Rapid Separation of Radioactive Strontium by Solvent Extraction with TTA-Hexone

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It is an important problem at present to develop a rapid method of separating and estimating radioactive strontium (^{89}Sr, and ^{90}Sr) contained in mixed fission products. Such a method is indispensable for devising a workable procedure for the chemical elimination of strontium from reactor wastes. Previously the authors attempted to separate the fission products into groups by solvent extraction, with TTA (*o*-thenoyl trifluoroacetone)-benzene[1], and cupferron-chloroform[2]. As a result of the experiment, it was found that by the solvent extraction with TTA-benzene at pH 6, and with cupferron-chloroform at pH 4, strontium, cesium, and ruthenium remained in the aqueous phase and the other fission products entered the organic phase. Hence the next problem to be solved is to recover the strontium retained by the aqueous phase after the extraction. The present paper describes an investigation on the separation of strontium from other fission products by liquid-liquid extraction.

TTA (*o*-thenoyl trifluoroacetone), dissolved in benzene, toluene, or xylene, is widely employed as a reagent for solvent extraction of zirconium and cerium from their acidic solutions[3], but there are few papers which treat of the separation from a solution of a given pH value. Khym, Tompkins and Cohen[4] have reported separation of ^{45}Ca, which was produced by Sc$(d, 2p)$ reaction, by solvent extraction with 0.5 M TTA-benzene from a solution of pH 9. As it seems advantageous to use a reagent-solvent phase of low concentration when the extraction is made, the present authors employed 0.05 M TTA-benzene for the purpose to examine the behavior of strontium. Belonging to the same family with calcium, strontium could not be extracted by the reagent-solvent phase though experiments were conducted over a wide range of pH of the aqueous solution. Afterward, various solvents other than benzene were tried and hexone (methyl isobutylketone) was found to be the best, both because of the high solubility of TTA in it and because of its superior power to effect the separation of strontium. In the following experiments 0.05 M TTA-hexone is always used as the extracting agent for the separation of strontium.

Experimental

Reagents, Materials and Apparatus.—*TTA* (*o-thenoyl trifluoroacetone*) imported from L. Light & Co. Ltd., England, was dissolved in hexone of extra pure grade to a concentration of 0.05 M. TTA-benzene was prepared by dissolving the reagent in thiophene-free benzene to a concentration of 0.05 M and 0.5 M.

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[1] T. Kiba, S. Ohashi and K. Yoshizawa, Unpublished paper, read at the 10th Annual Meeting of the Chemical Society of Japan (April, 1957).

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

[3] G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry", John Wiley & Sons, Inc. New York (1957).

[4] J. X. Kyhm, P. C. Tompkins and W. E. Cohen, USAEC, **MDDC-1214** (1947).

Radioactive Strontium.—^{90}Sr(^{90}Y) was imported from Oak Ridge National Laboratory, U.S.A. as nitrate in nitric acid solution, a part of which was diluted to 0.02 N nitric acid solution having an activity of about 10,000 cpm. per 0.2 ml. The mixed fission products (Batch No. 35), ^{45}Ca, and ^{106}Ru were imported from the Oak Ridge National Laboratory and used for the comparative investigation of the method.

Buffer Solution.—A system composed of 0.5 M acetic acid, ammonium acetate and aqueous ammonia was used, and its pH was measured by a glass-electrode pH-meter, Horiba Instrument Co., Japan.

Measurement of Radioactivity.—The radioactivity was measured as β-counting by a G-M counting set (No. 131 G-M tube, mica-window: 2.8 mg./cm^2, counting efficiency for ^{90}Sr(^{90}Y): 11.7%, "100" scalor, Kobe Kogyo Co. Ltd.).

Separatory Funnel.—The separatory funnel is a spindle-shaped vessel made of hard glass, with a capacity of 30 ml. In order to prevent the mixing of the two phases when being drained, a type with a small bore above the cock and a large bore below was chosen.

Shaking Machine.—Shaking of the content of the separatory funnel was done by means of an electric vertical oscillator performable 230 double strokes per minute. The equipment can handle six funnels at the same time.

Other chemicals were all of pure grade, and the utensils were of ordinary laboratory types.

