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ISOTOPE EFFECTS OF STRONTIUM IN CROWN ETHER CHROMATOGRAPHY

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ABSTRACT

A fundamental study was made on the chromatographic separation of strontium isotopes with the polymer-supported crown ether resin. Hydrochloric and nitric acids were chosen as the eluent solutions. In each of these systems, the heavier isotopes had been enriched in the front part of the strontium adsorption band. This result means that the heavier isotopes are preferentially fractionated into the solution phase. The largest single-stage separation coefficient (ϵ) for the ^{84}Sr and ^{88}Sr pair, 5.5×10^{-4} , was obtained with hydrochloric acid elution at 35°C. The observed separation coefficients from one-step separation procedures are much larger than those of ion exchange separation systems but smaller than those of crown ether extraction systems. Odd/even or anomalous isotope effects were not observed in the strontium-crown systems studied to date.

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INTRODUCTION

In 1976, Jepson and Dewitt (1) studied the separation of calcium isotopes by using 18-crown-6 compounds. The observed separation factor (α) for the ^{44}Ca and ^{40}Ca pair was $1.0010 (\pm 0.0002)$. Since then, many studies on the isotope effects of crown ethers have been carried out. Knöchel and Wilken studied sodium isotope effects with many macrocyclic polyethers, including crown ethers (2). Several researchers used chromatographic techniques to study isotope effects in crown-ether complex formation. Schmidhalter and Schumacher separated potassium isotopes by using dicyclohexyl-18-crown-6 as the eluent and obtained $\varepsilon = 0.00118 (\pm 0.00005)$ as the separation coefficient at -10°C (3). Kim et al. synthesized 15-crown-5 resin and used it in a chromatography column to separate lithium isotopes; $\alpha = 1.053 (\pm 0.005)$ (4). In 1990, Jepson and Evans carried out calcium isotope separation by column technique with a polymer-bound 18-crown-6 and obtained $\varepsilon = 0.0025 (\pm 0.0003)$ for the ^{40}Ca and ^{44}Ca pair (5).

Nishizawa et al. reported the isotope effects in liquid-liquid extraction with crown ethers and chromatography with cryptands. By using these processes, Nishizawa et al. determined isotope separation factors for many elements such as lithium (6), magnesium (7), nickel (8), zinc (9), strontium (10), and barium (10,11). They claimed that anomalous isotope effects of odd/even and spin dependence were found in these crown ether extraction systems. The odd/even isotope anomaly effect was observed at SrCl_2 concentrations above 2 M with 18-crown-6 compounds at $293.2 \pm 0.5 \text{ K}$ (10). The odd/even staggering isotope effects in chemical processes were first observed in the study on U(IV)-U(VI) chemical exchange achieved through the use of an ion exchange resin (12). Recently, the anomalous isotope effects were seen in Gd ion-exchange chromatography (13). The ion-exchange chromatographic technique is suitable for detecting small deviations in separation coefficients.

A number of studies have been done on the single-stage separation factors of isotopes with crown ethers in liquid-liquid extraction. Unlike column chromatography, a simple liquid-liquid extraction process is difficult to set up into a multi-stage system. For practical isotope separation, the isotopic anomalies, such as odd-even effects, must be considered in the column design. Because strontium has three even mass-number isotopes (^{84}Sr , ^{86}Sr , and ^{88}Sr) and one odd mass-number isotope (^{87}Sr), the odd/even isotope effects may be found in the chromatographic isotope separation with crown ether resin.

Recently, a strontium-selective 18-crown-6 resin named Sr-Spec was synthesized and commercially available. This resin effectively adsorbed and separated radioactive strontium (^{90}Sr) from other alkali, including alkaline earth metals, and a few actinide ions. A fast and convenient detection for ^{90}Sr in milk has been developed using Sr-Spec (14). In the present work, strontium isotope effects are studied by chromatographic technique with Sr-Spec.



EXPERIMENTAL DESIGN

Resin and Reagents

A commercially available crown ether resin, Sr·Spec, was purchased from Eichrom Technologies, Inc. (Darien, IL). The resin was produced by sorbing 4,4'(5')-Bis(*t*-butylcyclohexano)-18-crown-6 in a polymeric porous adsorbent (15). The particle size of this resin is 100–125 μm . All reagents used were of analytical grade and were used without further purification.

Chromatographic Operation

Four column experiments were performed. The conditions of each run are listed in Table 1. In runs 2 and 3, two glass columns (30 and 100 cm long), and in run 4 three glass columns (100 cm long) were connected in series with polytetrafluoroethylene (PTFE) tubes of 1 mm i.d. The i.d. of each column was 0.8 cm. A total of 5.3 g of Sr·Spec resin was packed in each 30 cm column, and 18 g of Sr·Spec resin was packed in the 100 cm column. The schematic diagram of the column system is shown in Fig. 1.

