A Study on Analysis of Carrier Free Radioisotopes by Paper Chromatography

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INTRODUCTION

The methods used for the chemical analysis of the ashes fallen on the No. 5 Fukuryu Maru are classified roughly, 1) the carrier free method by the use of ion-exchanger, and 2) the general chemical procedures by the use of carriers. The former method takes long time, while the latter is generally attended by radioactive contaminations. The procedure of ion-exchange separation is distinguished by that simplicity and nearly complete separability. And paper chromatography is similar to ion-exchange method both in the simplicity of the procedure and the principle of separation, and excels in that it takes shorter time. Further, one will be able to test the purity of a radioisotope easily but roughly. But it should be studied if a single operation of chromatography could separate ultramicro-quantities of elements with similar degree to ion-exchange method. Also, it will be useful to determine Rf-values of each elements in a tracer scale for a suitable developer both to the test of purity of element and to analytical purpose. For these purpose, we attempted the first dimensional paper chromatography in ascending method with radioisotopes which were produced as fission products of U or Pu and were assumed to survive comparatively long, on the basis of the fission yields and the half-lives : Ru-Rh, Zr-Nb, Y, Ce-Pr, I, Ca and Sr systems were examined.

PREPARATION OF SAMPLES

Ru–Rh : The dust which was gathered from a deck of the No. 5 Fukuryu Maru was treated with aqua regia. To the solution, NH_4OH was added to be slightly alkaline, obtained reddish-brown precipitate (which contained ferric hydroxide) was filtered, and dissolved in a little amount of conc. HCl, and then iron was removed by continuous extraction with ether. After the aqueous solution was treated with $HClO_4$-H_2O_2 to remove ether and its decomposition products, evaporated to nearly dryness several times with conc. HCl. The residue was taken up with HCl, added NH_4OH to just alkaline, and the precipitated hydroxides were dissolved in HCl and pH was adjusted to 1.0 with conc. NH_4OH. The solution was poured onto a ion-exchanger bed (Amberite IR-120, 80~120 mesh, 0.5cm² × 15cm)

to adsorb the fission fragments of U (or Pu) on the upper layer of the bed. The bed was washed with 100 ml of 0.1N-HCl with a flow-rate of 3 ml/cm²·min. and the effluent solution was evaporated to a small volume, which was used as a sample of Ru-Rh. Because I^{131} had been removed before the ion-exchange process, radio-active elements in the anion group obtained by the ion-exchange separation was assumed actually to be only Ru and Rh. An aliquot of the sample solution thus obtained was taken in a glass dish (3 cm by diameter), dried up on a water bath and the β-ray absorption curve was measured. The result is shown in Fig. 1.
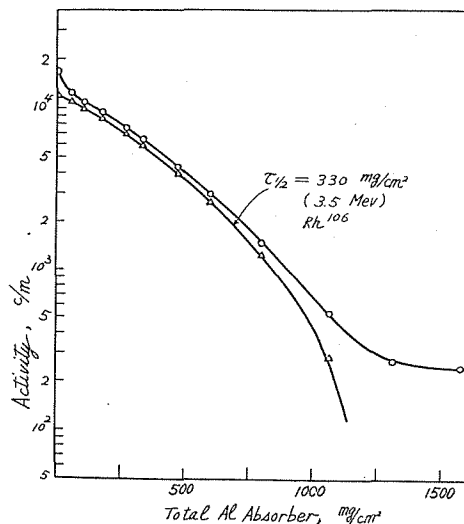

Fig. 1 : β-ray Absorption curve, Ru-Rh (original sample) : Applied potential ; 1350 V, Geometry ; sample 3rd shelf, absorber 2nd shelf.

Ru^{106}, whose half life is one year, ought to survive in a considerable amount at the time when Fig. 1 was measured. But owing to the weak β-rays (max. energy : 0.04 Mev.), this could not be detected with the counter used. Rh^{106} ($T_{1/2}$ = 30 sec.) which is produced as a daughter product of Ru^{106} and radiates two kinds of β-rays —— 3.5 Mev and 2.3 Mev. —— was detected accompaning with Ru^{103}. But Rh^{106} will not be able to be detected when the radioactivity of a sample is weak.

Because of a better discovery of Ru with the above method than that with the distillation method with $KMnO_4$-H_2SO_4, this sample was used for chromatography, in spite of a partial evaporation of Ru at the treatment with $HClO_4$-H_2O_2 and some contamination which was distinguished from Ru-Rh activity after a chromatogram was developed.

Zr-Nb : The dust which was gathered on a deck of the No. 5 Fukuryu Maru was put in a porcelain crucible, moistened with few drops of dil. NaOH, ashed,