Procedure.—In a 30 ml. separatory funnel, place 0.2 ml. of the solution of the mixed fission products or the radioactive nuclides, and add the buffer solution of a definite pH to make 6 ml. Then pour 2 ml. of the organic solvent into the vessel, and stopper tightly. Shake the vessel for five minutes with the electric vertical oscillator. After the phases have disengaged, take out the aqueous layer into a second funnel. Re-extract the aqueous phase in the second funnel with 2 ml. of the organic solvent for five minutes. To the organic phase retained in the first funnel, add 5 ml. of the buffer solution and shake for another five minutes. Combine the aqueous phases of the first and the second funnel in a vessel, and the organic phases in another, and evaporate the content in a porcelain counting dish, and measure the radioactivity with the G-M counting set. Plot the decay curve of the activity or draw a Harley plot to identify the nuclide contained in the sample.

1) The experiments were carried out with 0.5 M TTA-benzene, 0.05 M TTA-benzene, and 0.05 M TTA-hexone at different pH of the solution to determine the optimum pH for the separation of strontium.

2) Some experiments with TTA-hexone were carried out with the buffer solution of the optimum pH for the separation of strontium, containing a known amount of barium nitrate, magnesium nitrate, or calcium nitrate, in order to examine the effect of salts present in the solution on the extraction of strontium.

3) The behavior of calcium in the solution was examined using ^{45}Ca as tracer, and was compared in detail with the behavior of strontium.

4) The effect of such agents as EDTA (disodium ethylenediaminetetra-acetate) and ammonium citrate as masking agent on the extraction was examined.

5) For the purpose of rapidly isolating the radioactive strontium from the aged fission products, a two-step extraction was attempted: a solution of the gross fission products was first treated with 0.05 M TTA-benzene at pH 7, and after the organic layer was discarded, the remaining aqueous phase was shaken with 0.05 M TTA-hexone at pH 8. The radioactivity was measured in each case. The radioactive strontium, ^{89}Sr and ^{90}Sr, came out in the last organic phase.

Results and Discussion

The percentage of the material recovered by extraction from the solution of the fission products of different pH by 0.05 M TTA-benzene and 0.05 M TTA-hexone is shown in Fig. 1. The percentage extraction was computed as the ratio between the counting rate of the organic phase to that of the original solution. Before the counting, the organic phase was, of course, evaporated and dried in a counting sample pan, and the original activity taken in the solution was determined for 0.2 ml. of the stock solution of the fission products.

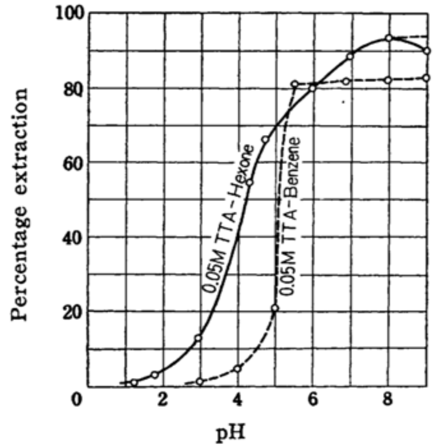

Fig. 1. Effect of pH on the extraction of gross fission products by TTA-benzene and TTA-hexone.

Comparing the results obtained by the extraction with TTA-benzene and TTA-hexone with each other, the amount extracted at pH 8 is greater by the latter than by the former. Since it has been confirmed[1] that after extraction with TTA-benzene at pH 6, strontium, cesium

TABLE I

EXTRACTION OF ^{90}Sr(^{90}Y) BY 0.05 M TTA-HEXONE

pH of the solution pH	^{90}Sr(^{90}Y) taken cpm.	Extracted in org. phase cpm.	Retained in aqueous phase cpm.	Extracted %
7	10,050	7,610	2,400	75.8
8	9,220	9,190	30	99.6
9	9,220	9,125	96	98.9