Prior to each experiment, the resin was treated with pure water to remove impurities. The washed resin was conditioned with 3 M HNO_3 in runs 1 and 2, and with 2 M HCl in runs 3 and 4. In runs 1 and 2, 0.1 M Sr^{2+} in 3 M HNO_3 was fed into the 30 cm column, and the adsorbed Sr^{2+} ions were eluted with 3M HNO_3 . In run 3, adsorption chromatography was performed with a feed solution of 0.1 M Sr^{2+} ions in 2 M HCl . To consider the effects of Sr concentration on the separation coefficient, the dilute solution of 0.01 M Sr^{2+} in 2 M HCl was used in run 4, where the adsorbed Sr ions were eluted with 1.8 M HCl . The solutions were fed into the columns by a high-pressure pump that created a flow rate of 0.33 cm^3/min in every experimental run. The operating temperature was $35 \pm 2^\circ\text{C}$ and was controlled by circulating the temperature-regulated water through the column jackets.

Table 1. Experimental Conditions

	Run 1	Run 2	Run 3	Run 4
Migration length (cm)	30	130	130	300
Feed solution	0.1 M Sr in 3 M HNO_3	0.1 M Sr in 3 M HNO_3	0.1 M Sr in 2 M HCl	0.01 M Sr in 2 M HCl
Eluent	3 M HNO_3	3 M HNO_3	—	1.8 M HCl
Temperature ($^\circ\text{C}$)	35 ± 2	35 ± 2	35 ± 2	35 ± 2
Flow rate (ml/min)	0.33	0.33	0.33	0.33
Band velocity (cm/min)	0.30	0.33	0.69	0.73



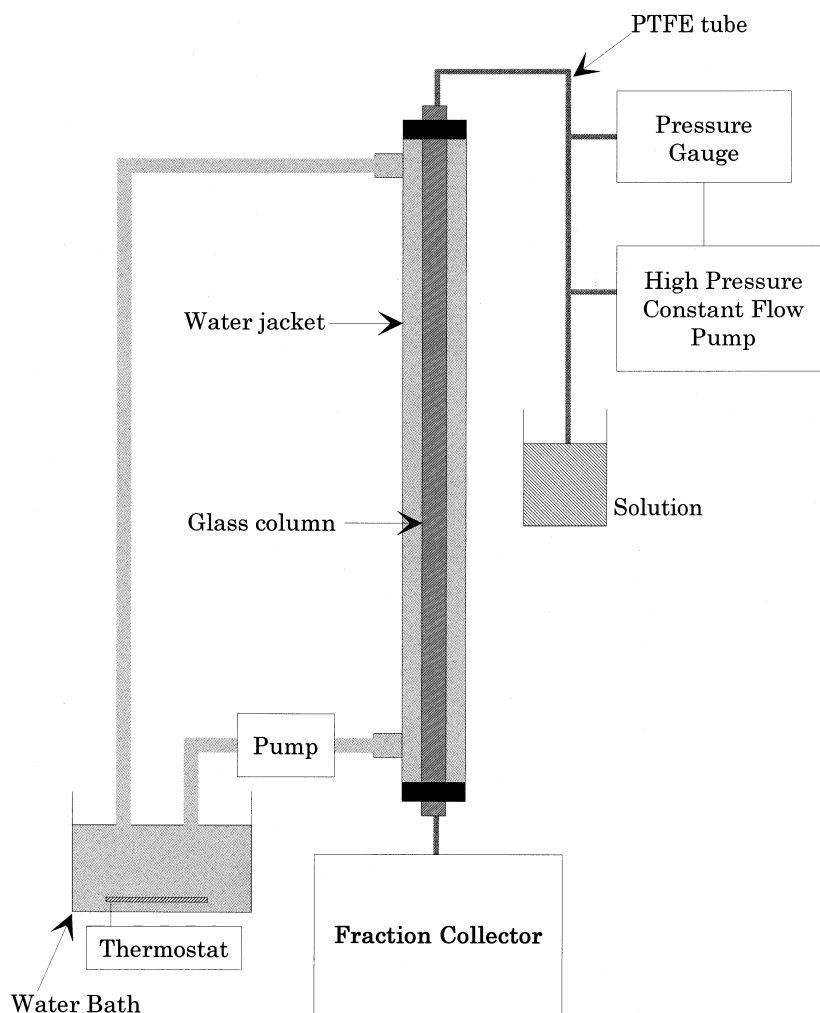


Figure 1. Schematic of separation column system.

