Ion-Exchange Separation of Fission Products[*1]

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Ion-exchange methods were studied for fission product separation in order to find a suitable separation procedure to prepare pure carrier-free radioactive isotopes and for radiochemical assay purpose. In this field we can refer to the prominent works which were performed during the War by American scientists. Their method, published in 1947(1) and 1948(2), consisted of the application of a cation-exchange chromatography. They used oxalic acid as the eluent for zirconium and niobium, and alkaline earths. Ruthenium, iodine and tellurium were grouped in the filtrate of sample solutions passed through hydrogen-form (HR) cation exchanger. The extension of this method, however, has not much been reported, in spite of recent considerable development of ion-exchange separation techniques(3).

The purpose of our studies was to find a systematic separation method for the fission product mixture, taking into account the minor constituents which are distributed in so-called " trough " region on the curve of the fission yield vs. mass number. For this purpose, both cation- and anion-exchange experiments were carried out using individual radioactive isotopes of these elements. Our interest was especially directed to the change of the exchange behavior caused by the formation of different oxidation states or of different ionic species.

The preliminary experiments showed that an anion-exchange method is not practical for the extraction of the transition elements, antimony and tellurium in the form of chloride complexes from the mixture. It owed to the complex behavior of ruthenium which is usually one of the main constituents in gross fission products. Then in this study a cation exchange was applied to the first step of group separation and various eluents were tested for fractional elution of cesium, rare earths and alkaline earths. However, characteristic behavior of antimony, tellurium and some transition elements to anion exchanger was found to be useful for their mutual isolation.

Measurement of Radioactivity

In this work the behavior of the elements was observed in their carrier-free state whenever possible. The counting device was G-M counter with ordinary scaler or with a self-recording rate meter. The effluents from the ion-exchange column were either collected and evaporated on a glass plate for counting, or led directly under

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[*1] This communication was presented at the XVth Congress of International Union of Pure and Applied Chemistry held on 13th of September, 1956 at Lisbon.

1) E. R. Tompkins, J. X. Khym and W. E. Cohn, *J. Am. Chem. Soc.*, **69**, 2769 (1947).

2) W. E. Cohn, G. W. Parker and E. R. Tompkins, *Nucleonics*, **3**, No. 5, 22 (1948).

3) K. A. Kraus and F. Nelson, Report presented at the International Conference on the Peaceful Uses of Atomic Energy (Genève, 1955), A/CONF 8/P/837.

the mica end-window of the counting tube through a spiraled vinyl tube.

Ion-exchange Behavior of Individual Element

Ruthenium :—The solution chemistry of ruthenium is fairly complex. We have performed some experiments with carrier-free ruthenium using a cation exchanger, Dowex 50, and several kinds of anion exchanger, Dowex 1, Dowex 3, Amberlite IRA-400, Amberlite IRA-411 and Amberlite IR-4B. The gross fission products[*2] were imported from the United States, Atomic Energy Commission (US, AEC).

Ruthenium-106 was presented in the stock solution (4 M nitric acid solution) and was found to be fractionated into the following three groups according to the behavior towards the ion exchangers (Table I).

TABLE I

BEHAVIOR OF CARRIER-FREE RUTHENIUM ON ION-EXCHANGE RESINS

Species	Content	Ion-exchange behavior
Neutral part	26%	Passed through a mixed bed of anion- and cation-exchangers (RCl+HR).
Anionic part	20%	Adsorbed on anion exchanger (RCl or RNO_3).
Cationic part	54% (by difference)	Adsorbed on HR from dilute acid solution.

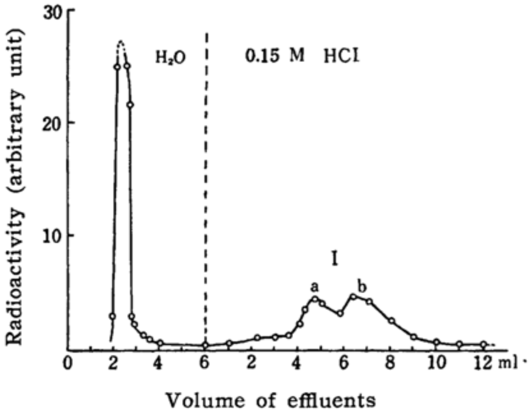

Fig. 1. Elution curve of cationic ruthenium.
Column: Dowex 50-X10, 3 ml. (HR form)

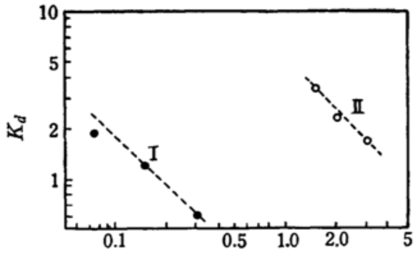

Fig. 2. Cation exchange of cationic ruthenium in $HClO_4$ solutions.
I: weakly retained species.
II: strongly retained species.
K_d's (ml./g.) were calculated from column experiment by
$$K_d=(V-I)/M$$
where V: volume of effluents flowed until the elution of the peak,
I: void volume of the column,
M: weight of dry resin (g.).