treated with HF three times in a platinum crucible, fused with Na_2CO_3–K_2CO_3 and the fused mass was dissolved in HCl. The insoluble residue was treated again with HF, dissolved in HCl and the residue was discarded, for radioactivity was scarcely detected in the residue. Ammonium hydroxide was added to the solution to precipitate hydroxides, which was dissolved as little amount of HCl as possible, and the insoluble part was discarded after washed 3 times with 3N–HCl. The filtrate and the washing solution was put together, pH was adjusted to 1.0 with NH_4OH and adsorbed on a bed of Amberite IR–120 (80~120 mesh, 0.5 cm²× 15 cm). After anion group was eluated with 100 ml of 0.1 N–HCl with a flow-rate of 3 ml/cm². min., Zr~Nb was eluated with 0.5% oxalic acid with the same flow-rate. The effluent was treated with $HClO_4$–H_2O_2, and after evaporated up several times with conc. HCl, the solution was made to 6 N–HCl acidic. From this solution, Zr and Nb was extracted to chloroform by shaking with chloroform, 6 %-cupferron solution and saturated Na_2SO_3 solution.[1) The same extraction procedure was repeated two times and each chloroform layer was put together, which was washed with HCl and 6 %-cupferron solution. From the chloroform layer, Zr and Nb was re-extracted by shaking with 10 ml of 6 N–HCl and few drops of bromine water for one minute in a interval of ten minutes, re-
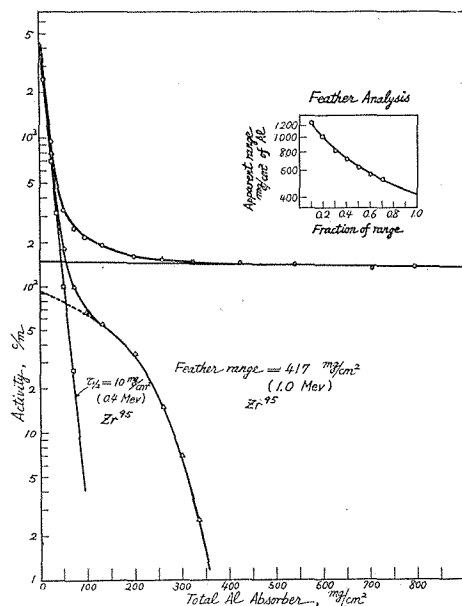

Fig. 2 : β–ray Absorption Curve, Zr–Nb
(original sample) : Applied potential ;
1350 V, Geometry ; sample 3rd shelf,
absorber 2nd shelf.

peating ten times. Organic compounds were removed from acid layer by shaking with three portions of 1 ml of $CHCl_3$. After destroying organic materials remain-

ing in the acid solution by shaking with few drops of bromine water, the solution was concentrated to a suitable volume and was used as a sample of Zr and Nb for chromatography. Toyo Filter Paper-No. 52 was wet with a part of this sample solution, dried and cut in 1 cm width, which was used for the measurement of β-ray absorption curve which is presented in Fig. 2.

The purity of the sample thus obtained which was discussed in Paper VII of this book seemed to be sufficient.

Y: After eluating Zr and Nb as oxalate as mentioned above, Y was eluated with 5 % citrate (pH 3.2) with a flow-rate of 3 ml/cm². min. After the effluent was treated with $HClO_4$-H_2O_2, perchlorate was expelled by evaporating up three times with conc. HNO_3, and the nitric acid solution was concentrated to a suitable volume and used as a sample of Y for chromatography. Fig. 3 shows β-ray absorption curve of this sample measured on a filter paper in the same way as in the case of Zr-Nb.
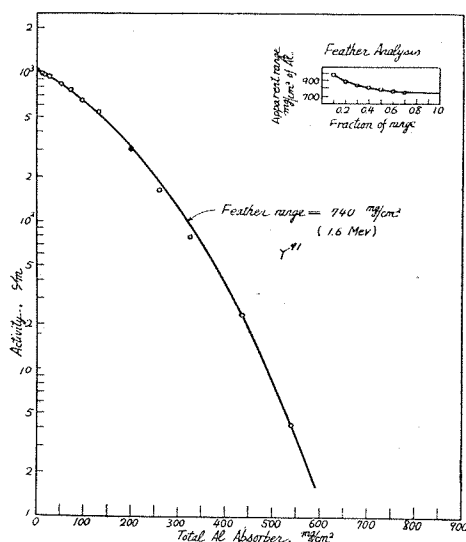

Fig. 3 : β-ray Absorption Curve, Y (original sample) : Applied potential ; 1350 V, Geometry ; sample 3rd shelf, absorber 2nd shelf.

Ce-Pr: After eluating Y as citrate as mentioned above, Ce group was eluated with 5 % citrate (pH 3.4) with a flow rate of 3 ml/cm². min. The effluent was treated in the same way as in the case of Y and the nitric acid solution was used as a sample of Ce-group for chromatography. Fig. 4 shows β-ray absorption curve of the sample measured on a mica film. It is assumed that main component of Ce-group at the time of the measurement was Ce^{141} and its daughter Pr^{144}, on the basis of fission yield and half life.
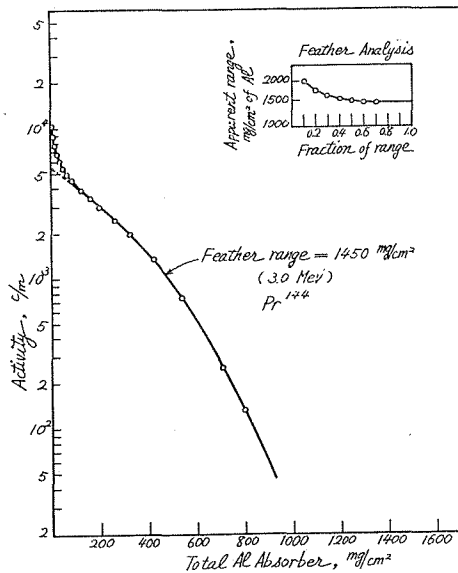
Fig. 4 : β-ray Absorption Curve, Ce-Pr
(original sample) : Applied potential ; 1350 V,
Geometry ; sample 3rd shelf, absorber 2nd shelf.