Analysis

The concentration of strontium in the effluent fractions was determined by high performance liquid chromatography (IC-500S, Yokogawa-Hokushin, Musashino-city, Tokyo, Japan) in runs 1–3 and by flame analysis (SAS/727, Daini-Seikosha, Matsudo-city, Chiba, Japan) in run 4. The isotopic ratios of $^{84}\text{Sr}/^{88}\text{Sr}$, $^{86}\text{Sr}/^{88}\text{Sr}$, and $^{87}\text{Sr}/^{88}\text{Sr}$ in samples taken from the front and rear parts of the adsorption strontium band were measured by using a mass spectrometer



MAT261 (Finnigan MAT, Bremen, Germany) with a double-filament surface ionization source. The sample ionization unit of the mass spectrometer consists of two rhenium filaments; one of them is an ionizing filament (I.F.) and the other is a vaporizing filament (V.F.). An aliquot of the sample solution containing 2–5 μg strontium in the form of $\text{Sr}(\text{NO}_3)_2$ was loaded on the V.F. and dried by charging electricity in the V.F. under atmospheric pressure. Then the sample ionization unit with the V.F. was placed in the ion source of the mass spectrometer. Thereafter electric current was passed through the I.F. and V.F. filaments. Naturally occurring strontium has four stable isotopes, ^{84}Sr (0.56 atom %), ^{86}Sr (9.86 atom %), ^{87}Sr (7.00 atom %) and ^{88}Sr (82.56 atom %). Rubidium and krypton have stable isotopes of ^{84}Kr , ^{86}Kr , and ^{87}Rb ; these isotopes overlap the atomic mass numbers of strontium isotopes. Because krypton is a rare gas, it does not affect strontium mass spectrometry analysis. However Rb is easily ionized due to its relatively low ionization potential and ^{87}Rb can be found with ^{87}Sr in mass spectrometry analysis. The existence of ^{87}Rb in samples was monitored with ^{85}Rb in which mass spectrometric peaks do not overlap with those of strontium isotopes. Thus, strontium mass spectrometric analysis was initiated when the ^{85}Rb beam intensity became small and negligible, which occurred after heating the I.F. at approximately 3 A and V.F. at approximately 0.6 A for 1 hour.

RESULTS AND DISCUSSION

Chromatograms and Strontium Adsorption

The concentration profiles of the eluted strontium adsorption band and the measured isotopic ratios are presented in Figs. 2–5. The breakthrough volumes of runs 1 and 2 are proportional to the column lengths. However, although the columns were of the same length, the breakthrough volumes were different between runs 2 and 3. Sr·Spec adsorbs strontium more effectively in the nitric acid system than in hydrochloric acid system. The distribution factor of Sr ions in the HCl eluent system is estimated to be almost one-half of that in HNO_3 eluent system.

The total adsorption of strontium in the adsorption medium (Q) is given by the following equation:

$$Q = C_0 (V_{\text{FB}} - V_{\text{d}}) \quad (1)$$

where C_0 is the concentration of Sr in the feed solution; V_{FB} is the volume of the breakthrough point, where the concentration is $C_0/2$; and V_{d} is the dead volume (void volume) of the column. The experimental values of the total adsorptions calculated from Eq. (1) were as follows: 2.5 mmol (run 1), 10 mmol (run 2), 3.1 mmol (run 3), and 0.63 mmol (run 4). One gram of Sr·Spec can maximally adsorb approximately 0.43 mmol of strontium because the resin contains approximately 0.43 mmol of 18-crown-6 compounds per gram (15). Hence, the theoretical value



