| | 5% Cupferron | 3 ml. | Chloroform | 5 ml. |
| 3 | Aqueous solution after the second step extraction<br>5.4 M $NH_3$ | 27 ml.<br>1 ml. | 0.05 M TTA in hexone | 10 ml. |
| 4A | Aqueous solution after the third step extraction<br>11 M HCl—4.4% $SnCl_2 \cdot 2H_2O$ | 27 ml.<br>23 ml. | TBP-kerosene (1 : 2) | 10 ml. |
| 4B | Aqueous solution after the third step extraction<br>11 M HCl—11% $NH_2OH \cdot HCl$ | 27 ml.<br>23 ml. | TBP | 50 ml. |

TABLE III. EXTRACTION OF FISSION PRODUCTS

| Step | Phase | $^{95}$Zr—$^{95}$Nb | $^{144}$Ce | $^{147}$Pm | $^{90}$Sr—$^{90}$Y | $^{106}$Ru | $^{137}$Cs |
|---|---|---|---|---|---|---|---|
| 1 | Org. phase | 98.9 | 0.3 | 0.0 | 0.0 | 0.0 | 0.4 |
| | Aq. phase | 0.3 | 99.3 | 98.2 | 99.5 | 99.8 | 98.1 |
| 2 | Org. phase | 84.2[a] | 99.4 | 99.6 | 53.2($^{90}$Y) | 0.5 | 0.6 |
| | Aq. phase | 2.0[a] | 0.5 | 0.5 | 46.2($^{90}$Sr) | 99.6 | 101.6 |
| 3 | Org. phase | 60.7 | 100.0 | 99.6 | 99.4 | 1.2 | 0.4 |
| | Aq. phase | 37.8 | 0.0 | 0.6 | 0.5 | 99.6 | 99.6 |
| 4A | Org. phase | 9.3[b] | 1.0[b] | 14.8[b] | 0.8[b] | 98.5[b] | 0.0[b] |
| | Aq. phase | 90.7 | 99.0 | 85.2 | 99.2 | 1.5 | 100.0 |
| 4B | Org. phase | 27.6[b] | 8.8[b] | 13.3[b] | 0.0[b] | 93.9[b] | 0.6[c] |
| | Aq. phase | 72.4 | 91.2 | 86.7 | 100.0 | 6.1 | 82.2 |

a. Some of $^{95}$Zr and/or $^{95}$Nb was lost probably by the adsorption.

b. These values were calculated from the total activities and the activities in the aqueous phase.

c. This value was obtained by the stripping of $^{137}$Cs from the organic phase with 15 M nitric acid. The loss of $^{137}$Cs in the 4B step was unaccountable.

step is the extraction of zirconium-95 and niobium-95 from a 3 M hydrochloric acid solution into chloroform with cupferron. The second step is the extraction of rare earth nuclides, i. e. cerium-144, promethium-147, and yttrium-90 from an acetate buffer solution of pH 4 to 5 into chloroform with cupferron. The third step is the extraction of strontium-90 from an acetate buffer solution of pH 8 into hexone with TTA. The fourth step is the extraction of ruthenium-106 from a 5 M hydrochloric acid solution into a mixture of TBP and kerosene (1 : 2) in the presence of stannous chloride. Another method for the fourth step is the extraction of ruthenium-106 from a 5 M hydrochloric acid solution into TBP in the presence of hydroxylamine. Thus cesium-137 remains is the last aqueous solution. The detailes of the extraction procedures are tabulated in Table II. The distribution of each radioactive nuclide in the aqueous and organic phases in each extraction step was determined. The results are summarized in Table III, in which the data shown under the step-like line in each column were obtained only for reference. Recovery on the stripping of the radioactive nuclides from the organic phase is shown in Table IV. The data given in Tables III and IV are mean values obtained from three or four experiments.

TABLE IV. RECOVERY OF NUCLIDES FROM ORGANIC PHASE BY STRIPPING

| Nuclide | Stripping agent | Number of stripping | Recovery % |
|---|---|---|---|
| $^{95}$Zr—$^{95}$Nb | 10 M $HNO_3$ | 2 | 83.9 |
| $^{144}$Ce | 3 M $HNO_3$ | 1 | 98.4 |
| $^{147}$Pm | 3 M $HNO_3$ | 1 | 88.8 |
| $^{90}$Y | 3 M $HNO_3$ | 1 | 98.8 |
| $^{90}$Sr | 3 M $HNO_3$ | 1 | 98.4 |
| $^{106}$Ru | 15 M $HNO_3$ | 3 | 99.8 |

In the first step oxalic acid is added to the solution to prevent the adsorption of zirconium-95 and niobium-95 onto a glass vessel by forming complexes with these nuclides. Hydroxylamine protects cupferron from oxidation with air and a trace amount of nitric acid. The data disclose that by the first step extraction only zirconium-95 and niobium-95 are extracted as cupferrates into the organic phase and all other nuclides are left in the aqueous phase. The zirconium-95 and niobium-95 extracted in the organic phase can be stripped with 10 M nitric acid as shown in Table IV.