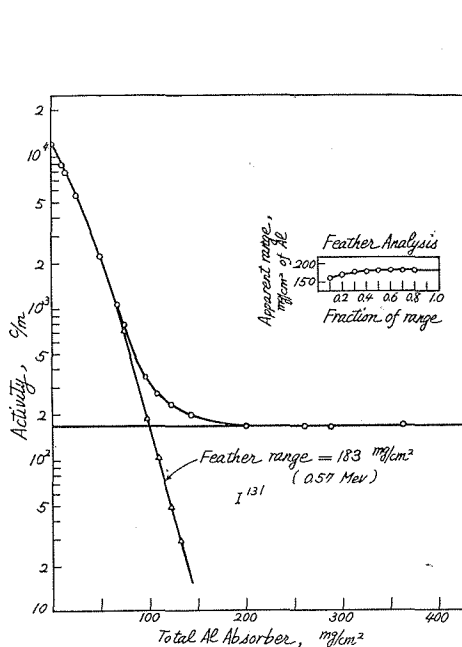**I, Ca, Sr :** Because we could not separate enough quantities of radioactive

Fig. 5 : β-ray Absorption Curve, I
(original sample) : Applied potential ; 1350
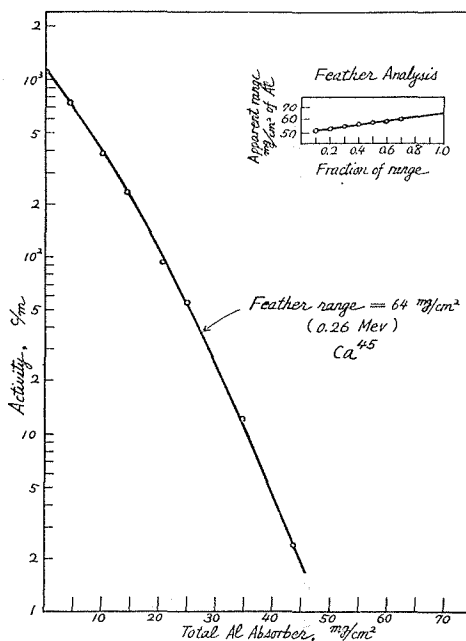V, Geometry ; sample 3rd shelf, absorber
2nd shelf.

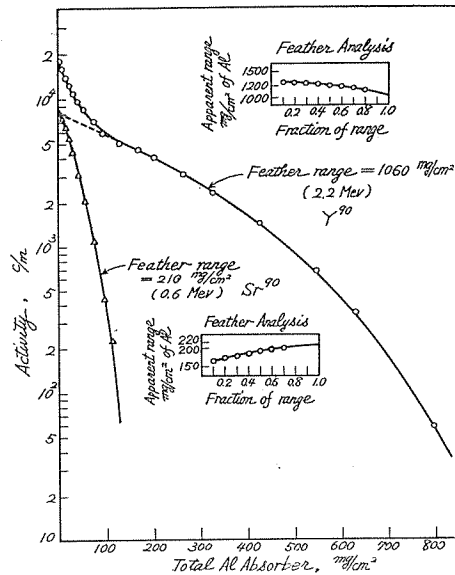Fig. 6 : β-ray Absorption Curve, Ca
(original sample) : Applied potential ;
1350 V, Geometry ; sample 3rd shelf,
absorber 2nd shelf.

I, Ca and Sr from the ash of the No.5 Fukuryu Maru, we used I^{131}, Ca^{45}, Sr^{90} imported from U. S. A. for chromatography. Ca^{45} which existed as a induced activity in the Bikini Ashes and was not a main component of them, was selected because of its biological importance. Fig. 5, 6 and 7 show β-ray absorption curves of I^{131}, Ca^{45}, and Sr^{90}, respectively, measured on filter paper.

Fig. 7 : β-ray Absorption Curve
Sr (original sample) : Applied potential ; 1350 V,
Geometry ; sample 3rd shelf, absorber 2nd shelf.

CHROMATOGRAM

Oxine-chloroform, oxine-butanol, acetylacetone-butanol, mandelate, cupferron-chloroform cupferron-carbon tetrachloride, tartrate, citrate and oxalate were tested for developer of the samples obtained by the above mentioned procedures. About 0.03 ml of each sample solution was attached on a Toyo Filter Paper-No. 52 at the height of 6 cm from a lower end, stood to dryness, and developed with ascending method by dipping 1 cm of the lower end of filter paper. After development, the strip was stood to dryness, cut by 1 cm bands and each piece of paper was measured for radioactivity with a G-M counter. Specially the measurement was done with a piece of paper cut into 0.5 cm band in the neighbourhood of a maximum of activity. Thus a maximum point of activity was determined and the result was plotted. Each peak was assigned by measurement of β-ray absorption curve.

1) **Oxine-CHCl$_3$** : Oxine (8-hydroxyquinoline) purified by steam distillation was dissolved in CHCl$_3$ to be 2% solution. Each sample was developed with the

developer at 22.0~22.3°C for 4~5 hrs.

