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Separation of Barium and Radium as Their TTA-complexes by Extraction Chromatography

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Synopsis. Satisfactory separation of a trace amount of radium from miligram amount of barium was attained on a column of 1.5 M TTA–MIBK (Daiflon) system. An HETP value as low as 0.47 mm was obtained with a column $0.98\phi \times 30$ cm at flow rate of 0.17 cm³ per minute. Distribution ratio of radium estimated from this column technique was compatible with the liquid-liquid extraction data.

Solvent extraction of radium has been investigated in several extraction systems in view of synergistic effect.[1–3] However, no report seems to have appeared on the separation of radium from barium matrix, because of their similar chemical properties. The separation of tracer level radium from barium matrix is desirable in view of not only analytical chemistry but also geochemistry.

Akaza studied the extraction of barium, strontium, calcium, and magnesium with 2-thenoyltrifloworoacetone (TTA)–methyl isobutyl ketone (MIBK),[4,5] the results being extended to extraction chromatography.[5,6] In this note, a further application of the same TTA–MIBK extraction system to radium(II), the extraction chromatographic separation of radium from miligram amounts of barium, and separation of alkaline earth metal ions involving radium are described.

Experimental

Radioactive Tracers. ^{140}Ba ($t_{1/2}$=12.8 d) was used as a tracer of barium. ^{223}Ra ($t_{1/2}$=11.68 d) was obtained from ^{227}Ac by milking.

Batch Extraction of Radium(II) in TTA–MIBK. A buffer solution consisting of 0.5 M ammonium acetate–aqueous ammonia–acetic acid was employed to adjust the pH of the aqueous solution. The final pH of extraction was measured immediately after the two phases had been separated, whereas γ-activity of ^{223}Ra in each phase was counted with a NaI(Tl) scintillation counter 6 h after the separation.

Column Preparation. The column was prepared by the method previously reported.[6] A glass chromatographic column with water jacket was employed to keep the column temperature constant.

Test Solutions and Eluting Solutions. Fifty mililiters of the test solution which has a similar composition to that of eluting solution was used for the column experiment. Eluting solutions were prepared by the method reported.[6]

A fraction collector was employed to collect an adequate fraction of the eluate. In some cases, a microtube pump, Tokyo Rikagakukikai Co., Model MP-11, was used to feed a solution on the column. Tigon tube was employed for solution transport.

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Results and Discussion

The extraction of radium as TTA-complex into MIBK was carried out with TTA in various concentrations. The results are shown in Fig. 1. Quantitative extraction was attained at pH 6.5< in 1.5 M TTA–MIBK, these conditions being preferable for the separation of relatively large amounts of alkaline earth metal ions from each other. The half extraction pH ($pH_{1/2}$) of radium(II) could be estimated as 6.0 in the same system, and that of barium as 5.2 from the previous data.[4] Thus, the difference between $pH_{1/2}$ values suggests the possibility of the separation of barium and radium as their TTA-complexes by extraction chromatography.

The separation of alkaline earth metal ions involving radium(II) was carried out on a 1.5 M TTA–MIBK column ($0.98\phi \times 19$ cm). The results are shown in Fig. 2. First, radium and barium were eluted with a solution of pH 6.5, giving some overlapping of two elution curves, secondly, strontium and calcium were eluted with a solution of pH 5.5, and finally magnesium with 0.1 M hydrochloric acid. The concentration of each metal ion in each fraction was determined by γ-counting for radium and barium and by atomic absorption spectrophotometry for strontium, calcium and magnesium, respectively. The results, except for radium, are in line with those reported.[5] ^{140}La was caught firmly on the column and eluted down together with magnesium (Fig. 2).

In order to achieve complete separation between radium and barium, the column was replaced by a longer one ($0.98\phi \times 30$ cm, $0.98\phi \times 40$ cm, and $0.97\phi \times 42$ cm). Figure 3 shows the results obtained.

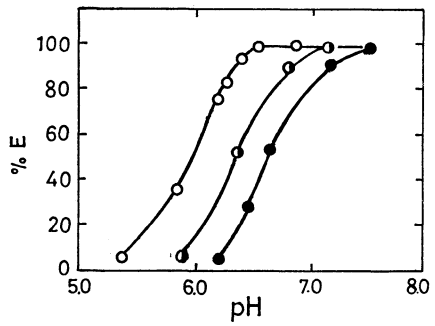

Fig. 1. Extraction curves of radium(II) with TTA in MIBK.
Aqueous phase: 10 cm³ of 0.5 M buffer solution, organic phase: 10 cm³, 1.5 M TTA-MIBK —○— 0.5 M TTA-MIBK —◑— 0.2 M TTA-MIBK —●—, shaking time: 30 min.

Table 1. Performance of the 1.5 M TTA-MIBK column

Column	Column size		D(pH 6.7)	N	HETP (mm)
(a)	0.98ϕ×30 cm	Ra	51±3	650±30	0.47±0.02
		Ba[a)]	126±5	840±40	0.36±0.03
(b)	0.98ϕ×40 cm	Ra	44±2	675±30	0.59±0.02
		Ba[a)]	93±5	773±40	0.52±0.03
(c)	0.97ϕ×42 cm	Ra	48±2	560±30	0.75±0.02
		Ba[b)]	105±5	815±40	0.52±0.03

Void volum; (a) 9±2 cm³, (b), (c) 12±2 cm³. a) Ba 0.5 mg. b) Ba 5.0 mg.

