*A Rapid Method for Determining Alkali and Alkaline Earth Elements Using an Ion Exchanger**

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The present authors previously reported[1] that fission products can be separately eluted more easily and rapidly by using a buffer solution of formic acid and ammonium formate as the elutriant than by using any other elutriants. As reported in that paper, even when fission products in a sample coexist with large amounts of other elements or carriers, they can be completely separated.

Many researchers have separated alkali metals[2-7] and alkaline earth elements[8-10] by using an ion exchanger. They have tried to analyse a mixture of alkali and alkaline earth elements containing other metal ions by using an ion exchange resin; moreover, separation of sodium, potassium, magnesium and calcium ions, which are abundant in nature, has been successful[6,11,12]. They did not, however, include in their experiments such rare elements as cesium or barium. Without including the cesium ion in their experiments, some researchers have stated that univalent ions and divalent ions can easily be separated with an ion exchanger[13,14]. However, the separation between cesium and magnesium ions would be difficult because the cesium ion is eluted last among alkali metals and the magnesium ion is eluted first among alkaline earth elements. The authors conducted systematic experiments on these elements with an ion exchanger and finally succeeded by using the buffer solution of 1 M formic acid and 1 M ammonium formate (the formate buffer solution).

Experimental and Discussion

Selection of an Elutriant.—Separation of alkali metals from alkaline earth metals has been conducted by using hydrochloric acid as an elutriant, when cesium was not included. To find out whether efficient separation can be realized when cesium is present, the following experiment was carried out. 0.1∼1 meq. of potassium, cesium and magnesium ions, respectively, were mixed and passed into the column, Dowex 50, X12, 200∼250 mesh, 1.1×15 cm., H$^+$-saturated resin, (exchange capacity, ca. 37 meq.), and eluted chromatographically with 1 N hydrochloric acid or 0.5 N hydrochloric acid at the flow rate of 1 ml./min. The effluent was divided into 10 ml. fractions. After evaporation of the fractions potassium and cesium in each fraction were determined from chloride content using silver nitrate standard solution and fluorescent indicator, and magnesium was determined by EDTA standard solution and Eriochrom Black T(EBT) indicator after the pH of the fractions had been adjusted to 10 with ammonium hydroxide.

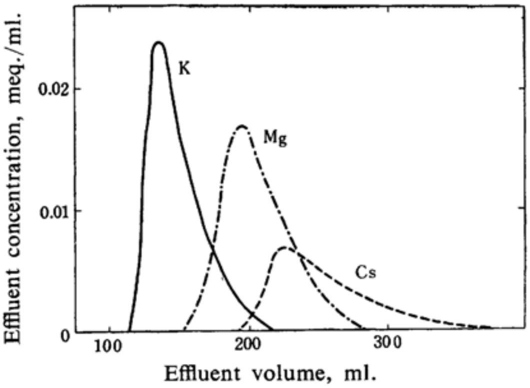

Fig. 1. Elution curves of K$^+$, Cs$^+$ and Mg^{2+} with HCl.
Column: Dowex 50, X12, 200∼250 mesh, 1.1×15 cm.
H$^+$-saturated resin.
Elutriant: 1.0 N HCl.
Flow rate: 1.0 ml./min.

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

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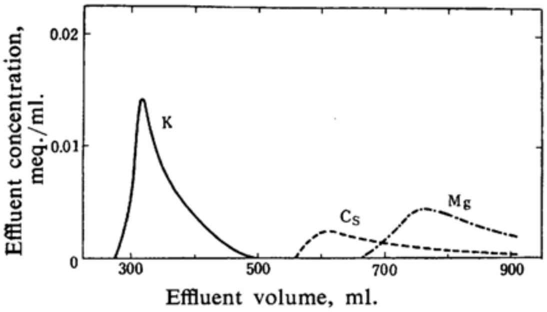

Fig. 2. Elution curves of K^+, Cs^+ and Mg^{2+} with HCl.
Column: Dowex 50, X12, 200~250 mesh, 1.1×15 cm.
H^+-saturated resin.
Elutriant: 0.5 N HCl.
Flow rate: 1.0 ml./min.