Y, I, Ca and Sr did not move from the original point and Zr–Nb was not separated from one another forming a wide band at Rf value of about 0.88. Ru–Rh was separated into three peaks, two of which (Rf = 0.24 and Rf = 0.39) was both assigned to be Ru^{103} from the β-ray absorption curves. Beta–ray absorption curve of a peak of Rf = 0.24 was presented in Fig. 8 in which a strong β-rays of Rh^{106} could not be measured owing to the weak activity of the sample. Two peaks of Ru–Rh were assumed to be occured by a effect of iron presented. Ce–Pr forms two peaks, both of which are equilibrium mixtures of Ce^{144}–Pr^{144} as are shown in Fig. 9. A soft component of Fig. 9 gives a similar absorption curve to Fig. 12 and is assumed to be Ce^{144} (Feather range = 76 mg/cm²; 0.3 Mev.).
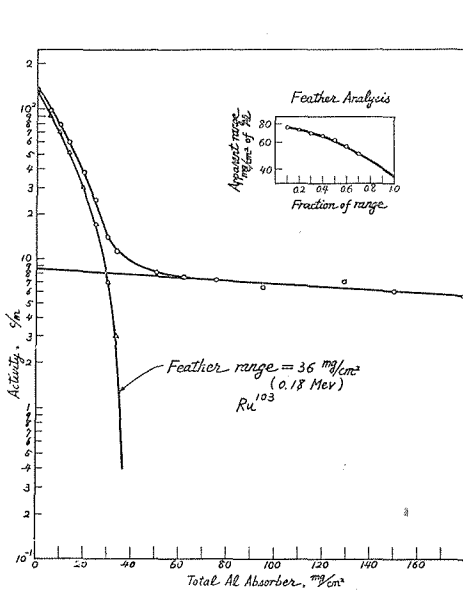

Fig. 8 : β-ray Absorption Curve, Ru^{103} : Applied potential ; 1350 V, Geometry ; sample 3rd shelf, absorber 2nd shelf.
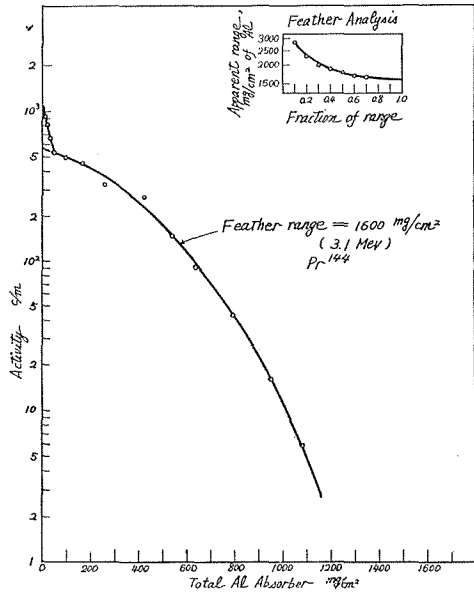
Fig. 9 : β-ray absorption Curve, Ce^{144}–Pr^{144} : Applied potential ; 1350 V, Geometry ; sample 3rd shelf, absorber 2nd shelf.

2) **Oxine–Butanol**: Oxine was dissolved in butanol saturated with water to be 1% solution. The chromatogram was developed with this solvent at 22.0~22.3°C for 4.5~5 hrs.

Two peaks on the chromatogram of Ru–Rh is both Ru^{103} as in the case of 1). The β-ray absorption curve of Y^{91} remained at the original point is shown in Fig. 10. Ce–Pr remained also at the original position, β-ray absorption curve of which is shown in Fig. 11, and the soft component is Ce^{144} as is shown in Fig. 12.

Iodine was separated into two peaks (Rf = 0 and Rf = 0.16), both of them are I^{131} as are obvious from Fig. 13 and Fig. 14. Calcium remained at the original point,

β-ray absorption curve of which is shown in Fig. 15. Strontium was separated into two peaks (Rf = 0 and Rf = 0.70) and it is assumed that, as in the case of 3) unmoved
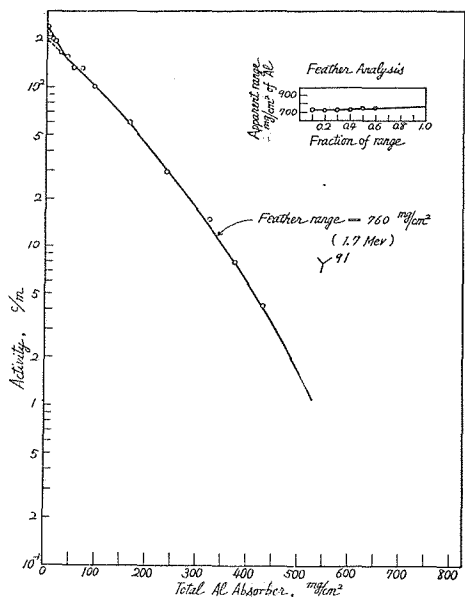
Fig. 10 : β-ray Absorption Curve, Y^{91} : Applied potential ; 1350 V, Geometry ; sample 3rd shelf, absorber 2nd shelf
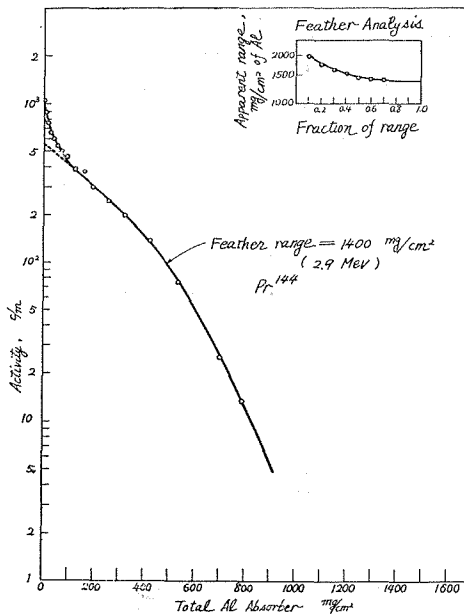
Fig. 11 : β-ray Absorption Curve, Ce^{144}–Pr^{144} : Applied potential ; 1350 V, Geometry ; sample 3rd shelf, absorber 2nd shelf
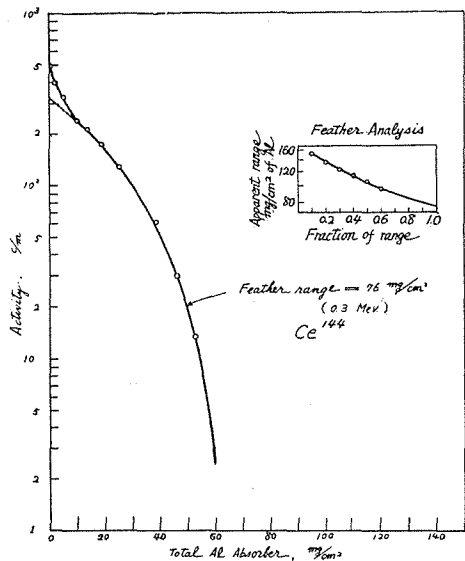
Fig. 12 : β-ray Absorption Curve, Ce^{144} : soft component of Fig. 11 Applied potential ; 1350 V, Geometry ; sample 3rd shelf, absorber 2nd shelf