TABLE II

EXTRACTION OF ^{90}Sr(^{90}Y) WITH VARIOUS SOLVENTS AT pH 8

Reagent-solvent	^{90}Sr(^{90}Y) taken cpm.	Separation into the phases cpm. (%)	Note: Nuclide and its radiochemical purity
0.5 M TTA-Benzene	8,020	Org. Phase 4,490 (56.0%)	^{90}Y+^{90}Sr
		Aq. Phase 3,530	^{90}Sr
0.05 M TTA-Benzene	7,750	Org. Phase 4,290 (55.3%)	^{90}Y (98%)
		Aq. Phase 3,460	^{90}Sr (98～100%)
0.05 M TTA-Hexone	7,540	Org. Phase 7,510	^{90}Sr+^{90}Y
		Aq. Phase 30	None

and ruthenium remain in the aqueous phase, the increase in counting rate of TTA-hexone phase should perhaps be attributed to strontium. The following experiment will confirm this supposition.

A solution containing ^{90}Sr(^{90}Y) was adjusted to a different pH, and the extraction was carried out with 0.05 M TTA-hexone. The partition of the radioactivity between the aqueous phase and the organic phase was determined as the ratio of their counting rates. As shown in Table I the ^{90}Sr(^{90}Y) was completely transferred into the organic phase.

The results of the extractions carried out with 0.05 M TTA-benzene, 0.5 M TTA-benzene, and 0.05 M TTA-hexone, respectively, are illustrated in Table II. By the extraction with TTA-benzene all the ^{90}Y was transferred into the organic phase and the ^{90}Sr remained in the aqueous phase. On the other hand, by the extraction with TTA-hexone both the ^{90}Sr and the ^{90}Y went into the organic phase. When the two-step extraction is performed, that is, when the solution is extracted first with 0.05 M TTA-benzene and then 0.05 M TTA-hexone, the latter organic phase contains ^{90}Sr alone.

The distribution coefficient and the equilibrium constant were measured at 20°C when the extraction of ^{90}Sr with TTA-hexone was performed from aqueous solution of pH 8.05. Writing the formula for TTA as HT, the reaction involved can be described by the following equation:

$$\mathrm{Sr^{2+}}_{aq}+2\mathrm{HT}_{org}=\mathrm{SrT_2}_{org}+2\mathrm{H^+}_{aq}$$

in which subscript *org* refers to organic phase and *aq* to adueous phase. The equilibrium expression may be written as follows,

$$K=[\mathrm{SrT_2}]_{org}\cdot[\mathrm{H^+}]^2_{aq}/[\mathrm{Sr^{2+}}]_{aq}\cdot[\mathrm{HT}]^2_{org}$$

In this case the aqueous phase is a buffer solution of pH 8.05, that consists of 0.5 M ammonium acetate and aqueous ammonia, so the hydrogen ion concentration, $[\mathrm{H^+}]_{aq}$ could be considered as being kept constant before and after the extraction. Then,

$$K'=[\mathrm{SrA_2}]_{org}/[\mathrm{Sr^{2+}}]_{aq}\cdot[\mathrm{HT}]^2_{org}$$

The distribution coefficient of strontium, q, can be written as

$$q=[\mathrm{SrA_2}]_{org}/[\mathrm{Sr^{2+}}]_{aq}$$

so

$$K'=q/[\mathrm{HT}]^2_{org}$$

$$\log K'=\log q-2\log[\mathrm{HA}]_{org}$$

As the concentration of radioactive strontium is far less than that of TTA in the organic phase, $[\mathrm{HA}]_{org}$ may be considered as being invariable during the extraction. Before the experiment, ^{90}Sr had been separated from ^{90}Sr(^{90}Y) by the extraction with 0.05 M TTA-benzene at pH 7 as described above, and the ^{90}Sr retained in the aqueous solution was used for the purpose. Six ml. of hexone containing TTA of various concentrations was mixed with the same volume of the aqueous solution of pH 8.05, which contained the radioactive strontium. After a separatory funnel was shaken for thirty

TABLE III

DISTRIBUTION OF ^{90}Sr BETWEEN TTA-HEXONE AND BUFFER SOLUTION OF pH 8.05, AT 20°C

Concn. of TTA in hexone M	Activity in aq. phase I_{aq} (cpm.)	Activity in org. phase I_{org} (cpm.)	Distribution coeff. q	$\log_q$	$\log K'$
0.0005	3516	126	0.03583	−1.4458	5.16
0.001	3255	104	0.03195	−1.4955	4.50
0.005	2694	840	0.3118	−0.506	4.10
0.01	2256	1422	0.6303	−0.2005	3.80
0.05	232	3495	15.065	+1.178	3.78
0.1	243	3531	14.531	+1.162	3.16
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TABLE IV

DISTRIBUTION OF ^{90}Sr(^{90}Y) BETWEEN TTA-HEXONE AND BUFFER SOLUTION OF pH 8.05, AT 20°C.