When 1 N hydrochloric acid is used, potassium and cesium can be partially separated from each other, but magnesium and cesium can not be separated at all although magnesium begins to be eluted shortly before the elution of cesium (Fig. 1). When 0.5 N hydrochloric acid is used, potassium and cesium can be separated completely, but cesium and magnesium can not be separated although cesium begins to be eluted shortly before the elution of magnesium (Fig. 2). Based on these results, it can be concluded that, when cesium and magnesium are to be separated completely, a much longer column and a larger amount of a very dilute hydrochloric acid must be used. In other words, hydrochloric acid is not a practical elutriant for separating cesium from magnesium. The effect of the concentration of hydrochloric acid on the elution of magnesium, as seen in Figs. 1 and 2, can be understood by the fact that the magnesium ion forms $MgCl^+$ complex ion with the chloride ion. Therefore, in order to separate magnesium from cesium, it is essential to use an acid or salts other than chloride. As previously reported[1], when a formate buffer solution was used as the elutriant, cesium and magnesium were completely separated. This elutriant could be prepared and preserved easily and after-treatment of the effluent was done easily because ammonium formate could be sublimed easily and completely. Thus, it was decided to use the formate buffer solution as the elutriant, and separation of elements by using the buffer solution was examined.

Examination of Methods for Analyzing Alkali and Alkaline Earth Elements. — (A) *Alkali metals.*—The following two methods were used for determination of alkali metal ions in an effluent.

i) When an effluent containing alkali metals is evaporated and the residue is heated with infrared lamp or electric heater to remove ammonium formate completely, only alkali formate remains. A small amount of hydrochloric acid is added to the alkali formate and evaporation is repeated. The chloride content of the residue is determined by silver nitrate standard solution and fluorescent indicator;

TABLE I. THE EFFECT OF AMMONIUM FORMATE ON THE DETERMINATION OF ALKALI IONS BY SILVER NITRATE TITRATION METHOD

Metal	Added, mg.	Method of evaporation	Found, mg.		
Na^+	3.63	Water bath	3.93	5.60	
	3.63	Infrared lamp	3.63	3.65	
	3.63	Heat after using water bath	3.63	3.62	3.63
K^+	7.53	〃	7.55	7.53	7.57

TABLE II. THE EFFECT OF AMMONIUM FORMATE ON THE DETERMINATION OF ALKALI IONS BY FLAME PHOTOMETRIC METHOD

Metal	Wavelength	Added, p. p. m.	Brightness of flame in various solutions		
			H_2O	0.5 M NH_4HCOO	1 M NH_4HCOO
Li^+	671 mμ	10~100	100	100±1	99±1
Na^+	589	10~100	100	100±1	99±1
K^+	766	10~100	100	100±1	99±1
Rb^+	420	10~100	100	100±5	100±5
Cs^+	455	10~100	100	100±5	100±5

Apparatus: Shimadzu-flame photometer, Type QB-50.
Fuel: H_2 gas
The brightness of ions in distilled water are set on 100.

TABLE III. THE EFFECT OF AMMONIUM FORMATE ON THE DETERMINATION OF ALKALINE EARTH IONS WITH EDTA

Metal	Indicator	Added, meq.	Found, meq. (average) in various solutions			
			H_2O	0.1 M NH_4HCOO	1 M NH_4HCOO	2 M NH_4HCOO
Mg^{2+}	E. B. T.	0.225	0.225	0.225	0.224	
Ca^{2+}	E. B. T.	0.108	0.108	0.108	0.108	
Sr^{2+}	E. B. T.	0.165	0.165	0.165	0.164	*
	P. C.		0.164	0.165	0.165	*
Ba^{2+}	E. B. T.	0.148	0.15**	0.15*	0.15**	*
	P. C.		0.148	0.148	0.149	*

E. B. T.: Eriochrom Black T

P. C.: Phthalein Complexone

* : End point of titration can not be detected.

**: End point is not clear.

then, alkali content can be determined from the chloride content. The results are shown in Table. I.

ii) Alkali content in an effluent is determined directly by flame photometric method. The effect of a large amount of ammonium and formate ions upon the determination of alkali metals must be carefully examined. As given in Table II, however, interference of ammonium formate is not found in 0.5 M ammonium formate solution, and is found slightly in 1.0 M.

(B) *Alkaline earth elements.*—Alkaline earth elements are titrated by EDTA solution containing the magnesium ion using EBT indicator. The formate ion does not interfere, as shown in Table III. It is necessary to adjust pH over 9.5 for the titration with EDTA. As the effluent has a buffer action, the use of an indicator will be preferable, since it does not obscure the end point of the titration by EDTA and changes its color at pH 9.5. Thymol blue indicator satisfies the conditions. One drop of 0.1% water solution of thymol blue is added to an effluent to be titrated, and ammonium hydroxide is added until the color of the solution changes from yellow to blue and then the solution is titrated by EDTA with EBT indicator. As shown in Table IV, the values obtained by EDTA titration are about 1% lower than the added values, and therefore the observed value must be corrected. In some cases strontium and barium are determined by EDTA standard solution and phthalein-complexone indicator.

