*A Rapid Method for Determining Fission Products Contained in Waters Using an Ion Exchanger**

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It is essential to select a proper elutriant in order to separate many constituents in solutions by ion exchange resins. Many elutriants have been used by various researchers[1-7]; among them citrate buffer is used most extensively. However, most of these methods are time-consuming, and the preparation and preservation of elutriants are sometimes rather difficult. Moreover, it is often troublesome to treat the effluent for further chemical or radiochemical examinations. This paper deals with a procedure for rapid and easy separation of alkali, alkaline earth and rare earth elements contained in mixed fission products, by using the formate buffer solution.

A good elutriant should have the following characteristics: 1) There must be complete separation of elements; degree of separation can be expected from the complexity constants between cations in a sample and the anion of the complexing agent used as an elutriant[2,8,9]. When the complexity constants of various cations in the sample differ considerably from each other, these cations can be eluted separately

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* A part of this work was done at Kobe University, Kobe.

1) R. H. Diamond, K. Street, Jr. and G. T. Seaborg, *J. Am. Chem. Soc.*, **76**, 1461 (1954).

2) E. R. Tompkins, J. X. Khym and W. E. Cohn, ibid., **69**, 2769 (1947).

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

4) K. Kimura, E. Minami, M. Honda et al., *Japan Analyst* (*Bunseki Kagaku*), **3**, 335 (1954).

5) B. H. Ketelle and G. E. Boyd, *J. Am. Chem. Soc.* **73**, 1862 (1951).

6) E. C. Freiling and L. R. Bunney, ibid., **76**, 1021 (1954).

7) R. C. Vickery, *J. Chem. Soc.*, **1952**, 4357.

8) F. H. Spedding et al., *J. Am. Chem. Soc.*, **69**, 2777 (1947).

9) E. R. Tompkins and S. W. Mayer, ibid., **69**, 2859 (1947).

as the elutriant passes through a column of ion exchanger. 2) Buffer solutions having various pH values should be prepared easily and should be stable. 3) The reagent must be vaporized easily and completely because it is essential that all coexisting materials, other than a compound of the element in question, be removed before radioactive assay. 4) Besides these conditions, the reagents of high quality can be obtained at low cost. From the result of this experiment a formate buffer solution was proved to satisfy these conditions* and to be the best elutriant.

Experimental

Elutriants.—The following elutriants were used for the present experiment:

(A) Hydrochloric acid: 0.2 N.

(B) Oxalic acid: 0.5%.

(C) A buffer solution of 1 M formic acid and 1 M ammonium formate (a formate buffer solution): As shown in Fig. 1, the buffer solutions having various pH values can be prepared by mixing 1 M formic acid solution with varying quantities of 1 M ammonium formate solution.

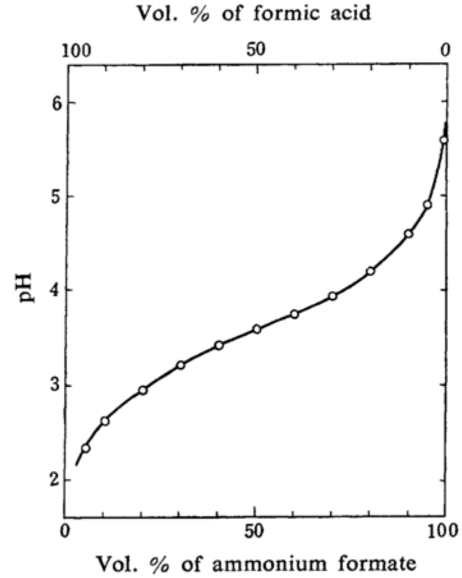

Fig. 1. pH of the buffer solution prepared by mixing 1 M formic acid and 1 M ammonium formate solution.

Columns.—Two columns were used:

No. 1, Dowex 50, X8, 100~150 mesh, 1.0×8.0 cm., H^+-saturated resin, (exchange capasity, ca. 14 meq.).