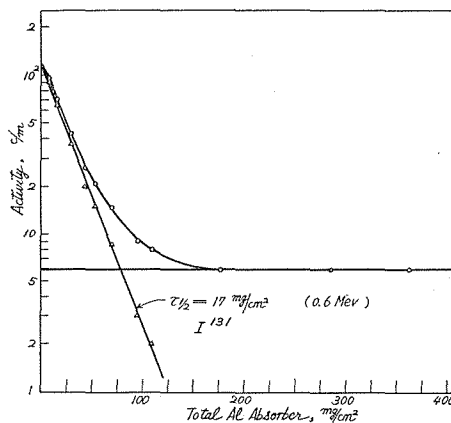Fig. 13 : β-ray Absorption Curve, I^{131} : Applied potential ;1350 V, Geometry ; sample 3rd shelf, absorber 2nd shelf

one is Y^{90} and elevated one to Rf value of 0.70 is Sr^{90} which contained Y^{90} produced as a daughter of Sr^{90} after Sr^{90} was separated. A relatively shallow valley between the two peaks is perhaps occured by Y^{90} activity produced from Sr^{90} which ascended to Rf value of 0.70.
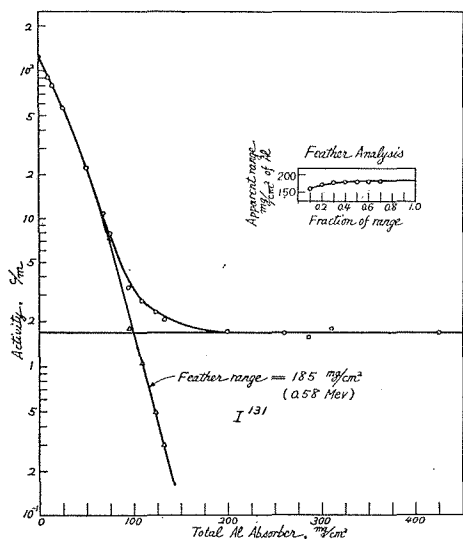
Fig. 14 : β-ray Absorption Curve, I^{131} :
  Applied potential ; 1350 V, Geometry ;
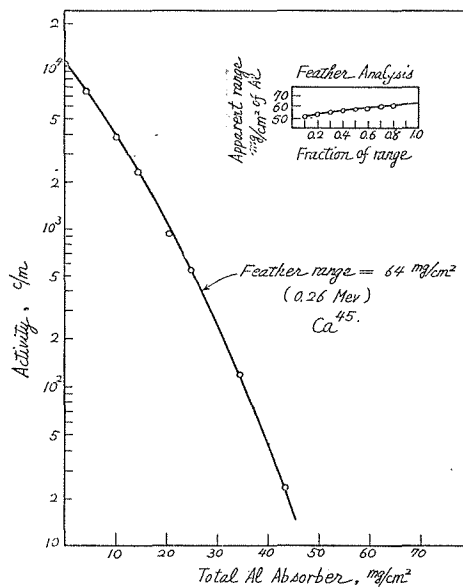 sample 3rd shelf, absorber 2nd shelf.

Fig. 15 : β-ray Absorption Curve, Ca^{45} :
  Applied potential ; 1350 V, Geometry ;
  sample 3rd shelf, absorber 2nd shelf.