TABLE IV. THE EFFECT OF pH-INDICATOR ON THE DETERMINATION OF ALKALINE EARTH IONS WITH EDTA

Sample solution: Mg^{2+} is contained in 50 ml. of 0.5 M ammonium formate solution.

pH-indicator: 0.1% Thymol Blue-water solution; 1 drop

Metal chelate indicator: Eriochrom Black T

Added; meq., Mg^{2+}	Found; meq., Mg^{2+}	Error, %
0.022_5	0.022_3	−0.9
0.045_0	0.044_5	−1.1
0.067_5	0.067_0	−0.7
0.090_0	0.089_0	−1.1
0.112_5	0.111_5	−0.9
0.135_0	0.133_5	−1.1
0.157_5	0.156_0	−1.0
0.180_0	0.178_0	−1.1
0.202_5	0.200_0	−1.2
0.225_0	0.223_5	−0.7

Examination of Conditions for the Separation of Alkali and Alkaline Earth Elements.—It is desirable to use a short column and a small

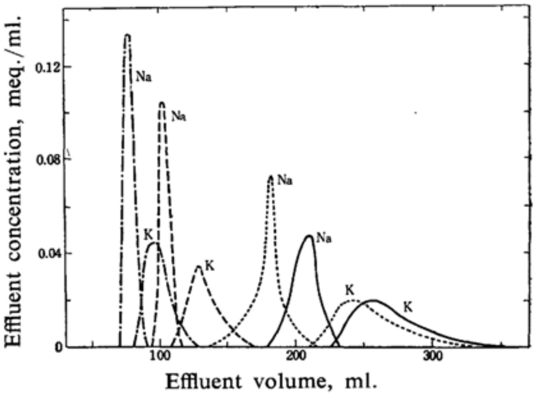

Fig. 3. Elution curves of Na^+ and K^+.

Column: Dowex 50, X8, 100～150 mesh, 1.1×8 cm.

Flow rate: 1.0～1.1 ml./min.

Resin form and elutriant:

—— H^+-saturated resin, with 0.1 M ammonium formate solution

…… NH_4^+-saturated resin, with 0.1 M ammonium formate solution

---- H^+-saturated resin, with 0.2 M ammonium formate solution

-·-·- H^+-saturated resin, with the buffer solution, pH 3.2

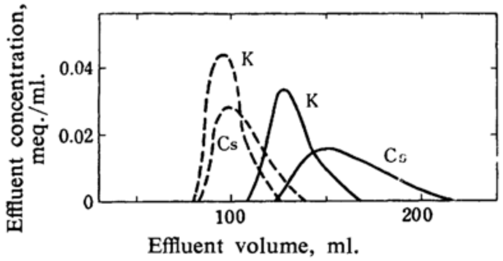

Fig. 4. Elution curves of K^+ and Cs^+.
Column: Dowex 50, X8, 100～150 mesh, 1.1×8 cm., H^+-saturated resin.
Flow rate: 1.0 ml./min.
Elutriants:
—— 0.2 M ammonium formate solution.
---- the buffer solution, pH 3.2.

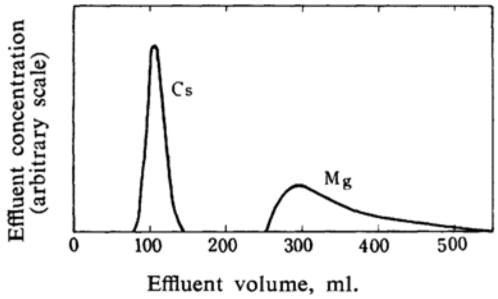

Fig. 5. Elution curves of Cs^+ and Mg^{2+}.
Column: Dowex 50, X8, 100～150 mesh, 1.1×8 cm., H^+-saturated resin.
Elutriant: the buffer solution, pH 3.2.
Flow rate: 0.50 ml./min.

