Separation of RaD, RaE and RaF by Ion Exchange

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There are several well-known procedures for the separation of RaD, RaE and RaF, e.g., coprecipitation with a suitable carrier, electrochemical separations, extractions of some complex compounds formed with organic reagents, and methods using radiocolloid formation. Recently Polonium has been extracted as dithizonate[1], and ThC has been separated from ThB by the use of radiocolloid formation[2]. These elements can also be separated from each other by means of paper partition chromatography[3]. As anion exchange resins are reported to be very effective for the separations of Zr, Hf, Nb, Ta and Pa[4], rare earths[5] and transition elements[6], etc.[7], the author studied the carrier-free separation of RaD, RaE and RaF using anion exchangers. It was found, in the hydrochloric acid solutions of suitable concentrations, that remarkable differences in the degree of adsorption of these elements for the resin could be successfully utilized for the ion exchange separation.

These ions adsorbed on the top of the column of Amberlite XE-98 (IR-411), a lower cross-linked strongly basic type resin, can be eluted successively, using 2 or 3N hydrochloric acid for RaD, conc. hydrochloric acid for RaE and finally dil. nitric acid or perchloric acid for RaF, respectively. Radioactive assay proved the radioactive purity of each fraction to be nearly 99.9%.

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2) M. Ishibashi, Y. Kusaka and M. Oyabu, presented at Annual Meeting of the Chemical Society of Japan (Kyoto, April, 1953).
3) W. J. Friersln and J. W. Jones, *Anal. Chem.*, **23**, 1447 (1951). E. E. Dickey, *J. Chem. Education*, **30**, 525 (1953).
4) K. A. Kraus and G. E. Moore, *J. Am. Chem. Soc.*, **73**, 2900 (1951).
5) E. H. Huffman and R. L. Osawlt, *J. Am. Chem, Soc.*, **72**, 3323 (1950).
6) K. A. Kraus and G. E. Moore, *J. Am. Chem. Soc.*, **75**, 1460 (1952).
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Experimental

Preparation of The Stock Solution of the Mixture of RaD, RaE and RaF.—The mixture of carrier-free RaD, RaE and RaF was extracted by digestion with aqua regia from a radon tube which had been used over these two years. From the extracted solution, stock solution of the mixture in conc. nitric acid (14N) was prepared by repeated evaporations and additions of nitric acid.

Radioactive Measurement.—Radioactive measurement was performed with a Geiger-Muller counter and a Lauritsen electroscope. The Geiger-Muller tube used was an end-window type, with thin mica window of 1.8 mg/cm^2 thickness.

Preparation of samples for radioactive assay: The radioactive substances were collected with ferric hydroxide. One ml. of 1 mole/l ferric nitrate solution was added to the radioactive solution, and ferric hydroxide precipitate, produced by the addition of dil. ammonium hydroxide solution, was filtered through a Gooch crucible and was collected on a disk of filter paper. The precipitate was dried using an infrared lamp and was used for assays. Ferric hydroxide was found to be a suitable carrier for the collections of RaE and RaF, but not fitted for RaD. One of the experiments showed that about 20% of RaD was retained in the solution without being carried down. But, since the procedure of preparing the samples is simple and time-saving this hydroxide was usually used as a carrier for RaD whenever a complete recovery was not necessary. Lead sulphide, if necessary, was used instead of ferric hydroxide.

The differences in disintegration properties of RaD, RaE and RaF favoured the identification of each species*.

Preliminary Experiments.—In order to find a good condition for the separation, the elution of the individual ion was investigated, using.

* The radioactive properties of these species have been sammarized as follows by G. T. Seaborg et al. (1953):

Symbol	Element	Half-life	Type of disintegration (Mev)
RaD	Pb	22 years	β (0.018) γ (0.047)
RaE	Bi	5.0 days	β (1.17)
RaF	Po	140 days	α (5.3) γ (.077)

hydrochloric acid solutions of various concentrations. The columns used were of Amberlite XE-98 (65-120 mesh), 3 cm. × 0.9 cm. diameter in size, and were preliminarily conditioned with 3NHCl. One drop of the stock solution was taken as a sample. The radioactive ions in the effluents were successively collected by coprecipitation with ferric hydroxide and their activities were measured. While the isolated RaD is expected to show an increase in the β-activity, the β-activity of RaE has to decrease because of its decay. So RaD and RaE are easily identified by duplicate measurements of their β-activities within a interval of a few days. RaF was identified by means of a Lauritsen electroscope because on its α-emitting property. The data of the elution experiments with 3N, 6N and conc. HCl are illustrated in Fig. 1 (No. 1-No. 3). Since RaF is