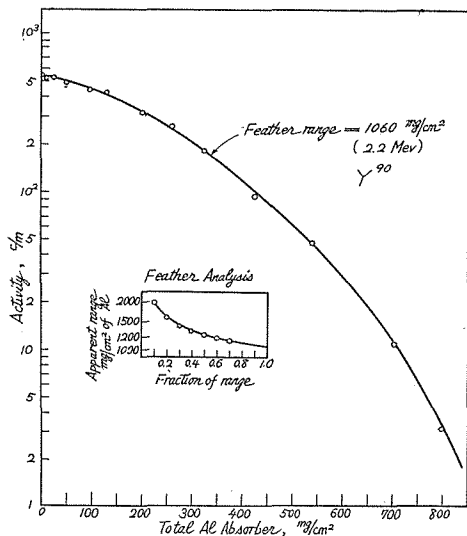3) **Acetylacetone-Butanol**: The developer is consisted of 100 ml of butanol,

Fig. 16 : β-ray Absorption Curve, Y^{90} :
  Applied potential ; 1350 V, Geometry ;
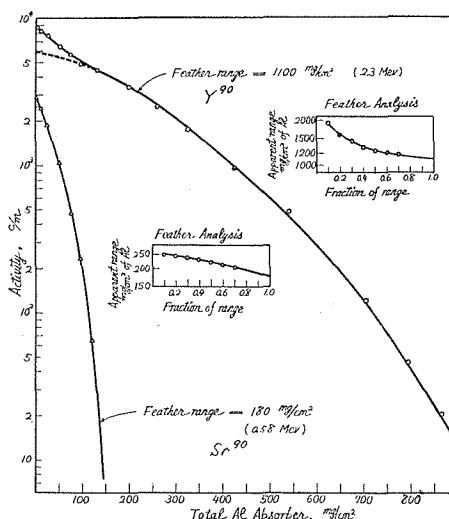 sample 3rd shelf, absorber 2nd shelf.

Fig. 17 : β-ray Absorption Curve, $Sr^{90} - Y^{90}$:
  Applied potential ; 1350 V, Geometry ;
  sample 3rd shelf, absorber 2nd shelf.

30 ml of acetylacetone, 6 ml of HAc and 65 ml of H_2O.[2] The sample was developed at 60~65°C.

Ce-Pr formed one sharp peak (Rf = 0.08) and a broad band (from R = 0.70 to R = 0.87). The former was identified to be Ce^{144} which contained Pr^{144} as a daughter, but the latter could not be identified owing to a little activity.

Activities remaining at the original point and ascended to Rf = 0.13 on the chromatogram of Sr were identified to be Y^{90} and Sr^{90}, respectively (Fig. 16 and Fig. 17). It seems that equilibrium had been reached between Sr^{90} and Y^{90} when the absorption curve was measured.

4) Mandelic acid: Five percent aqueous solution of mandelic acid was prepared and pH was adjusted with conc. NH_4OH. The developement was performed at 22.0~22.2°C within 4~4.5 hrs.

(a) pH 2.0: All the sample formed each one peak. A peak of Sr (Rf = 0.81) is Sr^{90} in equilibrium with Y^{90} (Fig. 18). In this case, Y is not separated from Sr because Rf values of them are alike.
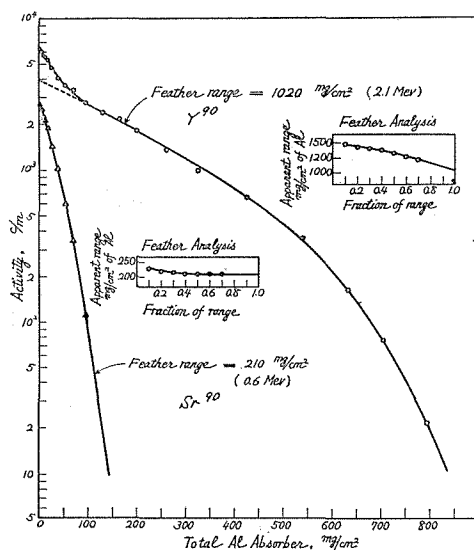

Fig. 18 ; β-ray Absorption Curve,
Sr^{90}-Y^{90} : Applied potential ; 1350
V, Geometry ; sample 3rd shelf,
absorber 2nd shelf.

(b) pH 2.9: This case is similar to the case of pH 2.0. Iodine formed two peaks, both of which are I^{131} as in the case of 2).

(c) pH 5.2: Zr-Nb formed a wide band about Rf value of 0.5 and a sharp peak at Rf = 0.79. It may be assumed that the band is Nb^{95} and the peak is Zr^{95}