Concn. of TTA in hexone M	Activity in aq. phase. I_{aq} (cpm.)	Activity in org. phase I_{org} (cpm.)	Distribution coeff. q	$\log_q$
0.001	1778	1772	0.997	−0.0015
0.005	1486	2151	1.448	+0.1606
0.01	1156	2418	2.092	+0.3205
0.02	399	2784	6.978	+0.8437
0.04	265	3505	13.226	+1.1214
0.05	105	3364	33.04	+1.5190

minutes and the phases were disengaged, each phase was poured out through the stem and the activity measured in the ordinary way. The results are shown in Table III, from which it is found that the distribution coefficient increases with the concentration of TTA in hexone and that the 0.05 M TTA-hexone is preferable for the extraction of strontium. Table IV shows the results of the same experiments which were carried on ^{90}Sr (^{90}Y) under the same condition.

To examine the effect of the amount of strontium carrier added to the solution, extraction of ^{90}Sr(^{90}Y) was performed in the presence of various amounts of strontium nitrate in the buffer solution of pH 8. In this case 2 ml. of 0.05 M TTA-hexone was used as organic solvent, corresponding to 100 μg. equivalent to the chelating agent. More than 98% of the ^{90}Sr went into the organic phase in the presence of up to 1 μg. equivalent (45 μg.) of strontium carrier, and this seemed to be the upper limit of the amount of the strontium carrier that could coexist with ^{90}Sr in this extraction.

On the other hand, the extraction of ^{45}Ca with TTA-hexone was attempted in the presence of calcium carrier by the same procedure in order to obtain some information on the behavior of the metal in the solvent extraction. The calcium could be completely extracted till the amount of the carrier reached 20 μg. equivalent. Calcium seems to be chelated more tightly than strontium with TTA. The results of the above experiments are illustrated together in Fig. 2.

The effect of other alkaline earth metals —calcium, magnesium and barium—that might be present in the solution was investigated as follows. Various amounts of the metallic salt were added to the solution and the extraction of ^{90}Sr(^{90}Y) was done at pH 8 by 0.05 M TTA-hexone according to the above procedure. The activity of the ^{90}Sr(^{90}Y) separated in the organic phase was measured to find the percentage recovery of the ^{90}Sr(^{90}Y) in each case. Fig. 3 illustrates the relation between the amounts of the other coexisting ions and the recovery of the ^{90}Sr(^{90}Y). From the figure, it is found that barium and calcium do not affect the extraction till their amounts reach 8 μg. and 4 μg. equivalent, respectively, but magnesium gives a remarkable influence upon the extraction and more than 1 μg. of it should not be present.

To separate the ^{90}Sr selectively into the organic phase from the ^{90}Sr(^{90}Y), the solution containing ^{90}Sr(^{90}Y) was first adjusted to pH 7, and the extraction was done with 0.05 M TTA-benzene, by which ^{90}Y could be completely transferred out of the solution into the organic phase as shown in Table V. The aqueous phase retained after the extraction was adjusted again to pH 8, and a second extraction was done with 0.05 M TTA-hexone. Thus