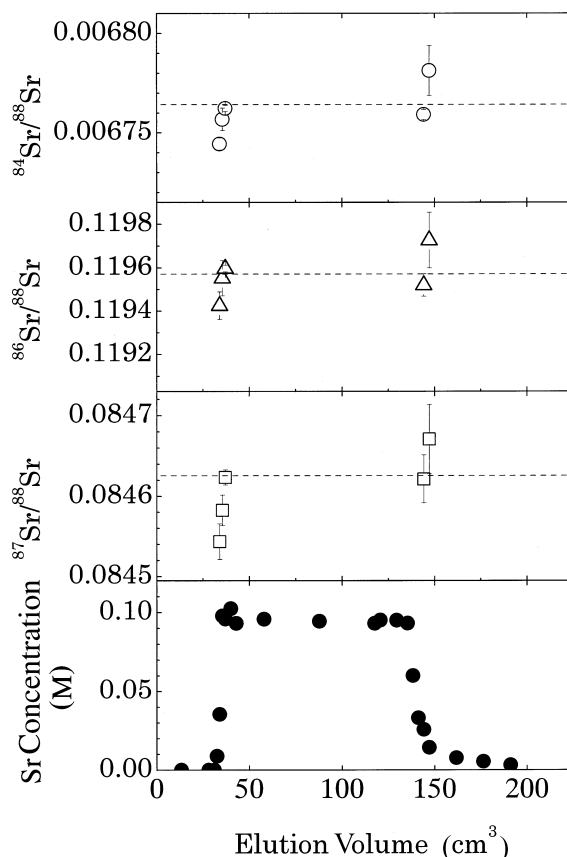


Figure 2. Chromatogram and the isotopic ratios of the effluent fractions for run 1. Measured isotopic ratios are denoted by $^{84}\text{Sr}/^{88}\text{Sr}$ (\circ), $^{86}\text{Sr}/^{88}\text{Sr}$ (\triangle), and $^{87}\text{Sr}/^{88}\text{Sr}$ (\square), respectively. The horizontal dotted lines indicate the natural abundance feed-isotopic ratios for each isotope pair.

of the adsorption capacity were calculated as 2.3 mmol, 10 mmol, 10 mmol and 23 mmol for runs 1, 2, 3, and 4, respectively. The experimental values of runs 1 and 2 were almost the same as the theoretical values; however, the experimental values of runs 3 and 4 were smaller than the theoretical values. These results show that theoretical adsorption values can be obtained in the nitric acid system.

Because the breakthrough points of the front boundaries are 67cm^3 in run 3 and 155cm^3 in run 4, the breakthrough points appear proportional to column length and were not dependent on the concentration of Sr ions in the feed solutions. This suggests that the adsorption mechanism of Sr^{2+} on the resin in an HCl solution is quite different from that observed in ion exchange chromatography and is similar



to the separation found using solvent extraction. When the distribution factor is large and solvent extraction is used, adsorption is easily attained, but elution becomes difficult. The nitric acid system, in which a long tail was observed in the rear boundary of run 2, also is characterized by elution problems. See Fig. 3.

Counter-anion dependencies of cation extractability by crown ethers have been studied (6,16). In most cases, crown ethers extract cations effectively when extraction systems contain bulky and soft anions such as NO_3^- , SCN^- , and ClO_4^- . The present work resulted in findings consistent with those of previously published reports.

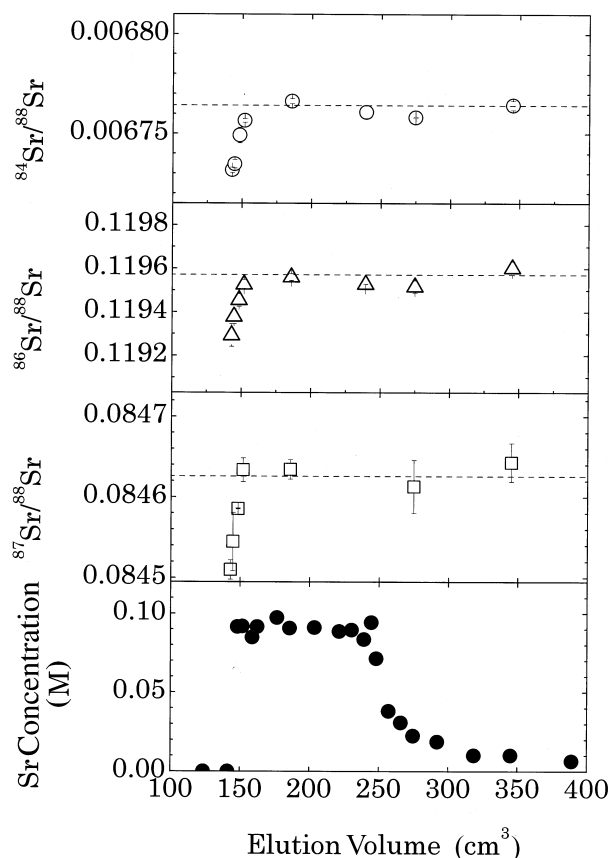


Figure 3. Chromatogram and the isotopic ratios of the effluent fractions for run 2. Measured isotopic ratios are denoted by $^{84}\text{Sr}/^{88}\text{Sr}$ (\circ), $^{86}\text{Sr}/^{88}\text{Sr}$ (\triangle), and $^{87}\text{Sr}/^{88}\text{Sr}$ (\square), respectively. The horizontal dotted lines indicate the natural abundance feed-isotopic ratios for each isotope pair.