No. 2, Dowex 50, X8, 200~250mesh, 1.0×20 cm., H^+-saturated resin, (exchange capacity, ca. 35 meq.).

Flow Rate.—0.3~0.4 ml./min.

Sample Solution of Mixed Fission Products.—The fission products mixture used in this experiment had been supplied from ORNL, U. S. A., and was three years old. Nitric acid was added to the fission product solution, and was evaporated on a water bath. More nitric acid was added to the residue. And 0.1~1 ml. of the nitric acid solution (concentration, approx. 10 μc/ml.) were diluted with 5~10 ml. of 0.2 N hydrochloric acid. This hydrochloric acid solution was used as a sample solution.

Procedure.—(A) The sample solution is passed through the column No. 1.

(B) Ruthenium is eluted with about 20 ml. of 0.2 N hydrochloric acid*[4]. The column is washed by passing 10~20 ml. of distilled water.

(C) Next, zirconium, niobium and uranium are eluted together by passing 50~70 ml. of 0.5% oxalic acid[3,4]. The column is washed with 10~20 ml. of distilled water.

(D) When the formate buffer solution of pH 3.2 (1 M formic acid : 1 M ammonium formate=7 : 3, in volume) has passed through the column, cesium is eluted in the effluent of a quantity between 50 and 110 ml. Thymol blue is used as indicator because cesium begins to be eluted after the thymol blue indicator in the effluent changes to yellow.

(E) When the formate buffer solution of pH

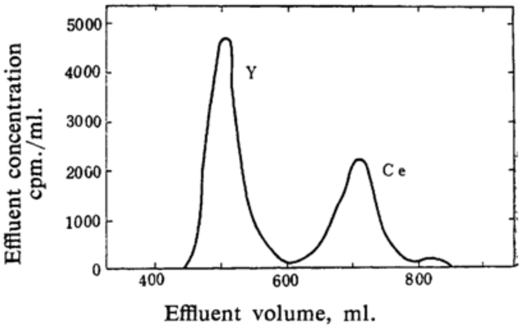

Fig. 2. Separation of rare earth elements.
Column: No. 2.
Elutriant: the buffer solution, pH 3.8.
Flow rate: 0.2~0.3 ml./min.

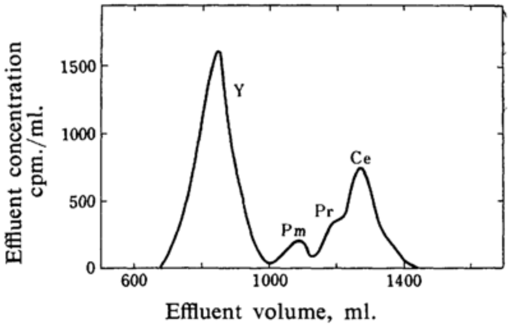

Fig. 3. Separation of rare earth elements.
Column: No. 2.
Elutriant: the buffer solution, pH 3.6.
Flow rate: 0.2~0.3 ml./min.

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* They will be discussed in detail elsewhere.

* If I and Te are present, they are eluted together with Ru.

3.8 (1 M formic acid : 1 M ammonium formate=4 : 6, in volume) has passed through the column, all rare earth elements are simultaneously eluted in a fraction between 50 and 170 ml. of the effluent. After this fraction of the effluent has been vaporized, the residue containing rare earth elements is dissolved in a small amount of dilute hydrochloric acid. The resultant solution is passed through the column No. 2, and rare earth elements are adsorbed on it. When the formate buffer solution having pH 3.8 has passed, rare earth elements are separated into yttrium and cerium groups, as shown in Fig. 2. When the formate buffer solution having pH 3.6 (1 M formic acid : 1 M ammonium formate=1 : 1) is used, cerium group elements are further separated into promethium, praseodymium and cerium fractions, as shown in Fig. 3.

(F) After ruthenium, zirconium, niobium and cesium and rare earth elements have been removed, strontium is eluted by passing about 120 ml. of the formate buffer solution of pH 4.2 (1 M formic acid : 1 M ammonium formate=2 : 8) through the column No. 1.