The major part of the cationic ruthenium, adsorbed on a cation exchanger, was easily eluted with hydrochloric acid solution stronger than 0.1 M. The elution curve showed two reproducible peaks (Fig. 1). But a small percentage of cationic ruthenium was adsorbed rather strongly, and a more concentrated mineral acid was needed for its rapid elution.

The affinites, distribution coefficients (K_d), of these two cationic species to a cation exchanger are shown with reference to hydrogen-ion concentration (Fig. 2). The inclination of two linear curve suggests that both species are probably univalent cations.

When the stock solution of fission products was treated with concentrated hydrochloric acid, evaporated to dryness and then dissolved in dilute hydrochloric acid solution, all the ruthenium was converted into an anionic species which passes through the column of cation exchanger. After being kept standing more than one week, however, two cationic species were found again from this solution.

This phenomenon might be attributed to the hydrolysis of the anionic chloro-complex formed by the treatment with concentrated hydrochloric acid. In this case, two peaks which could be refered to weakly retained cationic ruthenium were not resolved into separate peaks. This fact is in contrast to the experiments (Fig. 1) using original stock solution of the gross fission products.

The anionic part of ruthenium was

[*2] The sample used in this experiment was sufficiently aged, so that its composition was rather simple, i. e. it consisted of chiefly rare earths, strontium-90, cesium-137, ruthenium-106 and their daughters. Antimony-125 was found in the filtrate of the cation exchanger through which the sample solution had passed. The activity was ca. 0.1 % of total. The data as far as obtained suggest the sample being cooled for 3~4 years[4)].

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

strongly adsorbed from acid solution on strongly basic anion exchangers such as Dowex 1, Dowex 2, Amberlite IRA-400 and Amberlite IRA-411. It was eluted out with 12 M hydrochloric acid in two broad peaks. On the other hand, it was noticed that the weakly basic anion exchangers, Dowex 3 and Amberlite IR-4B, react irreversibly with ruthenium in hydrochloric acid solutions.

Detection of rhodium-106, the short lived daughter of ruthenium-106, was easily performed from this anionic part of ruthenium. Rhodium was found in the effluents of 6~12 M hydrochloric acid passed through with a high flow rate. The decay curve of the activities of rhodium was drawn with an automatic recording rate-meter and it showed $T_{1/2} = 31.1$ seconds (Fig. 3).

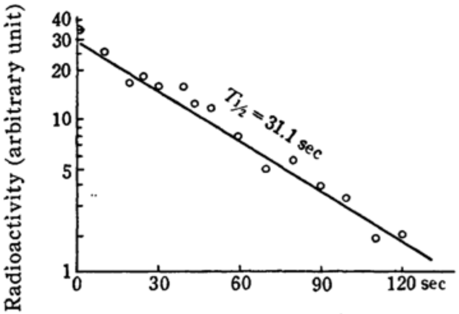

Fig. 3. Decay curve of rhodium-106 isolated by anion exchange.

Antimony:—The tracer used was antimony-124 imported from the U.S., AEC. It contained 20 microgram Sb/ml. as a carrier, and was stocked in 6 M hydrochloric acid. Appreciable volatility of the activity was noticed during the evaporation of the solution. Then, if necessary, a few milligrams of antimony, Sb(V), were added and the activity was precipitated as antimony(III) sulfide.

Cation exchange. Antimony(V) was passed quantitatively through a cation exchanger in dilute acid solution. On the other hand, antimony(III) which was obtained by reduction with sulfur dioxide was adsorbed completely.

The adsorbability of antimony(III) by cation exchanger indicated the presence of univalent cation, possiblity SbO^+. That is, the plot of log K_d vs. log (HCl) has the slope of about one in the range of 0.05~0.3 M HCl (Fig. 4). These two species of antimony, Sb(V) and Sb(III), were separated from each other by a simple procedure (Fig. 5). Antimony(III) was also easily eluted out with dilute solution of oxalic acid from cation exchangers.

