CHROM. 15,247

CALCIUM ISOTOPE ENRICHMENT BY MEANS OF COUNTER-CURRENT ELECTROMIGRATION USING AN ION-EXCHANGE RESIN AS MIGRATION MEDIUM

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(Received July 29th, 1982)

SUMMARY

A new apparatus was designed and constructed for calcium isotope enrichment by means of counter-current electromigration. Experiments have been carried out under conditions where the temperature and migration length were varied. The separation coefficient per unit mass was found to vary from $1.3 \cdot 10^{-4}$ to $8.7 \cdot 10^{-4}$ depending on the conditions, however, most values were larger than those obtained by ion-exchange chromatography. The mass effect was also observed clearly, $-\mu^+ = 0.0035$. The atomic fraction of ^{48}Ca increased from its original value of 0.185 % to 0.226 % after 5 weeks of migration under moderate conditions, yielding 144 mg of the enriched calcium.

INTRODUCTION

Calcium isotope enrichment has been investigated by several methods, including ion-exchange chromatography[1-5], amalgam–water distribution[7], electromigration in molten salt[8] and electromigration in a cation-exchange membrane[9]. However, the isotope effects reported were much smaller than those expected from the large mass differences among calcium isotopes (^{48}Ca–^{40}Ca). For example, ion-exchange chromatographic processes have shown isotope effects smaller than $3 \cdot 10^{-4}$ per unit mass for calcium isotopes, whereas *ca.* $7 \cdot 10^{-4}$ per unit mass for uranium isotopes[10,11].

In the present work, a counter-current electromigration technique was employed to obtain a larger isotope effect. The feasibility of routine operation of the separation apparatus was also examined. Counter-current electromigration using aqueous solutions was attempted by Madorsky and co-workers[12-14] in NBS, and its performance was improved by use of an ion-exchange resin as migration medium by Hirai and Kakihana[15]. We also used an ion-exchange resin as the migration medium in the present work.

EXPERIMENTAL

Apparatus

The separation apparatus used is shown schematically in Fig. 1. The size of the migration column (Pyrex glass) is 60 × 2 cm. The two cathode chambers and two anode chambers were attached symmetrically at the top and the end of the column and they were separated from the column contents with a cation-exchange membrane. Platinum electrodes were employed. The temperature of the resin bed was regulated by circulating water from a thermostat through a glass tube (from H to I) placed in the centre of the resin bed, and when necessary a blanket was used to maintain the column temperature.
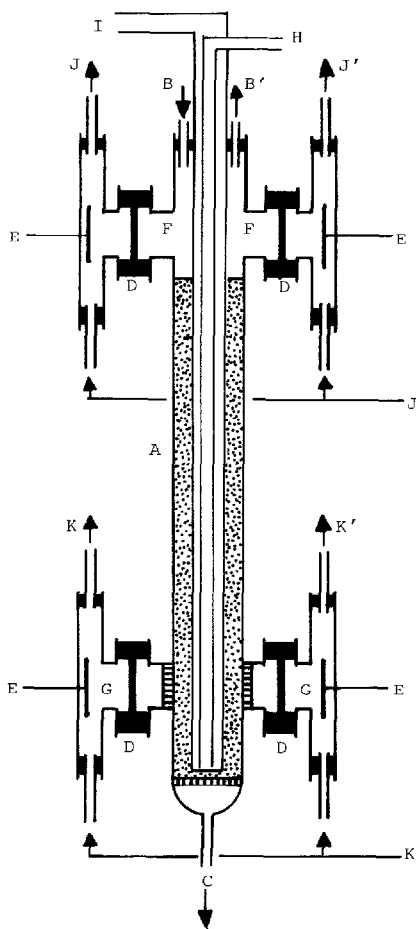

Fig. 1. Apparatus for calcium isotope separation. A = Ion-exchange column; B,B′ = feed solution inlet and outlet; C = effluent outlet; D = ion-exchange membrane; E = platinum electrode; F = cathode chamber; G = anode chamber; H,I = water inlet and outlet; J,J′ = cathode solution inlet and outlet; K,K′ = anode solution inlet and outlet.

Ion-exchange resin, membrane and reagents

A strongly acidic cation-exchange resin (PK-1) and a strongly acidic cation-exchange membrane (Aciplex-1), were used (Asahi Chemical Industry). The LiCl, LiOH, $CaCl_2$ and other reagents used were analytical grade.

Analysis

The calcium content in a sample fraction was determined by flame photometric analysis after separation of lithium from calcium by use of a small cation-exchange column. The calcium isotopic ratio was determined using a Varian MAT Model CH-5 mass spectrometer by the surface ionization technique.