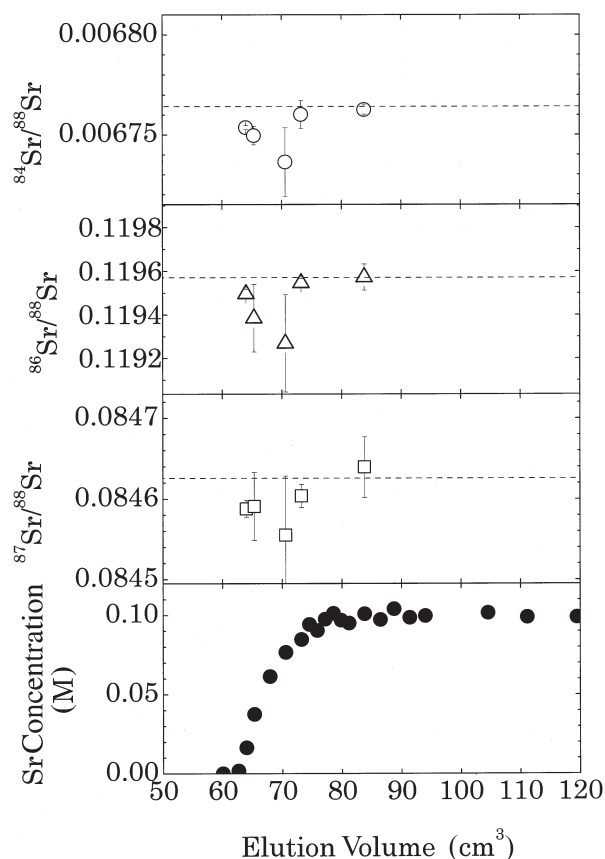


Figure 4. Chromatogram and the isotopic ratios of the effluent fractions for run 3. Measured isotopic ratios are denoted by $^{84}\text{Sr}/^{88}\text{Sr}$ (○), $^{86}\text{Sr}/^{88}\text{Sr}$ (△), and $^{87}\text{Sr}/^{88}\text{Sr}$ (□), respectively. The horizontal dotted lines indicate the natural abundance feed-isotopic ratios for each isotope pair.

Isotopic Distribution

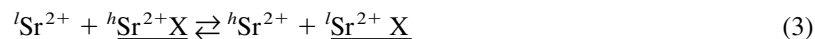
The measured isotopic ratios are presented in Figs. 2–5 along with chromatograms. A complex formation reaction of crown ether with strontium in an adsorbed band is described as:



where X is a crown ether compound and the underline represents the species in the organic resin phase. Equation (2) is rewritten into the isotopic exchange reaction



as:



where h and l represents heavier and lighter isotope, respectively.

According to the profiles of isotopic ratios shown in Figs. 2–5, the lighter isotopes were depleted in the front boundary region of the chromatography column. This result indicates that the lighter isotopes are enriched in the crown ether phase, and the equilibrium represented in Eq. (3) shifts to the right-hand term. This

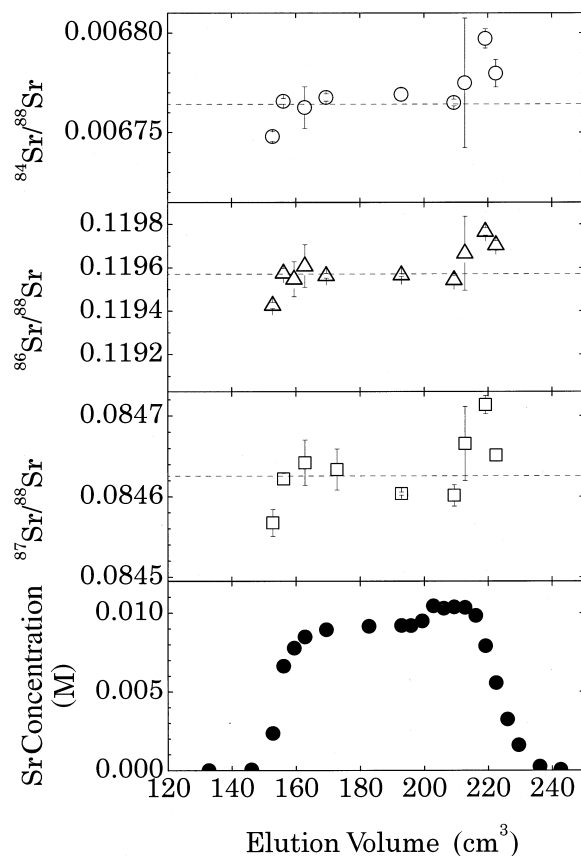


Figure 5. Chromatogram and the isotopic ratios of the effluent fractions for run 4. Measured isotopic ratios are denoted by $^{84}\text{Sr}/^{88}\text{Sr}$ (○), $^{86}\text{Sr}/^{88}\text{Sr}$ (△), and $^{87}\text{Sr}/^{88}\text{Sr}$ (□), respectively. The horizontal dotted lines indicate the natural abundance feed-isotopic ratios for each isotope pair.



tendency is the same as one shown in the previous studies on calcium and lithium isotope effects of crown ethers (4,5).