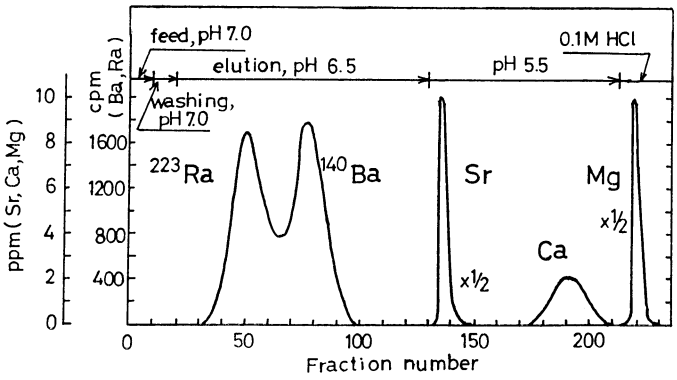

Fig. 2. Separation of alkaline earth metal ions on 1.5 M TTA-MIBK column.
Metal, loaded: 0.5 mg each (except radium), Daiflon: 5.5 g, one fraction: 5.0 g stationary phase: 7.8 cm³, temp: 20±1 °C column size: 1.0ϕ×19 cm flow rate; feed and washing: 0.2—0.3 cm³·min⁻¹ elution: 0.5 cm³·min⁻¹.

A test solution of pH 7.5 and an eluting solution of pH 6.7 were used, the flow rate of elution being 0.17-cm³ min⁻¹. Under these conditions excellent separation of trace radium(II) could be achieved from 0.5 mg, of barium(II) (Figs. 3 (a) and (b)), and also from 5.0 mg of barium(II) (Fig. 3 (3)). From these column experiments, distribution ratios of radium and barium ions were estimated (Table 1) by the well-known relation of $D=(E-F)/B$, where E is the volume of effluent in relation to the maximum of the eluted metal concentration, F the void volume of the column, and B the volume of the stationaly phase. The distribution ratio of radium shown as 44, 48, and 51 in Table 1 is somewhat large, but roughly compatible with the value 30 obtained in the liquid-liquid extraction under the same extraction pH. In order to elucidate the performance of extraction column in Fig. 3, a number of theoretical plates of column (N) and height equivalent to a theoretical plate (HETP) were estimated. N is given by the equation $N=E(E-F)/S^2$, where S is half width (ml) at 0.607 peak maximum. HETP is given by the column length divided by N. Thus the HETP value as low as 0.47 mm could be maintained on the column 0.98ϕ×30 cm long.

The elution of alkaline earth metal ions proceeds in the order of light element in conventional cation-exchange chromatography. However, elution takes place in the reversed order in extraction chromatography. Thus, the latter is appropriate for a precise

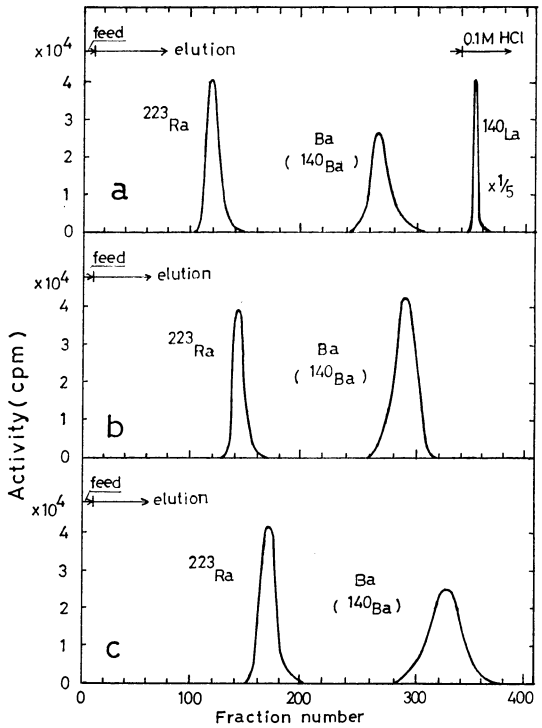

Fig. 3. Separation of barium and radium on 1.5 M TTA-MIBK column.
One fraction: 5.0 cm³, temp: 18±1 °C flow rate; feed: 0.1 cm³·min⁻¹, pH 7.5 elution: 0.17 cm³·min⁻¹, pH 6.7
(a) Column size: 0.98ϕ×30 cm, barium loaded: 0.5 mg Daiflon: 9.0 g, stationary phase 10.4 cm³, (b) column size: 0.98ϕ×40 cm, barium, loaded: 0.5 mg Daiflon: 12.0 g, stationary phase 15 cm³, (c) column size: 0.97ϕ×42 cm, barium loaded: 15.0 mg Daiflon: 12.0 g, stationary phase 15 cm³.

and delicate separation of trace amount of radium from other alkaline earth metals or barium matrix.

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