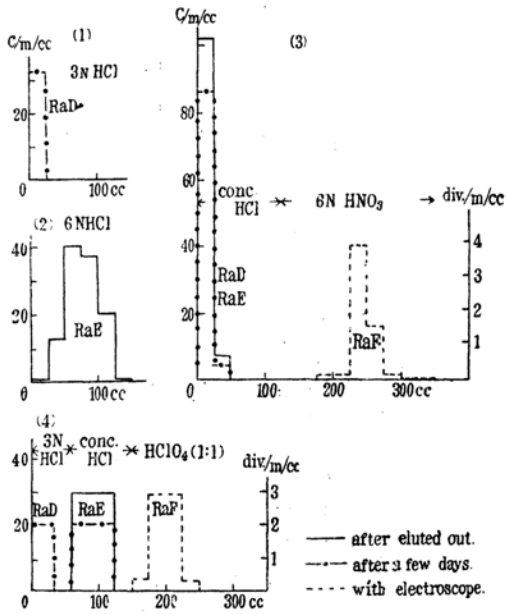

Fig. 1.

not detected in the effluents of the hydrochloric acid solution, in Experiment No. 3 6NHNO$_3$ was used to elute it. The considerable differences in the rate of elution of these ions indicate the desired separation as being possible. Thus, in Experiment No. 4 fractional elution of these ions were performed, i.e., RaD was eluted out with 3NHCl, RaE with conc. HCl and then RaF with HClO$_4$ (1:1). Perchloric acid was used because on its slight tendency to form a complex anion. The experimental results were parallel with this anticipation.

Separation for the Samples of Stronger Activities.—The experiments with samples of stronger activities were tried and each fraction of effluent was to check the extent of the separation. As a sample, one drop was taken out of the hydrochloric acid solution which had been prepared by evaporating the stock solution, followed by digesting it with conc. HCl. The activity of a sample was about 4×10^4 c/m. The columns used were of Amberlite XE-98 (65-120 mesh), 3 cm × 0.85 cm. diameter in size, and preliminarily condititioned with 2NHCl. Solutions of 2NHCl, conc. HCl and HNO$_3$ (1:1) were used as the eluent for RaD, RaE and RaF, respectively. From the effluent, successive drops were taken at suitable intervals on a small glass pan or a disk of filter paper and after being dried, their activity was determined to obtain the elution curve. The resulting elution curve is shown in Fig. 2. From each fraction of effluents I, I′, II,

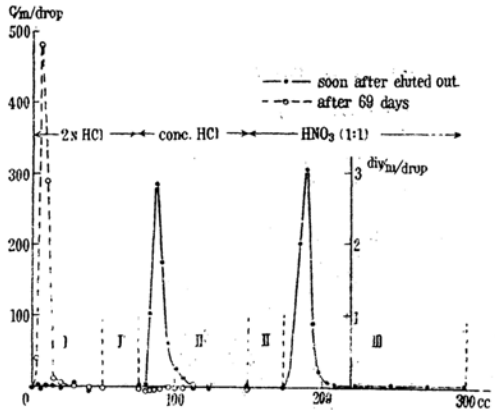

Fig. 2. Elution Curve.

Activities of each fraction were as following:

activity c/m \ fraction	I	I′	II	II′	III
after eluted out	390	1	41.5×10^3	1	0
after 35 days	39.7×10^3	0	270	2	−3
after 69 days	40.0×10^3	0	0	0	0

II′ and III, as shown in Fig. 2, the radioactive ions were carried down with ferric hydroxide precipitates and their activities were measured. In the cases of fraction I and II, aliquots of 1/10 and 1/15 of the originals, respectively, were used because of their stronger activities.

Examination of the Extent of Separation

1. Elution Curve.—From the elution curve illustrated in Fig. 2, the separation is considered to be satisfactory. Absence of activity in fraction I′ and II′ shows that the fractional elution was performed successfully. While it might be necessary to prevent the tailing of RaF, the quantity of RaF contained in the tailing of fraction III appears to be negligible when examined with some larger amounts of effluent.

2. Detection of RaE Contaminating RaD Fraction.—The activity of fraction I increased as shown in Fig. 3 due to the growth of the element, RaE. In this respect, the observed growth curve agrees with the theoretical one of RaE. Moreover, the observed activity 39±4 c/m, of RaE grown after one handred minutes from the

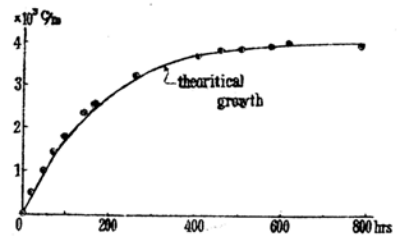

Fig. 3. Growth of RaE.

instant of the elution of RaD's peak, is in good agreement with the calculated value, 38.4 c/m:

$$4.02\times10^3(1-e^{-(0.693/5.0\times24\times60)\cdot100})=38.4.$$

The value 4.02×10^3 c/m is the activity of RaE existing at radioactive equilibrium with RaD before the separation. It was obtained from the measurement after 69 days taking into account of RaD's decay. From the results mentioned above it is considered that at the moment of elution, RaD is, to a great extent, free from RaE which coexisted before the separation.