The mass spectrometric analysis of the rear boundary was carried out in runs 1, 2, and 4. In run 1, light isotopes were enriched in the rear boundary region; however, in run 2, light isotopes were not enriched in the rear boundary region. The migration length of run 2 was more than four times as long as that of run 1. As a result, the rear boundary of the run 2 column was diffused gradually and the boundary sharpness was lost as migration proceeded. In such a case, the enrichment is not accumulated in a narrow region but diffused in a long tail of within the column.

Isotopic Separation Coefficients

An isotopic exchange reaction is expressed by



where K is the equilibrium constant, and X and Y represent ligands. A and A' represents heavier and lighter isotopes, respectively. This reaction equation can be divided into two elementary reactions as shown in Eqs. (5) and (6).



The equilibrium constant of Eqs. (5) and (6) are given by the reduced partition function ratios derived by Bigeleisen and Mayer (17):

$$\left(\frac{s}{s'}\right)f = \prod_i \frac{u_i}{u'_i} \frac{e^{-u_i/2}/(1 - e^{-u_i})}{e^{-u'_i/2}/(1 - e^{-u'_i})} \quad (7)$$

where s and s' are symmetrical numbers and $u_i = hv_i/kT$. The h and k are Plank and Boltzmann constants; ν represents vibration frequencies; and T is temperature.

The reduced partition function ratio for obtaining equilibrium constants for a symmetrical complexes represented by Eq. (5) can be given in the following simplified form:

$$\ln f_{(AX/A'X)} = \frac{\Delta M m_X n_X}{24MM'} \left(\frac{hv_X}{kT}\right)^2 \quad (8)$$

where ΔM is the mass difference; M is the mass of the heavier isotope; M' is the mass of the lighter isotope; n_X represents the number of ligands; and m_X and ν_X refer to the mass and the totally symmetrical stretching-vibration frequency of ligand X .



A similar reduced partition function ratio is given for Eq. (6), and the separation coefficient (or fractionation factor) ε of Eq. (3) is calculated by the following equation:

$$\varepsilon = \ln K = \ln f_{(AX/A'X)} - \ln f_{(AY/A'Y)} = \frac{\{m_X n_X (h\nu_X)^2 - m_Y n_Y (h\nu_Y)^2\} \Delta M}{24MM'(kT)^2} \quad (9)$$

Equation (9) shows that ε is proportional to the mass difference ΔM , and as a result is called the "normal mass dependence rule." In the present work, the isotopic separation coefficients for the isotopic pair of ^{84}Sr and ^{88}Sr ($m = 84, 86$, or 87) are calculated by the following equation:

$$\varepsilon_{m/88} = \frac{\sum q_i (1 + r_o)^{m_i} r_i - m r_o}{m r_o Q (1 + m r_i)} \quad (10)$$

where q is the amount of strontium in a fraction samples of effluent; Q is the total adsorption of strontium in the column as calculated from the experimentally derived breakthrough volume according to Eq. (1); $m r$ ($m r = m \text{Sr}^{88}\text{Sr}$, $m = 84, 86$, or 87) is the isotopic abundance ratio measured by mass spectroscopic analysis; and the subscripts i and o denote the i th fraction sample and feed solution, respectively. The calculated values of $\varepsilon_{m/88}$ from Eq. (10) are listed in Table 2 and plotted in Figs. 6 and 7 with fitting lines made by the method of least squares. Although a few data deviated from the lines fit by this method, we concluded that, as long as error ranges are considered, the separation coefficients are proportional to the mass difference in both systems. This result is consistent with the classical Bigeleisen-Mayer theory on isotope effects (17). The slope of each fitted line in Figs. 6 and 7 gives the average values of separation coefficients per unit of mass difference: 4.4×10^{-5} for run 1, 5.6×10^{-5} for run 2, 1.4×10^{-4} for run 3, 7.7×10^{-5} for run 4. These values correspond to ε s for $M = 87$ in Figs. 6 and 7. Because the experimental conditions of runs 1 and 2 are identical except for the column length, these two runs were expected to show the same separation coefficient. The average value of $\varepsilon/\Delta M$ was $(5.0 \pm 0.6) \times 10^{-5}$ for the nitric acid system. It is clear that the hydrochloric acid system shows the smaller adsorption capacity and, as mentioned before, larger isotope effects than the nitric acid system.