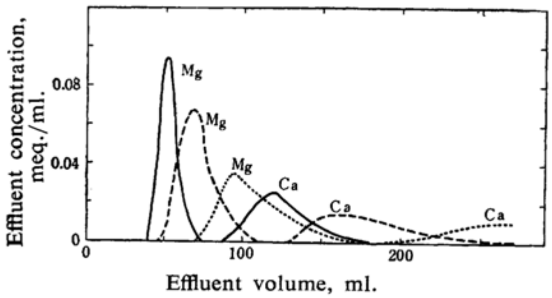

Fig. 6. Elution curves of Mg^{2+} and Ca^{2+}.
Column: Dowex 50, X8, 100～150 mesh, 1.1×8.5 cm., H^+-saturated resin.
Folw rate: 0.40～0.50 ml./min.
Elutriant: —— the buffer solution, pH 4.0
---- the buffer solution, pH 3.8
······ the buffer solution, pH 3.6

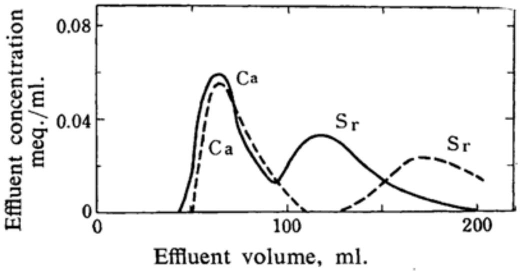

Fig. 7. Elution curves of Ca^{2+} and Sr^{2+}.
Column: Dowex 50, X8, 100～150 mesh, 1.1×8.5 cm., H^+-saturated resin.
Flow rate: 1.0 ml./min.
Elutriant: —— the buffer solution, pH 4.2
---- the buffer solution, pH 4.1

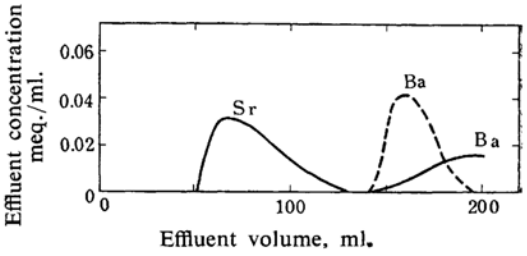

Fig. 8. Elution curves of Sr^{2+} and Ba^{2+}.
Column: Dowex 50, X8, 100～150 mesh, 1.1×8.5 cm., H^+-saturated resin.
Flow rate: 1.0 ml./min.
Elutriant:
—— the buffer solution, pH 4.5.
---- 2 M ammonium formate solution.

amount of elutriant for separation. To decide a suitable elutriant to be used with a column of Dowex 50, X8, 100～150 mesh, 1.1×8 cm., H^+-saturated resin, (exchange capacity, ca. 17 meq.), and at rate of 2～3 ml./min., elution curves were made as follows: An effluent was divided into fractions of 5～10 ml. and elements in each fraction were determined by the same method as shown above. The results are as follows:

(A) Separation of alkali metals.—It is known that separation factors of sodium, potassium and ammonium in cationic resin of sulphonic type are increased according to the series: sodium < ammonium < potassium. It is, therefore, expected that sodium and potassium can be easily separated when ammonium salt is used as an elutriant. Fig. 3 shows the elution curves of sodium and potassium when ammonium formate solution and the formate buffer solution are used. The separation of potassium and cesium, however, can not be conducted with this buffer solution, as shown in Fig. 4.

(B) Separation of cesium and magnesium.—As shown in Fig. 5, cesium and magnesium can be separated completely from each other by using the formate buffer solution having pH 3.2.

(C) Separation of alkaline earth elements.—The elution curves of magnesium and calcium, as shown in Fig. 6, are obtained when the formate buffer solutions of various pH are used as an elutriant. From Fig. 6, it can be seen

that magnesium and calcium can be easily separated by the buffer solutions. As shown in Fig. 7, calcium and strontium can be separately eluted by the buffer solution having pH 4.1. Finally, to separate strontium and barium, strontium is first eluted by the buffer solution of pH 4.5, and then barium is eluted by 2 M ammonium formate solution, as shown in Fig. 8.

(D) Separation of alkali and alkaline earth elements.—To separate completely alkali and alkaline earth elements, a column of 10 cm. in length may be used. This column length was determined by the plate theory⁶⁾ for two ions, sodium and potassium ions which are most difficult to separate in the above experiments.

Sodium and potassium can be separately eluted by using 0.1 M ammonium formate solution. For an early start of elution of sodium, 0.2 M ammonium formate solution may be passed through a column before 0.1 M ammonium formate solution is passed.