3. Detection of RaD Contaminating RaE Fraction.—A. Decay of RaE Fraction's Activity: The decay curve of RaE fraction (II) which was collected using ferric hydroxide is indicated in Fig. 4. Within the range of experimental error

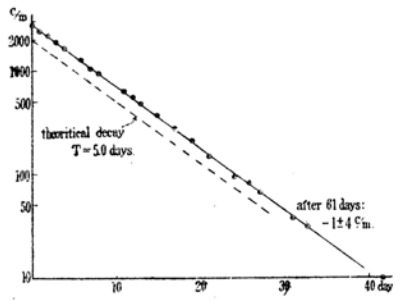

Fig. 4. Decay of RaE fraction.

the activity may be supposed to decrease in accordance with the half-life (5.0 days) of RaE. The sample was covered with a thin sheet of cellophane absorber and placed at 2 cm. under the window of a G.M. tube. So the α-rays from RaF were cut off and the activity of RaF resulting from RaE does not interfere with this determination.

B. Fearing the possibility that the amounts of RaD in the RaE fration were not satisfactorily collected with ferric hydroxide in the above experiment, a further expriement was undertaken. Using RaE which was separated from RaD by fractional elution, the same procedure was repeated and the activity of the RaD fraction was measured. The produres and results are shown in Table I. It may be said that contaminants in RaE separated as above are in the order of less than $1:10^4$.

4. Detection of RaD and RaE Contaminating RaF Fraction.—The radioactivity of ferric hydroxide precipitated from the aliquot of RaF

TABLE I

DETECTION OF RaD CONTAMINATING RaE FRACTION

Procedure:

Sample→RCl → (2N HCl 75 cc. → RaD fr. → evap. →*; 2N HCl 75 cc. → RaE fr.) conc. HCl 100 cc.

* 10 cc. of 2N HCl → RCl → (2N HCl 75 cc. → RaD fr.**; → RaE fr.***) conc. HCl 100 cc.

** (PbS) .....A

*** ($Fe(OH)_3$) .....B

activity c/m / sample	after a day	after 5 days
A	−1	−2
B	14.6×10^3	9.5×10^3

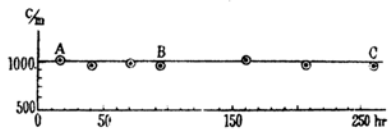

Fig. 5. Activities of RaF measuree with G. M. counter.

When the absorber (3.3 mg/cm² cellophane) is used, the activities are following:

at the time of	A	B	C
activity c/m	−1	−1	0

fraction was measured with a G.M. counter. As shown in Fig. 5, activities did not show any decrease for 10 days. The RaF radiations may be completely cut off when a cellophane sheet (3.3 mg./cm²) is used as an absorber. Hence it may be concluded that this fraction is not contaminated with RaD and RaE.

5. Detection of RaF Eluted in RaD and RaE Fraction.—Since it is difficult to detect the presence of a small amount of RaF in the presence of RaD and RaE, a pure sample of RaF was prepared by preliminary fractional elution and was tested with respect to the absence of RaD and RaE. The sample was treated again by the fractional elution method: 25 cc. of RaF solution (2NHCl) were passed through a column and then fractionation was performed with 50 cc. of 2NCHI, 50 cc. of conc. HCl and 150 cc. of HNO_3 (1:1). From each fraction, RaF was collected with ferric hydroxide and measured using a Lauritsen electroscope. The results are the following:

fraction	RaD	RaE	RaF
div./min.	0.10	0.12	104

It was found that about 0.1% of RaF leaked and contaminated both the fractions of RaD and RaE.

6. Ash of the Exchanger after the Experiment.—The exchange resins were burnt to ashes

and examined after the fractional elution experiment in order to investigate whether the radioactive components had been quantitatively removed or not. The results given in Table II indicate that 0.8% of RaF remained in the exchange resin and the other two species were eluted out quantitatively.

TABLE II

ASH OF EXCHANGER AFTER THE EXPERIMENT

sample / activity	eluted RaD and RaE	eluted RaF	ash of exchanger
c/m	8.28×10^3	—	2
c/m[1]	—	—	0
div./m	—	227	1.74

Each sample was prepared with carrier of ferric hydroxide (Fe (III) 0.4 m. eq.)
1) with 7.2 mg/cm² Al absorber.

Summary

RaD, RaE and RaF may be satisfactorily separated from each other by means of an anion exchanger, Amberlite XE-98. Carriers are not necessary. The use of an anion exchanger and strong acidities of eluents helps to prevent the formation of radiocolloids. This separation technique seems to be highly suitable for the preparation of carrier-free RaE and RaF tracer. It is efficient in separation and easy to manipulate.

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