In the second step aqueous ammonia is added to the aqueous phase remaining after the first step extraction to neutralize hydrochloric acid, and then ammonium acetate solution is added to adjust the pH of the aqueous phase to 4∼5. In order to complete the separation of rare earth nuclides the concentration of cupferron should be considerably high and the extraction should be repeated three times. Before each extraction with chloroform 3 ml. of a 5% cupferron solution is added to the aqueous phase. By this step cerium-144 and promethium-147 are extracted into the chloroform phase.

Strontium-90 and yttrium-90 in their radioactive equilibrium are separated from each other, the former being in the aqueous phase and the latter in the organic phase, as shown in the sixth column of Table III. The decay or the growth curve and the Harley plot of the activity in each phase indicates that the separation of the nuclides can be carried out completely. The rare earth and yttrium nuclides extracted in the organic phase can easily be stripped with 3 M nitric acid.

After the second step extraction, a small amount of aqueous ammonia is added to the resulting aqueous phase to raise the pH of the solution up to 8[3]. Then the third step extraction is carried out with a 0.05 M TTA-hexone solution. Two extractions complete the separation of strontium-90. The data in the sixth column of Table III shows that yttrium-90, if it could be present, by the later decay of strontium-90 is also extracted into the organic phase. The strontium-90 extracted in the organic phase can be stripped with 3 M nitric acid.

The fourth step extraction is that of ruthenium-106. It was found in the previous investigation[4] that ruthenium-106 can be extracted from 6 M hydrochloric acid solution with diphenyl thiourea dissolved in a mixed solvent of TBP and kerosene (1 : 2) in the presence of stannous chloride. However, it is difficult to strip the ruthenium-106 extracted in the mixed solvent into an aqueous phase. The present authors reexamined the extraction condition for ruthenium-106 and found that ruthenium-106 can be almost completely extracted, in the presence of stannous chloride from 6M hydrochloric acid solution with the mixed solvent of TBP and kerosene containing no chelating agent such as diphenylthiourea. Almost all of the ruthenium-106 extracted in the organic phase can be stripped with concentrated nitric acid, but a part of stannous chloride which is extracted from into the organic phase is also stripped with concentrated nitric acid. It is difficult to remove the stannous chloride from the nitric acid solution as well as to obtain the salt-free aqueous solution of ruthenium-106. So this method would not be suitable for preparing carrier-free ruthenium-106, but the procedure might be used as an analytical method for ruthenium-106 in the fission products.

Another method for the extraction of ruthenium-106 is as follows: ruthenium-106 can be extracted from 5 M hydrochloric acid solution in the presence of hydroxylamine with TBP which is not diluted with kerosene but is saturated with a 5 M hydrochloric acid solution. By this method about 94 per cent of ruthenium-106 is extracted and almost all of it is stripped with concentrated nitric acid from the organic phase. Some amount of hydroxylamine is also extracted with TBP and then also with concentrated nitric acid. But it is possible to decompose the hydroxylamine stripped together with ruthenium-106 by heating after neutralizing the nitric acid with aqueous ammonia. Then we can get the salt-free aqueous solution of ruthenium-106. Although the yield of ruthenium-106 is less than that obtained by the former method, this method is superior to the former one from the point of view of the preparation of carrier-free ruthenium-106.

## Summary

A new scheme for separating fission products, zirconium-niobium-95, cerium-144, promethium-147, yttrium-90, strontium-90, ruthenium-106 and cesium-137, by the four-step liquid-liquid extractions was presented. First, zirconium-95 and niobium-95 were extracted from a 5 M hydrochloric acid solution into chloroform with cupferron. Second, rare-earth nuclides, cerium-144, promethium-147 and yttrium-90 were extracted from an acetate buffered solution of pH 4 to 5 into chloroform with cupferron. Third, strontium-90 was extracted from an acetate buffered solution of pH 8 into hexone (methyl isobutyl ketone) with TTA (2-thenoyltrifluoroacetone). Fourth, ruthenium-106 was extracted from 5 M hydrochloric acid solution with TBP (tri-*n*-butyl phosphate)-kerosene in the presence of stannous chloride or extracted with TBP in the presence of hydroxylamine. then cesium-137 was left in the last aqueous solution. Strippings of nuclides extracted in the organic phases could be attained by shaking each organic phase with nitric acid.

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