Enrichment procedure

After packing the column with ion-exchange resin (Li^+), it was filled with dilute LiOH solution. Calcium chloride solution was introduced at the top of the column (from B), and allowed to overflow from B′ throughout the operation. An appropriate direct current was supplied by a constant current source, and at the same time a hydraulic flow of $CaCl_2$ through the column was initiated by activating a peristaltic pump connected to the bottom of the column at C. The calcium content of the cathode solution (F: 1 mol/dm^3 HCl) was kept low with a constant flow of fresh solution (from J to J′). The lithium ion concentration in the anode solution (G: 0.5 mol/dm^3 LiOH) was maintained with a constant flow (from K to K′) of fresh solution to the anode chamber.

Under the combined flow field, a part of the calcium ions move down the resin bed with the hydraulic flow against the electric current; on the other hand, the more mobile lithium ions migrate up the resin bed against the hydraulic flow. Thus, by balancing the hydraulic flow against the electric flow, it was not difficult to maintain a boundary between the calcium band and the lithium band at an appropriate position in the resin bed. A schematic view of the migration bands is given in Fig. 2.

In this separation process, in principle an electromigration, when the balancing is accomplished the heavier isotopes should be enriched in the frontal part of the calcium migration band. The velocity of the migration could be controlled by changing the flow-rates of the hydraulic and electric current. In addition, the boundary (Ca^{2+}–Li^+) is detectable by the naked eye in the present case, so that its control was easy.

After migration of a suitable distance, the boundary was moved downwards by gradually reducing the electric current flow. When the boundary reached the bottom of the column the effluent was collected in small fractions. In the present work, nine runs were carried out under different conditions, varying the temperature, migration time (migration length) and concentration of the feed solution. The experimental conditions and the separation coefficients obtained are listed in Table I.

RESULTS AND DISCUSSION

Selection of the supporting ion

To achieve a sharp boundary, the supporting ion should have following characteristics:

(a) ion-exchange absorption: $Ca^{2+} \gg M^{n+}$
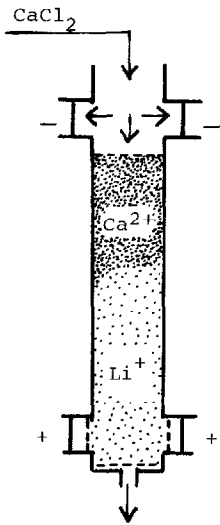
CaCl$_2$

Fig. 2. Schematic view of migration bands.

TABLE I

EXPERIMENTAL CONDITIONS AND SEPARATION COEFFICIENTS OBTAINED

Run No.	Temperature (°C)	Current density (mA/cm²)	Concentration of feed solution (mol/dm³)	Migration length (cm)	Separation coefficient per unit mass
1	82	109	0.5	382	$1.8 \cdot 10^{-4}$
2	52	109	0.5	386	$1.8 \cdot 10^{-4}$
3	24	109	0.5	387	$2.0 \cdot 10^{-4}$
4	76	162	0.5	657	$2.3 \cdot 10^{-4}$
5	75	213	0.5	639	$1.3 \cdot 10^{-4}$
6	81	109	0.5	890	$2.0 \cdot 10^{-4}$
7	80	109	0.5	2362	$1.8 \cdot 10^{-4}$
8	79	109	1.0	356	$4.1 \cdot 10^{-4}$
9	80	109	2.0	359	$8.7 \cdot 10^{-4}$

(b) electric mobility in the resin phase: $Ca^{2+} \gg M^{n+}$
(c) electric mobility in the solution phase: $Ca^{2+} > M^{n+}$

Although there are no simple ions which satisfy the above criteria, Li^+ and Zn^{2+} were tested as supporting ions. Typical results are illustrated in Fig. 3. Li^+ was selected on the basis of these results and also because the boundary (Ca^{2+}–Zn^{2+}) was not detectable with the naked eye.

Calculation of the separation coefficient, ε

The separation coefficient, $\varepsilon \ (= s - 1)$, was calculated from the analytical data using the following equation