(and Nb[95] as a daughter) in the similarity with the case of 4) (d). Of three

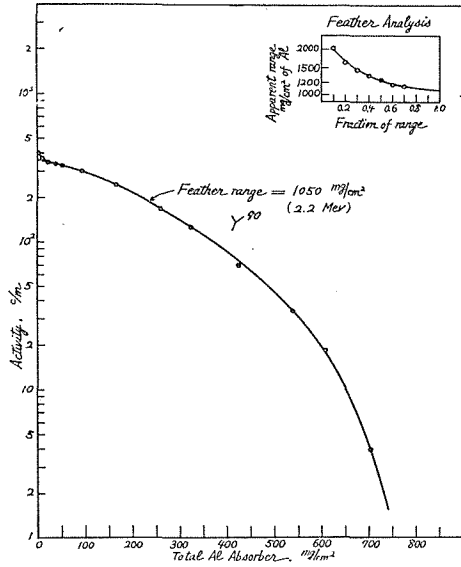Fig. 19 : β-ray Absorption Curve, Y[90] (Rf= 0.20): Applied potential ; 1350 V, Geometry; sample 3rd shelf, absorber 2nd shelf.
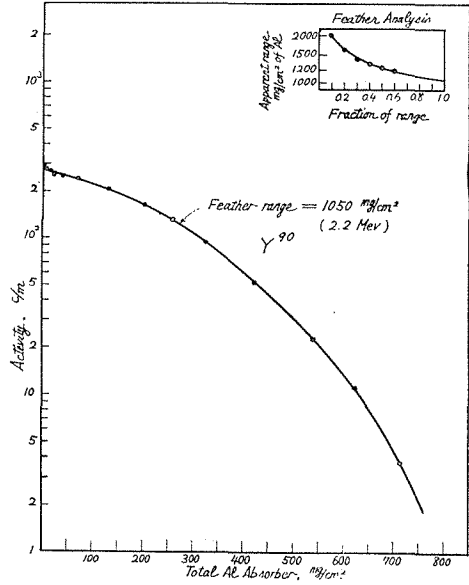
Fig. 20 : β-ray Absorption Curve, Y[90] (Rf= 0.20): Applied potential; 1350 V, Geometry; sample 3rd shelf, absorber 2nd shelf.
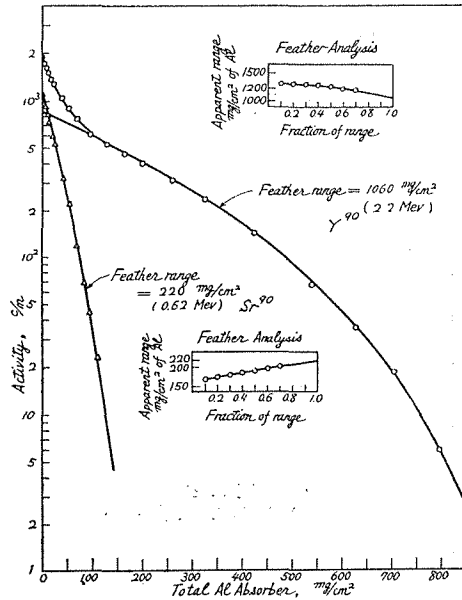
Fig. 21 ; β-ray Absorption Curve, Sr[90]-Y[90] : Applied potential ; 1350 V, Geometry ; sample 3rd shelf, absorber 2nd shelf

peaks of Sr two peaks at Rf=0.05 and 0.20 are mainly Y[90] and one at Rf=0.85 is

Sr^{90} which contains Y^{90} produced as a daughter after Sr^{90} was separated. (Fig. 19, Fig. 2^ .g. 21).

(d) pH 7.9: Of three peaks of Sr, two peaks at Rf = 0.34 and 0.53 are Nb^{95} and one at Rf = 0.82 is Zr^{95}. Fig. 22 shows a β-ray absorption curve of the first peak. This energy is large for Nb^{95}, owing to a little activity and a "lens effect" which occurs by a small distance between a sample and absorber: in this case, a special geometry was taken and a distance between sample and absorber was 0.3 cm. Another kind of β-rays of the sample could not be identified because there was no standard of F ather Analysis for this geometry. Fig. 23 shows β-ray absorption curve of e peak at Rf = 0.82.
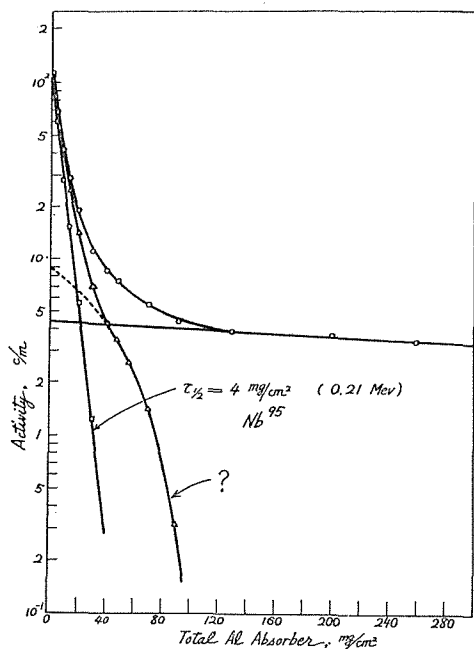

Fig. 22 : β-ray Absorption Curve, Nb^{95} : Applied potential ; 1450 V, Geometry ; sample 1st shelf, absorber 1st shelf.
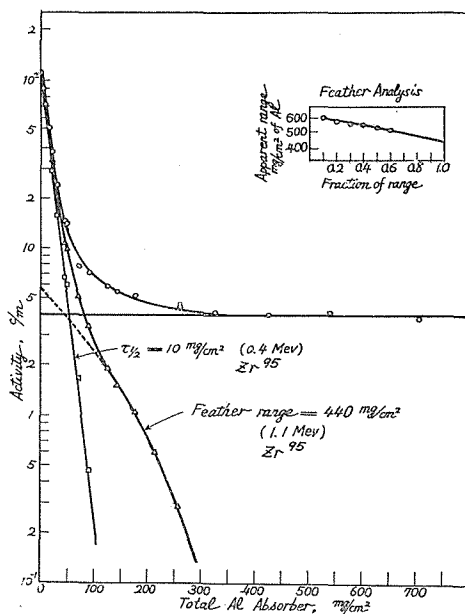
Fig. 23 : β-ray Absorption Curve, Zr^{95}– Nb^{95} : Applied potential ; 1350 V, Geometry ; sample 3rd shelf, absorber 2nd shelf.

Three peaks of Sr will be similar to those on the chromatogram developed by pH 5.2.