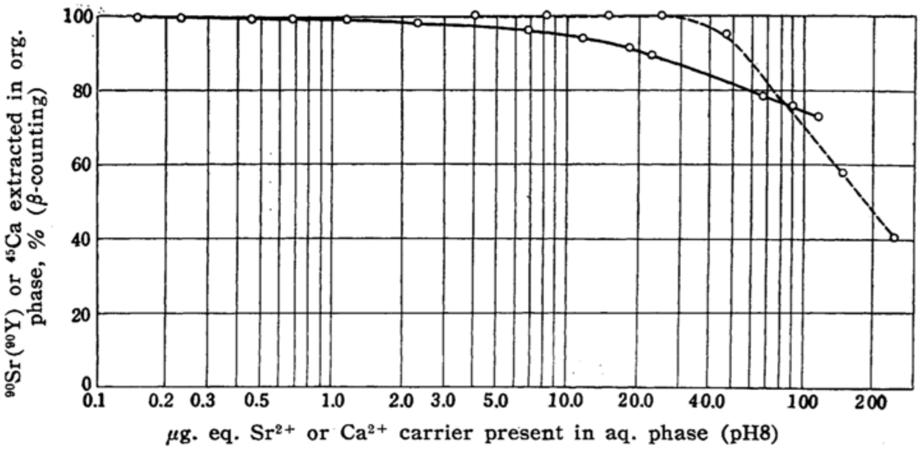

Fig. 2. Effect of strontium carrier on the extraction of ^{90}Sr(^{90}Y) and of calcium carrier on the extraction of ^{45}Ca by TTA-hexone.
—— strontium, ... calcium

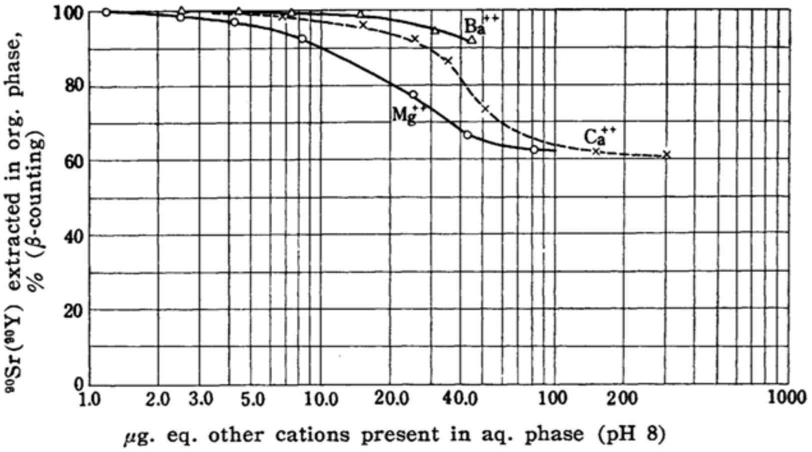

Fig. 3. Effect of the amounts of coexisting alkaline earth metals on the extraction of ^{90}Sr(^{90}Y) by TTA-hexone.

TABLE V

ISOLATION OF ^{90}Sr FROM ^{90}Sr(^{90}Y) BY THE TWO-STEP EXTRACTION

^{90}Sr(^{90}Y) taken cpm.	Taken up by the 1st org. phase (0.05 M TTA-benzene at pH 7) cpm.	Taken up by the 2nd org. phase (0.05 M TTA-hexone at pH 8) cpm.	Retained in aq. phase cpm.
16,590	8,890	7,186	510
17,050	9,440	7,328	280
Radiochemical purity	(^{90}Y: 99%)	(^{90}Sr: 100%)	

the strontium could be separated in the last organic phase. Table V shows the excellent results of the extraction.

The presence of a masking agent such as EDTA (disodium ethylenediaminetetra-acetate), and ammonium citrate may probably affect the extraction of ^{90}Sr(^{90}Y). Investigation was carried out to test this view, and was unsuccessful to keep the calcium in the solution by the masking effect of EDTA and to transfer the strontium into the organic phase; moreover, even the extraction of yttrium into the organic phase was markedly hindered. When a buffer solution consisting of ammonium citrate and aqueous ammonia was used to keep the solution at pH 8, only ^{90}Y could be extracted into the organic phase of TTA-hexone. The results obtained are shown in Table VI.

TABLE VI

EFFECT OF THE MASKING AGENTS ON THE EXTRACTION OF ^{90}Sr(^{90}Y) BY TTA-HEXONE

^{90}Sr(^{90}Y) taken cpm.	Ca^{2+} added μg.	EDTA added ml.	Extracted into org. phase %	Nuclide extracted
6,980	2,000	1	4.8_1	^{90}Y
7,040	1,000	1	9.1_2	〃
7,110	800	1	6.2_0	〃
6,890	400	1	2.8_1	〃
7,080	1,000	2	2.6_1	〃
6,650	600	2	1.5_8	〃

Note: One milli liter of EDTA solution corresponds to 566 μg. Ca^{2+}.