Table 2. Observed Separation Coefficients

	Run 1	Run 2	Run 3	Run 4
$\varepsilon(^{84}\text{Sr}/^{88}\text{Sr})$	$(1.7 \pm 0.42) \times 10^{-4}$	$(2.3 \pm 0.49) \times 10^{-4}$	$(5.5 \pm 0.75) \times 10^{-4}$	$(3.2 \pm 0.30) \times 10^{-4}$
$\varepsilon(^{86}\text{Sr}/^{88}\text{Sr})$	$(9.2 \pm 0.28) \times 10^{-5}$	$(9.7 \pm 0.33) \times 10^{-5}$	$(3.1 \pm 0.50) \times 10^{-4}$	$(1.3 \pm 0.20) \times 10^{-4}$
$\varepsilon(^{87}\text{Sr}/^{88}\text{Sr})$	$(5.0 \pm 0.28) \times 10^{-5}$	$(5.8 \pm 0.33) \times 10^{-5}$	$(1.4 \pm 0.49) \times 10^{-4}$	$(7.4 \pm 0.20) \times 10^{-5}$
$\varepsilon/\Delta M$	$4.4 \times 10^{-5*}$	$5.6 \times 10^{-5*}$	$1.4 \times 10^{-4*}$	$7.7 \times 10^{-5*}$

* Slope of Figs. 6 and 7.



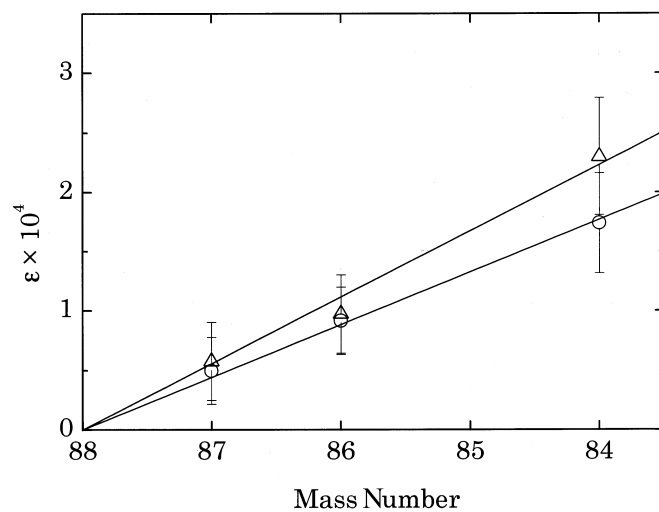


Figure 6. Strontium isotopic separation coefficients of the crown ether/nitric acid systems. Run1:○ and Run2:△.

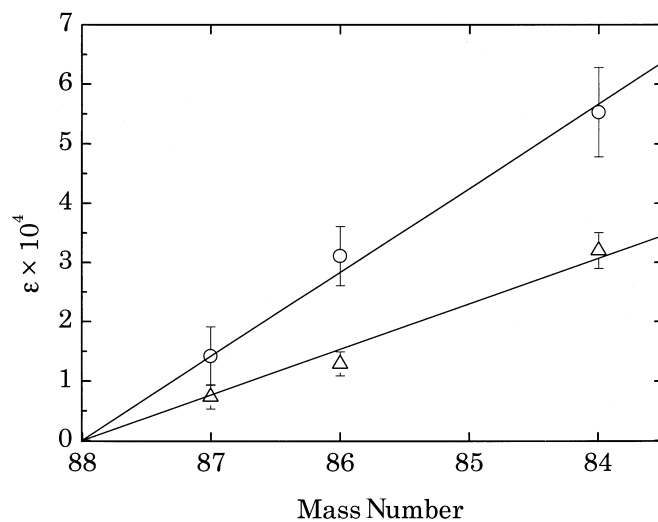


Figure 7. Strontium isotopic separation coefficient of the crown ether/hydrochloric acid system. Run3:○ and Run4:△.



All of the separation coefficients per mass difference obtained in the present work were smaller than the value of 5.1×10^{-4} obtained by a liquid-liquid extraction of strontium with 18-crown-6 compounds (10) but were larger than the values of $1.0\text{--}3.1 \times 10^{-6}$ observed from the results obtained by ion-exchange column chromatography (18).

The chromatographic adsorptions and elutions were made at rather high speed, as shown in Table 1, in the present work. The sharp boundary and the sharp isotopic enrichment observed in the chromatogram of run 1 suggest that the isotopic exchange reaction sufficiently proceeded in the adsorption band. Similarly, in the frontal band of run 2, a sharp boundary was shown and the height equivalent to a theoretical plate (HETP) value was calculated as 3 mm. The frontal band boundaries of Runs 3 and 4 were relatively broad and the isotopic enrichments at the front boundaries were not as sharp as that of run 1. Particularly in run 4, the migration speed may have been too fast to completely reach the isotopic equilibrium between the crown phase and the aqueous phase. The kinetic factor may be the reason that the isotope separation coefficient of run 4 was lower than that of run 3.