$$\varepsilon = \left[\frac{1}{Q} \cdot \frac{\Sigma f_i \ (R_i - R_0)}{R_0 \ (1 - R_0)} \right] \cdot \frac{1}{4}$$
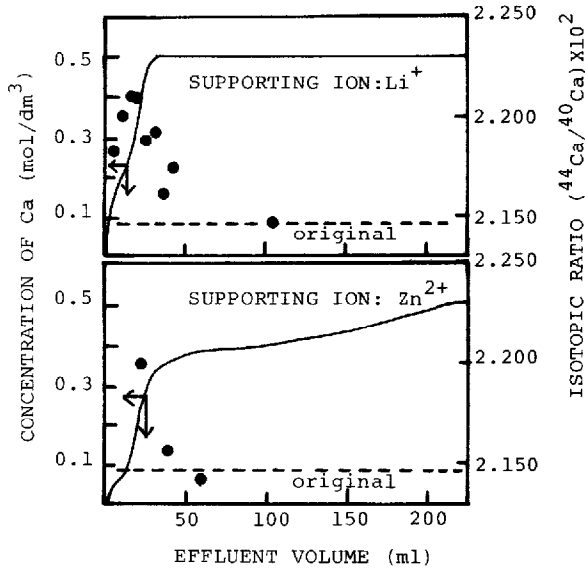
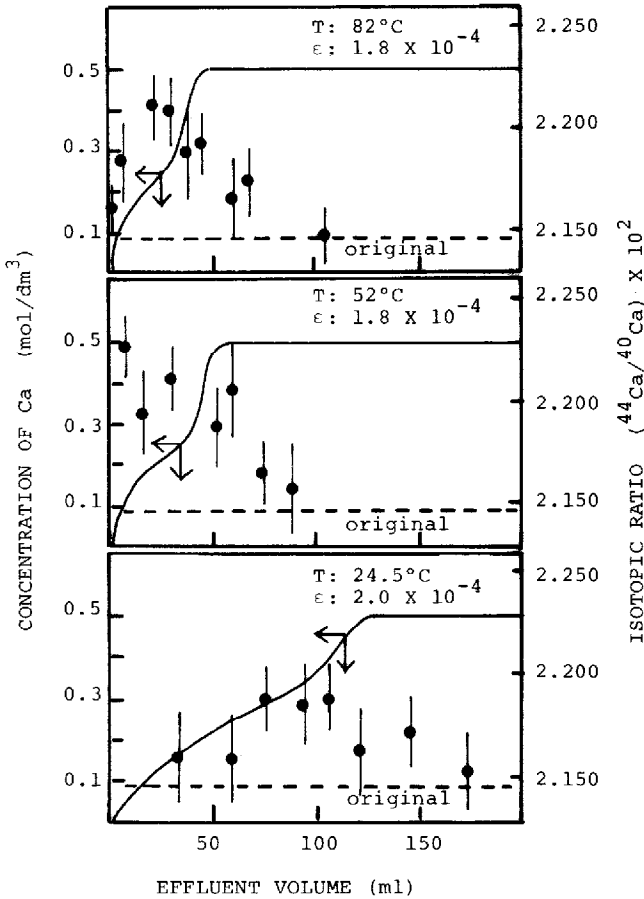Fig. 3. Supporting ion effect on the chromatogram and on the isotopic ratio, ε.

Fig. 4. Temperature influence on the chromatogram and on the isotopic ratio (runs 1, 2 and 3).

where Q is the total electric current (eq.   ), f_i the amount (eq.   ) of calcium in the ith fraction, R_i the atomic fraction of ^{44}Ca (or others) in the ith fraction and R_0 the atomic fraction of ^{44}Ca (or others) in the feed solution. The calculated value of ε is divided by 4 to yield the separation effect or isotope effect per unit mass for the case of ^{44}Ca–^{40}Ca; for other isotopes ε also indicates the isotope effect per unit mass in the present work, because calcium has six stable isotopes. The calculated values are listed in Table I.

Temperature effect on separation coefficient and chromatogram

In Fig. 4 the chromatograms and the profiles of the isotopic ratios obtained in runs 1, 2 and 3 are illustrated. An appreciable temperature effect was reported previously in the case of a molten salt medium, but in the present case no appreciable temperature effect on the separation coefficient was found. On the other hand, as expected from the temperature dependency of the rate of ion-exchange reactions, the boundary became sharper with increase in temperature.
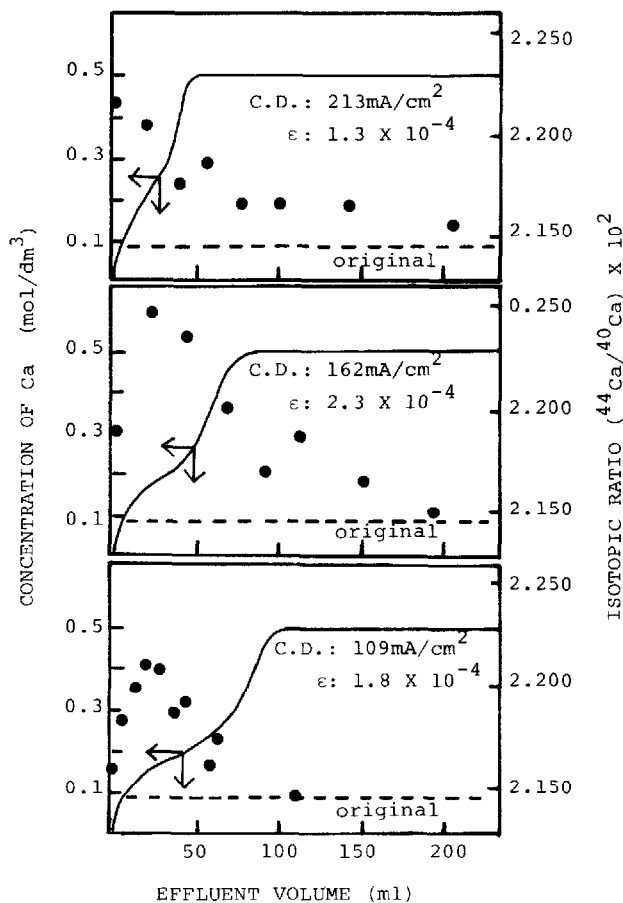