To separate potassium and cesium with the formate buffer solution, it is necessary to use a very long column and a large amount of the elutriant. Therefore first it was better to elute

TABLE V. DETERMINATION OF IONS IN MIXTURES

No.		Na^+	K^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
1	Added, meq.	0.481	0.493		0.450	0.434	0.412	0.403
	Found, meq.	0.491	0.488		0.453	0.432	0.424	0.40
	Error, %	+2.3	−1.0		+0.7	−0.5	+2.9	
2	Added, meq.	0.961	0.987	0.498	0.450	0.469	0.412	0.403
	Found, meq.	0.953	1.491		0.451	0.466	—	0.40
	Error, %	−0.8	+0.4		+0.2	−0.6		
3	Added, meq.	0.481	0.493	0.498	0.450	0.469	0.412	0.403
	Found, meq.	0.470			0.448	0.472	0.397	0.40
		(0.009)	(0.495)	(0.488)				
	Error, %	−2.3			−0.4	+0.6	−3.6	
		(−0.4)	(+0.4)	(−2.0)				
4	Added, meq.	0.961	0.987	0.498	0.450	0.469	0.412	0.403
	Found, meq.	0.965			0.451	0.469	—	0.40
		(0.000)	(0.982)	(0.495)				
	Error, %	+0.5			+0.2	−0.0		
			(−0.5)	(−0.6)				

The values in parenthesis are obtained by resorping the K^+ and Cs^+ fraction in longer column (1.1×15 cm.) and eluting with 0.5 N HCl separately (as shown in Fig. 2).

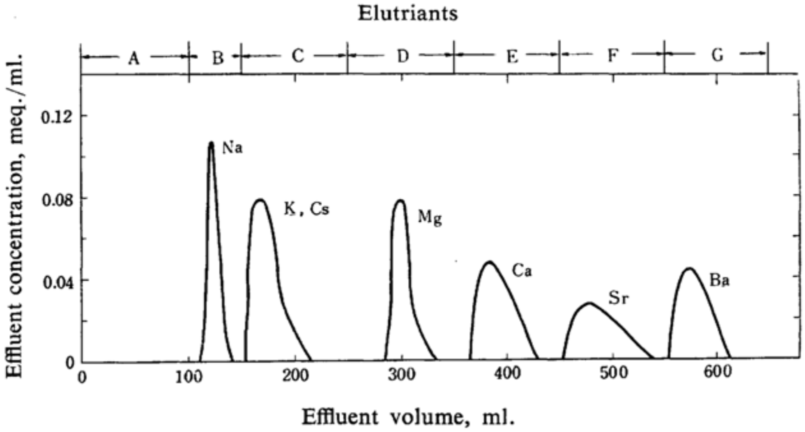

Fig. 9. Elution of alkali and alkaline earth elements.

Column: Dowex 50, X8, 1.1×10 cm., 100~150 mesh, H^+-saturated resin.

Flow rate: 2 ml./min.

Elutriants: **A** 0.2 M ammonium formate solution, **B** 0.1 M ammonium formate solution, **C** the buffer solution, pH 3.2, **D** the buffer solution, pH 4.0, **E** the buffer solution, pH 4.1, **F** the buffer solution, pH 4.4, **G** 2 M ammonium formate solution.

both simultaneously with the formate buffer solution of pH 3.2, and then to separate potassium and cesium by resorption and chromatographic elution with 0.5 N hydrochloric acid.

Cesium and magnesium can be separated by the formate buffer solution having pH 3.2. And the separation of magnesium, calcium, strontium and barium can be conducted by using the same buffer solution with different pH.

Using the column of Dowex 50, X8, or Amberlite IR-120, 100~150 mesh, 1.1×10 cm., and H^+-saturated resin, (exchange capacity, ca. 21 meq.), 0.5~1 meq. of sodium, potassium, cesium, magnesium, calcium, strontium and barium ions, respectively, are separated at a flow rate of 2~3 ml./min. The results are shown in Fig. 9 and Table V. Alkali and alkaline earth elements can be successfully separated from each other by the procedure shown in Fig. 9.

Summary

Alkali and alkaline earth elements, including their rare elements, can be separately eluted easily, rapidly and completely by the elutriants here described. This procedure and its modified procedures* can be applied to routine analysis of natural waters.

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* The modified procedures will be reported elsewhere.