^{90}Sr(^{90}Y) taken cpm.	0.1 M Ammonium citrate soln. ml.	Extracted in org. phase %	Nuclide extracted
7,600	5	60.52	^{90}Y
18,800	5	55.67	〃

TABLE VII

ISOLATION OF RADIOACTIVE STRONTIUM BY TWO-STEP EXTRACTION FROM THE MIXED FISSION PRODUCTS

The fission products taken cpm.	Extracted by 0.05 M TTA-benzene cpm.	Extracted by 0.05 M TTA-hexone cpm.	Retained in aq. phase cpm.
57,980	48,640	6,260(10.8%)	3,080
56,980	48,550	5,960(10.4%)	2,470
120,900	102,500	12,370(10.2%)	6,050

In order to separate the radioactive strontium from mixed fission products, the solution of the material was at first adjusted to pH 7 and extracted with 0.05 M TTA-benzene. By this treatment rare earths and yttrium were made go into the organic phase out of the solution, but ruthenium was not. The aqueous phase remaining after the extraction and the removal of the organic phase, was transferred into another separatory funnel, and adjusted to pH 8 with the addition of ammonia, and extracted with 0.05 M TTA-hexone. In this case the radioactive strontium was completely extracted into the organic phase. Only less than 5% of ruthenium presented in the solution was extracted together.

The organic phase containing radioactive strontium was transferred from the funnel into a counting pan and rapidly evaporated to dryness under an infrared lamp, and the activity was measured as usual. The results obtained are shown in Table VII, in which the percentage of the strontium, represented by the activity ratio to the total, coincides well with that obtained by the ion-exchange resin method for the separation of the same material[5].

The Harley plot for the activity of the separated strontium is shown in Fig. 4 with ^{32}P as standard. The plot indicates that the radioactive strontium consists of 64% ^{89}Sr and 36% ^{90}Sr. The above separation process can be performed without spending much time.

The strontium extracted in the organic phase can easily be taken in the solution by the stripping with nitric acid of various concentrations. However, as the evaporation of the organic phase of TTA-hexone proceeds rapidly under an infrared lamp, the stripping of the strontium seems unnecessary for the purpose. Thus, by

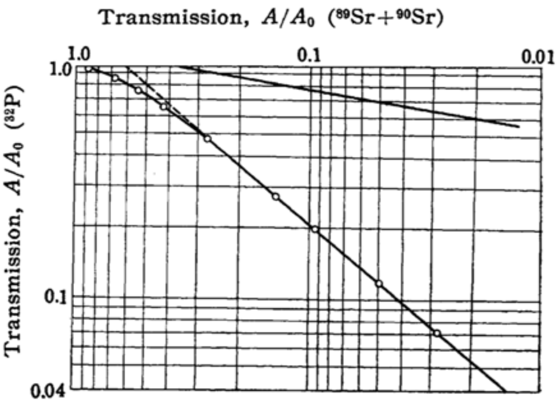

Fig. 4. Harley plot of the radioactive strontium separated in TTA-hexone from the gross fission products.

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[5] M. Honda, Y. Sasaki and H. Natsume, *Japan Analyst* (*Bunseki Kagaku*), 4, 240 (1955).

the two-step extraction method devised by the authors, radioactive strontium could be separated rapidly and efficiently from mixed fission products.

Summary

Radioactive strontium in mixed fission products could be rapidly separated by the two-step extraction deviced by the authors. The solution of the material was first adjusted to pH 7 and extracted with 0.05 M TTA-benzene. By this treatment rare earths and yttrium were made to go into the organic phase out of the solution. The remaining aqueous phase was transferred into another separatory funnel, adjusted to pH 8, and extracted with 0.05 M TTA-hexone. In this case the radioactive strontium was completely extracted into the organic phase. Only less than 5% of ruthenium present in the solution was extracted at the same time. Detailed data of the experiments on the extraction involving the determination of distribution coefficient, and the equilibrium constant were tabullated.

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