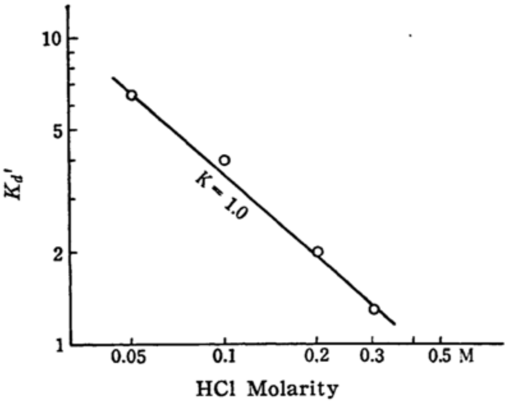

Fig. 4. Cation exchange of antimony(III) in HCl soln.
Exchanger: Dowex 50-X1
K_d': volume distribution coefficient corrected for swelling and measured by column method (Fig. 2).
(adsorption amount/ml. resin)/(concn. in soln.).
K: selectivity coefficient,
{SbOR/(SbO)}/HR/(H)}.

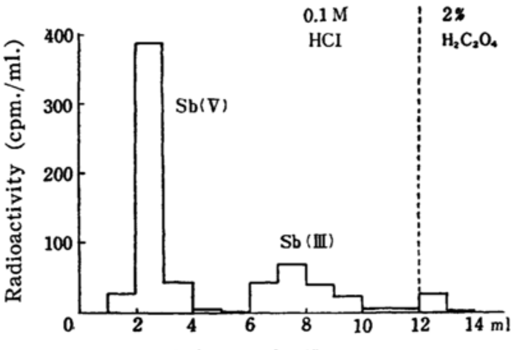

Fig. 5. Separation of Sb(V) and Sb(III).
Column: Dowex 50-X1, 5.5 ml. (capacity 2.10 meq.).

Anion exchange. High reproducibility was obtained by anion exchange using antimony(V) in hydrochloric acid solution, whereas antimony(III) showed quite complicated behavior. Reproducible results with anion exchangers who obtained by a preliminary treatment with hydrochloric acid solution containing free bromine. This treatment was necessary and effective to eliminate any irreversible reactions in the column. Bromine was retained in the resin phase as Br_3^- or Br_2Cl^-, and kept the proper oxidation state of antimony throughout the procedure. Elution constants are tabulated in Table II.

TABLE II

ELUTION CONSTANTS AND HCl CONCENTRATION IN ANION EXCHANGE[5]

Exchanger: Dowex 1-X4

	Concentration of HCl (M)					
	0.1	1	2	3	4	6
Sn(IV)	1.3*	<0.1	<0.1	<0.1	<0.1	<0.1
Te(IV)		1.3	0.1	<0.1	<0.1	<0.1
Sb(V)		1.3	1.3	1.0	0.3	<0.1
In(III)	1.3	0.5	—	0.3	—	0.3

* Maximum value of elution constant, 1.3, corresponds to no adsorption to anion exchanger. Elution constant $= v/(I+M\cdot K_d)$, v: column volume (see Fig. 2).

Tellurium:—The carrier-free tellurium-127 was obtained from the gross fission products, which were cooled for about three months, according to the processes described later. If necessary, a few milligrams of inactive tellurium were added in the form of chloride, and the activity was isolated in metallic tellurium precipitated with sulfur dioxide.

Cation exchange[6,7]. Tellurium(IV) was adsorbed by a cation exchanger and eluted out with dilute mineral acid. It behaves as a univalent cation such as $Te(OH)_3^+$ or $TeOOH^+$ in dilute perchloric acid solution. On the other hand telluium(VI) has no affinity towards cation exchangers.

Anion exchange[5,8]. The anion-exchange properties of tellurium(IV) in hydrochloric acid solution were studied using a few milligrams of tellurium tagged with tellurium-127. The results are tabulated in Table II. It was confirmed by some preliminary experiments that the carrier-free behavior was the same as the weighable amount of tellurium(IV) in both cation- and anion-exchange. The affinity of tellurium(VI) to anion exchanger is also negligibly small in acid solution.

Other minor constituents:—Some preliminary experiments were performed using the radioactive isotopes of cadmium, indium and tin (Fig. 6; Table II).

By cation exchange, using 0.5~1 M hydrochloric acid solution as an eluent, one can separate these elements, Cd, Sn(IV), Sb(III) and Te(IV), in one group from the gross fission products. By the following treatment with anion exchanger, cadmium and tin would be separated from antimony and from tellurium.