The method is summarized in Table I, and the results are shown in Fig. 4.

Radioactibity Measurement.—The effluent is divided into 5 ml.-fractions by means of a fraction collector, and 1~2 ml. of each fraction is transferred into a counting dish. Evaporation and sublimation of the effluent is done by heating the counting dish with an infrared lamp and an electric heater. After the formate is removed completely, the radioactivity is measured by using a G. M. counter. The nuclides can be identified from the decay curves and the absorption curves.

TABLE I. METHOD FOR SEPARATION OF FISSION PRODUCTS WITH CATION EXCHANGE RESIN

Sample (in dil. HCl)
↓
Column No. 1

Elutriant		Elements eluted
0.2 N HCl	20 ml.	Ru
(washed with water)		
0.5% oxalic acid	50~70 ml.	U, Pu, Zr, Nb
the buffer solution, pH 3.2	110 ml.	Cs (found in a effluent intermediate between 50 and 110 ml.)
the buffer solution, pH 3.8	170 ml.	Rare earth elements (found in a effluent between 50 and 170 ml.)
the buffer solution, pH 4.2	100 ml.	Sr
2 M ammonium formate solution	100 ml.	Ba

Rare earths fraction
(dissolved in dilute HCl after evaporation)
↓
Column No. 2

1) Y- and Ce-groups can be separated with the buffer solution, pH 3.8.
2) When the buffer solution having pH 3.6 is used, the elements of Ce-group can be separated partially.
3) To separate exactly, use the buffer solution having pH 3.3~3.4 or use a longer column.

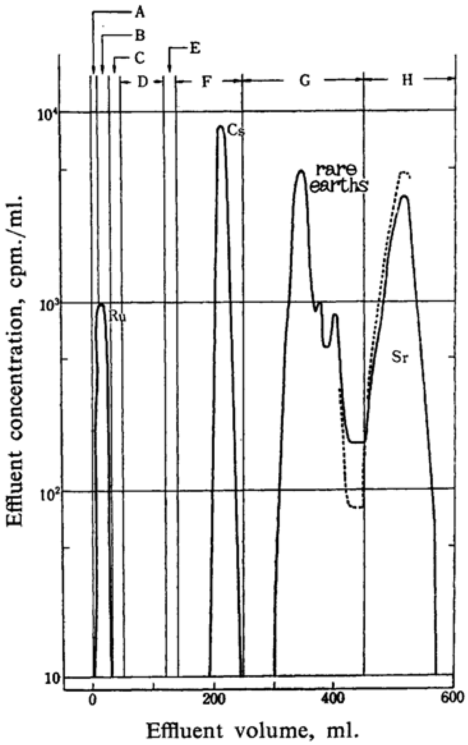

Fig. 4. Separation of fission products.
Column: No. 1.
Influents: A sample solution, B 0.2 N HCl, C H_2O, D 0.5% oxalic acid, E H_2O, F the buffer solution, pH 3.2, G the buffer solution, pH 3.8, H the buffer solution, pH 4.2.
Flow rate: 0.33 ml./min.
The curve in dotted line shows the radioactivity of each fraction 60 hours after the original measurements.

Discussion

Elution of Cesium.—Up to the present time, the elution of cesium has been conducted with hydrochloric acid or citrate buffer solution[10], but neither of these elutriants is satisfactory for the following reasons. When cesium is completely eluted with hydrochloric acid from the column, the adsorption band of strontium moves downward, and consequently, when a further separation of rare earth and alkaline earth elements is to be carried out, a part of

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

strontium is eluted together with the rare earth elements and the separation is incomplete. When a citrate buffer solution is used as the elutriant, the process is complicated because, to avoid the uncertainty of separating rare earth and alkaline earth elements, cesium and rare earth elements must be eluted together, and afterwards cesium and rare earth elements must be separated by resorption and chromatographic elution. Finally, it is very difficut to remove citrate from the effluent. When the formate buffer solution having a pH less than 3.4 is used, the adsorption bands of both rare earth and alkaline earth elements never move downward. Therefore cesium alone can be eluted completely by using the formate buffer solution having pH 3.2, as shown in Fig. 5. Ammonium formate and formic acid sublime easily and completely. Therefore, when the effluent containing cesium is evaporated, and an adequate acid is added to the residue and re-evaporated, pure and carrier-free cesium salts can be obtained.