Besides the developers mentioned above, cupferron–chloroform, cupferron–carbon tetrachloride, tartrate, citrate and oxalate was used to develope Zr–Nb. These reagents are considered to form salts or inner complex salts with niobium and zirconium. And the fact that, when Zr and Nb is developed with cupferron–$CHCl_3$ or cupferron–CCl_4, Rf value is the largest of all the developer attempted,

illustrates that cupferron-CHCl$_3$ is suitable to extracting reagent for a carrier free separation of Zr and Nb. And because carbon tetrachloride is superior to chloroform at unvolatility and easiness of separation from aqueous layer, cupferron-CCl$_4$ will be more suitable than cupferron-CHCl$_3$ for a carrier free extraction of Zr and Nb, at least concerning these properties.

5) **Cupferron–CHCl$_3$** : Cupferron was dissolved to saturation in chloroform, and the saturated solution was diluted two and four times with chloroform. These solutions were used as developers.

6) **Cupferron–CCl$_4$** : A saturated cupferron solution in carbon tetrachloride was used for a developer.

7) **Tartaric acid** : The 5% aqueous solution of tartaric acid was adjusted to each pH with conc. NH$_4$OH. The β-ray absorption curve of the peak (pH 2.20) is shown in Fig. 24.
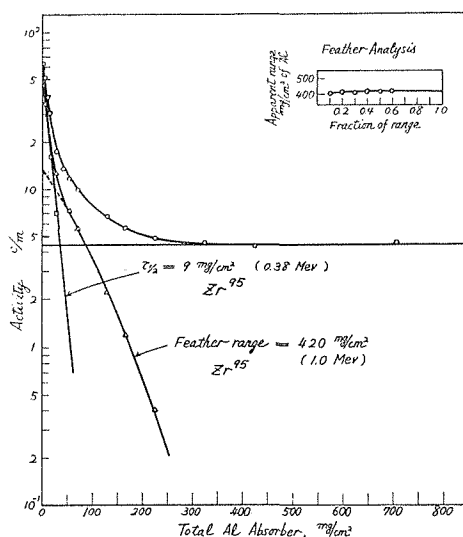

Fig. 24 : β-ray Absorption Curve,
Zr^{95}–Nb^{95} : Applied potential ; 1350 V, Geometry ;
sample 3rd shelf, absorber 2nd shelf.

8) **Citric acid** : The 5% aqueous solution of citric acid was adjusted to each pH with conc. NH$_4$OH, and was used to develope chromatogram.

9) **Oxalic acid** : The 0.5% aqueous solution of oxalic acid was adjusted to each pH with NH$_4$OH, and was used to develope chromatogram.

RESULTS AND DSICUSSION

Rf values on the chromatograms were listed in Table 1.

As is shown in Table 1, Zr and Nb were separable from one another only when develped with mandelic acid of pH 5.2 and pH 7.9. Elements of Ce-group seemed

to be separated mutually when developed with acetylacetone-butanol[3]. The separability between Ru and Rh could not be confirmed owing to a short life of Rh^{106}.

Table 1 Rf Values of the Peaks

		Ru–Rh	Zr, Nb	Y	Ce–Pr	I	Ca	Sr (Y)
Oxine–CHCl₃		0.39 0.24	0.88	0	0.92 0.83	0	0	0
Oxine–Butanol		0.47	0.56	0	0	0.16 0	0	0.70(0)
Acetylacetone–Butanol		0	0	0	0.08	0.36	0.07 ·	0.13(0)
Mandelic acid	pH 2.0	0.88	0.95	0.90	0.86	0.99	0.92	0.81
	2.9	0.85	0.81	0.92	0.88	0.54 0	0.92	0.83
	5.2	0.78	0.79 0.50	0.67	0.82	0.91	0.88	(0.20) 0.85(0.05)
	7.9	0.82	0.53 0.82 0.34	0.58	0.88	0.80	0.88	(0.25) 0.86(0.07)
	9.6	0	0	0.02	0.03	0.80	0.90	(0.36) 0.84(0.03)
Cupf. –CHCl₃	sat. /2 sat. /4		0.96 0.97					
Cupf. –CCl₄	sat. sat. /2		0.96 0.99					
Tartaric acid	pH 1.65 2.20 4.50 6.16		0.86 0.88 0.82 0.85					
Citric acid	pH 1.75 2.80 4.20 5.50		0.81 0.78 0.82 0.80					
Oxalic acid	pH 1.60 2.30 3.20 4.20		0.87 0.81 0.81 0.81					

The sample of Sr^{90} formed at least two peaks when Sr and Y had different Rf values, and one peak when these values were similar. In Table 1, Rf values of Y in the former case were shown in parentheses. Rf values of Y^{90} and Y^{91} differed especially when samples were developed with mandelic acid of pH 5.2 and pH 7.9. The original samples of them are both nitrate and temperature at which the chromatogram was developed is not so varied. Of other reason, effects of trace amount of iron and radioactive strontium is conceivable.

A study on chromatogram when several elements are co–existing is not reported. It will be possible to separate radioisotopes with a suitable combination of the developer described above when elements are limited. But for the sample containing many kinds of elements, a single operation of chromatography will not be able to perform separation, unless some extent of separation is conducted with other method.

Besides, at a solvent extraction of carrier free radioisotopes, following reagents are assumed to be effective :

1) Rare earths (Y, Ce~Pr) : Oxine-CHCl$_3$
2) Ca, Sr : Oxine-Butanol
3) I, Ru~Rh : Mandelic acid and suitable organic solvent (from ammoniacal solution of pH 10).

ACKNOWLEDGEMENT

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3) M. Lederer, Anal. Chim. Acta, **11**, 145 (1954) : After the completion of the manuscript of this paper, the authors have learned by this paper, that rare earths can be separated by the paper electrophoresis with citric acid medium.