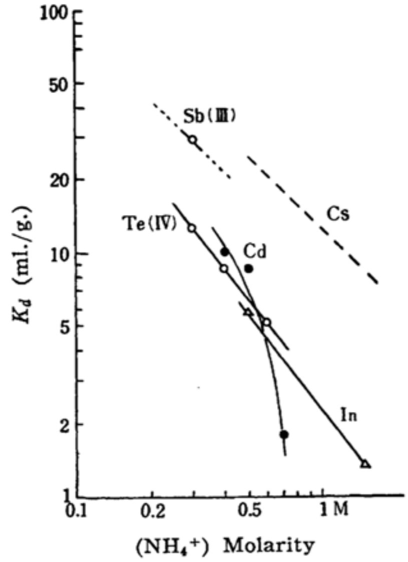

Fig. 6. Cation exchange of Cd, In and Te(IV) in HCl soln.
Exchanger: Dowex 50-X8.

Cesium, rare earths and alkaline earths:—The cation-exchange properties of cesium, rare earths and alkaline earths are rather well known. Some considerations, however, might be needed for the selection of the eluent for the separation of these elements which are adsorbed on the top of HR-form cation-exchange column.

In general, complexing reagent is most effective to remove rare earths from cation exchangers. But every complexing reagent, as far as the solution of its ammonium salt is used, elutes not only rare earths but also cesium from a column of HR-form cation-exchange resin with slightly different rates (Figs. 7 and 8). Therefore in this experiment cesium was eluted beforehand with ca. 1 M hydrochloric acid or 0.5 M ammonium salt of a mineral acid. The identification of the nuclide is possible from the position of the peak in the elution curves.

Detection of barium-137m, the daughter of cesium-137, was performed by cation-exchange separation. Cesium fraction was adsorbed again on the top of a cation-exchange column (NH_4R form), and barium activity was eluted out with ammoniacal 0.01 M EDTA solution. The effluents were directly led under the mica window of a counter tube through a vinyl tube, and the half-life of 2.60 min. was measured repeatedly with the same sample.

Acetate and EDTA were applied for the elution of rare earths and alkaline earths

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[5] Y. Sasaki, This Bulletin, **28**, 615 (1955).
[6] F. Aoki, ibid., **26**, 480 (1953).
[7] Y. Sasaki, *Japan Analyst* (*Bunseki Kagaku*), **4**, 637 (1955).
[8] Y. Sasaki, This Bulletin, **28**, 89 (1955).

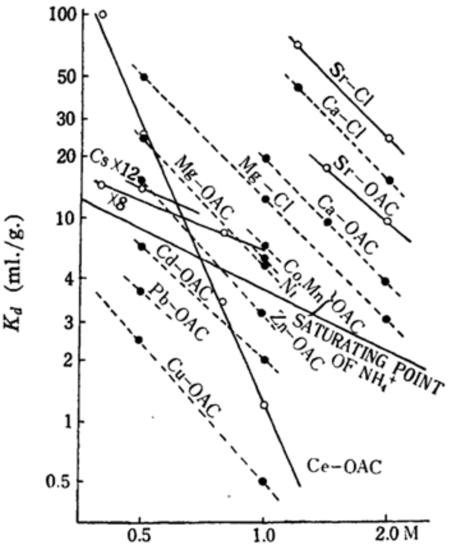

Fig. 7. Cation exchange of several elements in ammonium salt solutions.
Cs and Me—Cl: in NH_4Cl solutions.
OAc: $NH_4OAc+HOAc$ (pH 4.6).
Exchangers: Colloidal Dowex 50 (for alkaline earths); Dowex 50-X8 (for others).

from the cation-exchange column. Ammonium acetate has been used as a fractionating eluent by changing the concentration for the group of rare earths, some transition elements[9] and alkaline earths[10,11]. This eluent has an advantage over any other organic reagent in that it can easily be removed by simple evaporation. Therefore this eluent is not only useful for the titrimetric determination of carrier metals by complexometric method which enables us to compare the elution curves of carriers and activities, but also convenient for the counting of carrier-free nuclides without the difficulty arising from self-absorption.

EDTA is a valuable reagent for the separation of rare earths and alkaline earths, especially for the separation into individual elements by the careful control of the pH. The smaller solubility of the free acid, however, prevents the direct use of HR-form column. For the elution of alkaline earths the mixture containing 0.01 M EDTA and 0.1 M ammonium acetate could be used at the pH between 7 and 9 to separate each member successively.