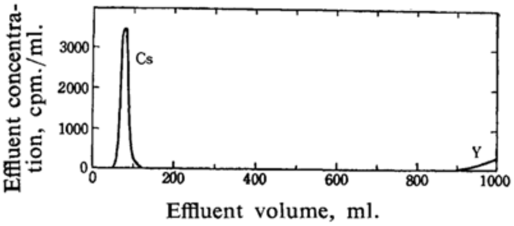

Fig. 5. Elution curve of Cs.
Column: No. 1.
Elutriant: the buffer solution, pH 3.3.
Flow rate: 0.40 ml./min.

Separation of Rare Earth and Alkaline Earth Elements.—As shown in Fig. 4, a fairly high radioactivity is found in the effluent intermediate between yttrium and strontium fraction. It is, however, possible to conclude that the radioactivity of this fraction is not due to the incomplete separation of rare earth from alkaline earth elements, but to the elution of ^{90}Y coming from ^{90}Sr adsorped on the column from the decay of this fraction.

When the formate buffer solution is used, lanthanum is to be eluted last among all rare earth elements to be eluted in the effluent. In other words, amoung rare earth elements lanthanum is the most difficult element to be separated from alkaline earth elements. The solution of fission products used in this experiment is not fresh; hence, it does not contain ^{140}La having a half-life of 40 hr. Complete separation of lanthanum from strontium is essential if the sample contains fresh fission products. For this purpose, separation of the two elements was examined by using nonradioactive strontium and lanthanum. One meq. of strontium and 1 meq. of lanthanum are passed through the column No. 1 and are adsorbed, and they are eluted by the formate buffer solution as described above. The effluent is divided into 5 ml.-fractions, and lanthanum and strontium in each fraction are determined by a semi-quantitative method, and the result is obtained as shown in Fig. 6. Fig. 6 also shows the result of 1 meq. of strontium and 1 meq. of mixed rare earth elements, viz., lanthanum, neodymium, praseodymium and cerium. From the figure, it can be seen that strontium is easily and completely separated from lanthanum and also from other rare earth elements by using column No. 1 with the buffer solution having pH 3.8. It can be concluded from this experiment that by using the formate buffer solution, rare earth elements and alkaline earth elements can be separately eluted even when fairly large amounts of carriers are present in the sample to be analysed.

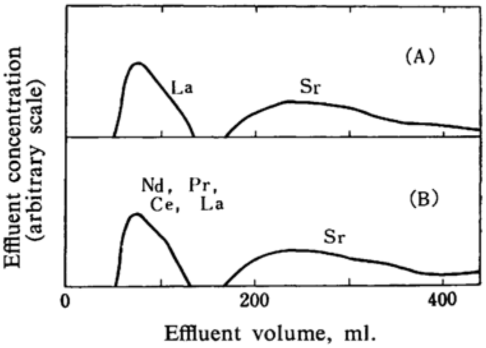

Fig. 6. (A) Separation of La-Sr, (B) Separation of rare earth elements-Sr.
Column: No. 1.
Elutriant: the buffer solution, pH 3.8.
Flow rate: (A) 0.24 ml./min., (B) 0.30 ml./min.