Local Isotope Enrichment

The isotopic separation coefficient (ϵ) is useful for evaluating column separation systems. However, because ϵ is calculated by the summation of many data, including errors of all the measured fractions (Eq. (10), the subtle deviation in isotope effects may be hidden in experimental error. To confirm the mass dependence of isotope effects, local isotope enrichment (α) and normalized isotope enrichment (β) are introduced and examined.

$$\alpha_{m/88} = \frac{([^m\text{Sr}]/[^{88}\text{Sr}])_i}{([^m\text{Sr}]/[^{88}\text{Sr}])_o} \quad (11)$$

$$\beta_{m/88} = (\alpha_{m/88})/(\alpha_{84/88}) \quad (12)$$

In the present work, β was calculated for eight samples, which showed large differences in isotopic ratios, selected from all runs. The isotopic ratios and β values of the selected eight samples are shown in Table 3. The average β values and errors were plotted as functions of mass number in Fig. 8. Figure 8 clearly shows the normal mass dependence of isotope effects: The isotope enrichment ratio increases proportionally with the mass difference of the related isotopic pair. All these results indicate that the isotope separation process proceeded in the manner expected based on the theory of normal mass dependence.

For the actual separation of isotopes, the crown-resin column system has the advantage of producing relatively large separation coefficients compared with



Table 3. Observed Isotopic Ratios and Normalized Isotope Enrichment (β)

Run	Sample Name	Isotopic Ratio			Normalized Isotope Enrichment		
		$^{84}\text{Sr}/^{88}\text{Sr}$ ($\times 10^{-3}$)	$^{86}\text{Sr}/^{88}\text{Sr}$ ($\times 10^{-1}$)	$^{87}\text{Sr}/^{88}\text{Sr}$ ($\times 10^{-2}$)	$\beta_{(84/88)}$	$\beta_{(86/88)}$	$\beta_{(87/88)}$
1	D23	6.7443	1.1943	8.4543	1*	0.414	0.330
1	E10	6.7813	1.1973	8.4621	1*	0.518	0.212
2	F41	6.7318	1.1929	8.4510	1*	0.483	0.284
2	F42	6.7348	1.1938	8.4545	1*	0.368	0.219
3	K38	6.7363	1.1927	8.4555	1*	0.611	0.201
4	T9	6.7480	1.1943	8.4567	1*	0.503	0.286
4	T33	6.7972	1.1977	8.4714	1*	0.336	0.214
4	T34	6.7800	1.1970	8.4652	1*	0.486	0.133

* Control

those of ion exchange systems and rendering the HETP value of 3 mm, which is small compared with those of other liquid-liquid extraction systems.

Recycled use of the resin without the need for regeneration is another advantage of the crown ether system. The adsorption band is eluted with acid from columns, and the columns are recharged with the strontium. Results from run 4

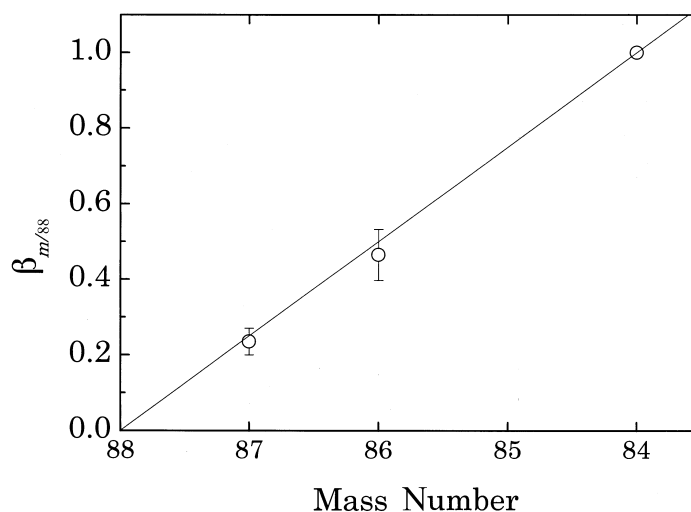


Figure 8. The normalized local isotope enrichment of strontium β averaged for eight samples in crown ether chromatography runs.



suggest that the acid concentration of the eluent may be lower than the Sr feed solution to facilitate the elution of the adsorption band.

CONCLUSIONS

The isotope effects of strontium were studied by using crown ether resin packed in columns. The lighter isotopes were enriched in the resin phase in both hydrochloric and nitric acid systems, and the isotope separation coefficients of strontium were experimentally determined. The largest value of ϵ per unit mass difference was 1.4×10^{-4} , which was obtained in a hydrochloric acid system. Although ϵ values were relatively small, Sr-Spec adsorbs strontium effectively in nitric acid systems. The local isotope enrichment is observed to increase proportionally with the mass difference of the related isotopic pair.

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