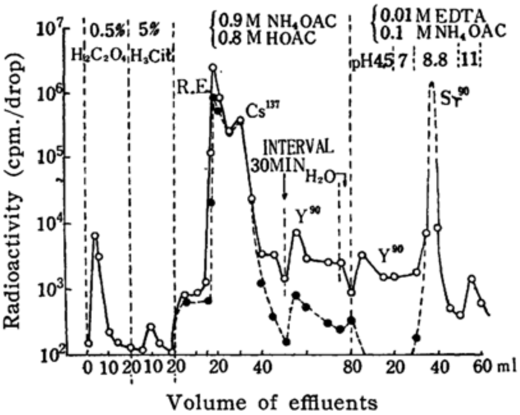

Fig. 8. Group separation with cation exchanger[4].
Sample: the fission products (Batch No. 19) (Oak Ridge Natl. Lab.) ca. 4 mc. in 4 M HNO_3 solution.
-○-○- measured just after the elution.
-●-●- measured after 2 months.
Column: Dowex 50-X8, 5 ml.

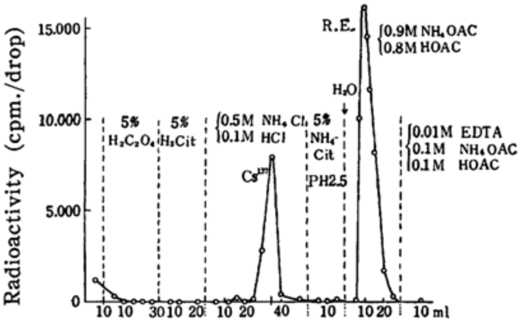

Fig. 9. Separation of cesium and rare earths[4]. (See Fig. 8)
Sample: 10~30 ml. fraction of NH_4OAc effluents in Fig. 8.
Column: Dowex 50-X8, 5 ml.

Systematic Separation Process

The properties of the elements described above could be applied to the systematic ion-exchange separation process for fission-product mixture. The possible scheme of such a process is outlined in Fig. 10. The sample of gross fission products free from heavy metals, is treated with concentrated hydrochloric acid, evaporated to dryness, and dissolved in a few milliliters of 0.1~0.2 M hydrochloric acid solution which contains free bromine. By these procedures, ruthenium is converted into anionic complexes, and bromine will oxidize antimony to its quinquevalent state. This solution is slowly passed through a small cation-exchange column (HR form),

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[9] M. Honda, *Japan Analyst* (*Bunseki Kagaku*), **4**, 384 (1955).
[10] M. Honda, ibid., **3**, 132 (1954).
[11] K. Kimura, E. Minami, M. Honda and others, ibid., **3**, 335 (1954).

and the column is washed with water. All ruthenium and antimony will be found in the effluents. The latter is treated with sulfur dioxide and passed through another cation-exchange column, which will take up antimony reduced to tervalent state. Oxalic acid (1%) or dilute hydrochloric acid (1 M) could be used for the elution of this element.

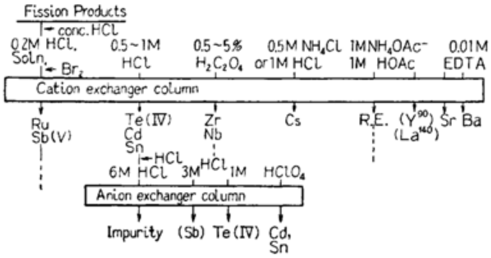

Fig. 10. Method of systematic separation of fission product mixture.

Tellurium(IV), cadmium and tin(IV) are eluted rapidly with 0.5~1 M hydrochloric acid from the former column. To the effluents, concentrated hydrochloric acid is added and the concentration of the acid is adjusted to 6 M. The impurities will be removed from this fraction by passing it through an anion-exchange column, Dowex 1–X4 (pretreated with 6 M HCl), and washing it with 6 M hydrochloric acid. Then carrier-free tellurium is eluted with 1 M hydrochloric acid. Finally, minor constituents, cadmium and tin, would be eluted out with perchloric acid or nitric acid.

After the elution of tellurium and others, zirconium and niobium will be eluted with 0.5~5% oxalic acid from the cation-exchange column. Cesium, rare earths and alkaline earths are then treated as illustrated in Figs. 8 and 9. If the addition of ammonium chloride is not favorable, the use of NH_4R-form cation exchanger and ca. 1 M ammonium acetate solution which is buffered with acetic acid can be recommended to separate rare earths from cesium. In this case, rare earths appear in the effluent with the added eluent and can be separated from cesium which has the elution peak at the same position as in the case in which HR-form resin is used.

In Figs. 8 and 9, citrate and oxalate were used to remove possible heavy-metal impurities.

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