Separation of Rare Earth Elements. — Since fresh fission products contain various kinds of the rare earth element, the authors conducted separation of rare earth elements as follows:

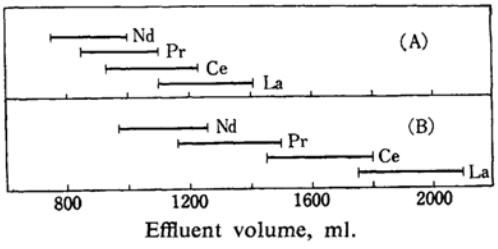

Fig. 7. Separation of rare earth elements.
Column: No. 2.
Elutriant: the buffer solution, (A) pH 3.6, (B) pH 3.4.
Flow rate: 0.25 ml./min.

a mixture of 1 meq. each of neodymium, praseodymium, cerium and lanthanum is adsorbed on column No. 2; the rare earth elements are eluted with the formate buffer solution. The effluent is divided into 10 ml.-fractions, and the elements in each fraction are determined. As shown in Fig. 7, the separation is incomplete when the formate buffer solution having pH 3.6 is used, but when the buffer solution of pH 3.4 is used the separation becomes rather complete. This procedure will be applied for the purification of rare earth elements.

Separation of Strontium and Barium.—With the same purpose as described in the preceding section, the authors carried out separation of strontium and barium by adsorbing 1 meq. of strontium and of barium on the column No. 1. As shown in Fig. 8, barium can be separated from strontium very easily and completely.

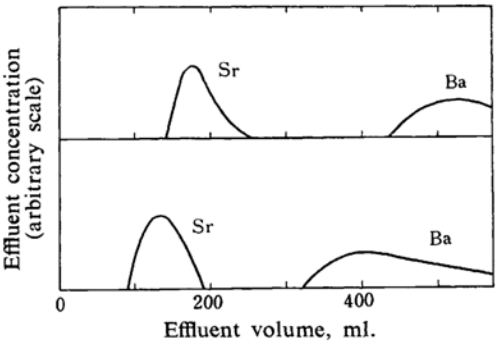

Fig. 8. Separation of Sr–Ba.
Column: No. 1.
Elutriant: the buffer solution, (A) pH 4.0, (B) pH 4.2.
Flow rate: (A) 0.40 ml./min., (B) 0.42 ml./min.

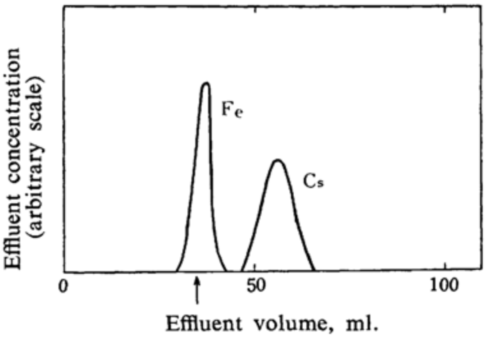

Fig. 9. Separation of Fe(3 meq.) from Cs.
Column: Dowex 50, X8, 1.1×10 cm., (100∼150 mesh) H^+-saturated resin.
Elutriant: the buffer solution, pH 3.2.
Flow rate: 2.0 ml./min.
Arrow indicates the point at which thymol blue indicator changes to yellow from red.

Separation of Fission Products from Iron.—To determine exactly fission products in natural waters by ion exchange resin, it is essential that the coexisting elements or carriers must be separated from fission products. Sodium, potassium, magnesium, calcium, ferric and aluminum ions are often found in natural waters, and barium and ferric ions are used as carriers. By using the formate buffer solution fission products can be separated easily from the other metals such as alkali, alkaline earth elements and iron. The separation of alkali and alkaline earth elements will be reported eleswhere[11], and the separation of iron and fission products is reported here; this is particularly important for the determination of fission products in natural waters. As shown in Fig. 9, the ferric ion is completely eluted before thymol blue indicator in the effluent changes from red to yellow. By using the buffer solution of pH 3.2, the ferric ion can be eluted long before cesium is eluted.

Summary

The essential point of this method is the use of the formate buffer solution. This method would be used for the analysis of fission products in natural waters and for the preparation of pure and carrier-free radioactive elements from mixed fission products.

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[11] H. Tsubota and Y. Kitano, This Bulletin, 33, 770 (1960).