Fig. 5. Influence of current density (C.D.) on the chromatogram and isotopic ratio (runs 5, 4 and 1).

Current density effect

In Fig. 5 the chromatograms and the profiles of the isotopic ratios obtained in runs 1, 4 and 5 are illustrated. By increasing the current density, the boundary became less sharp because Li$^+$ further invaded the calcium band owing to its higher migration velocity. The separation coefficient is influenced strongly by the current density and it seems to be optimum around 162 mA/cm^2 in run 4, as previously reported for lithium isotope separation using a cation-exchange membrane as migration medium[17].

Dependence of migration length on the separation coefficient and the accumulation of the isotope effect

Under moderate conditions (temperature 80°C, current density 109 mA/cm^2, concentration of CaCl$_2$ 0.5 mol/dm^3), long-distance migrations were carried out to examine the accumulation of the isotope effect with increasing migration distance. The results obtained from runs 1, 6 and 7 are illustrated in Fig. 6, the migration distances being 382 cm for 152.7 h, 890 cm for 346.6 h and 2362 cm for 896.4 h, respectively. The migration distance was calculated from the total electric current, the exchange capacity of the resin bed and the void fraction of the resin bed. Evidently, the separation coefficient was practically constant, which indicates that the separation
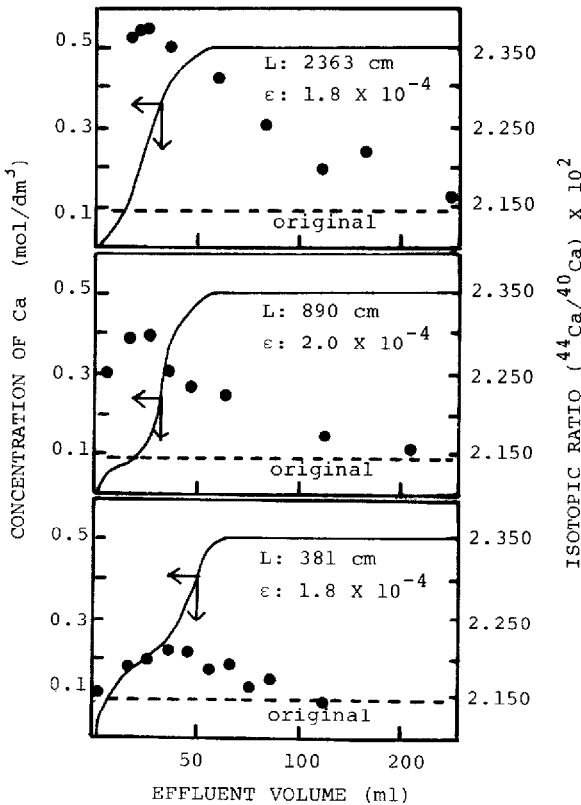

Fig. 6. Influence of migration length, *L*, on the chromatogram and isotopic ratio (runs 7, 6 and 1).

process is operating even over the long migration distances. The shapes of the chromatograms and also the profiles of the isotopic ratios are almost identical in the three migrations. These facts, together with the constancy of the separation coefficient, indicate that the technique and the apparatus are suitable to obtain enriched calcium isotopes on a laboratory scale. The largest isotopic ratios ($^{44}Ca/^{40}Ca$) obtained in each migration seem to be proportional to the migration length, and show that the isotope effect was accumulated steadily along the migration distance, under the present experimental conditions.

Feed solution concentration effect
        Two additional experiments were carried out using 1.0 and 2.0 mol/dm^3 CaCl$_2$ feed solutions to compare with run 1 (0.5 mol/dm^3 CaCl$_2$) the other conditions were as in run 1. In the case of higher concentrations, maintenance of a sharp interface became difficult, similar to the case at higher current density; however, satisfactory results were obtained as shown in Fig. 7. The separation coefficients obtained here are larger than those reported previously using an aqueous medium, and the separation coefficient increases significantly with increasing concentration of the feed solution.
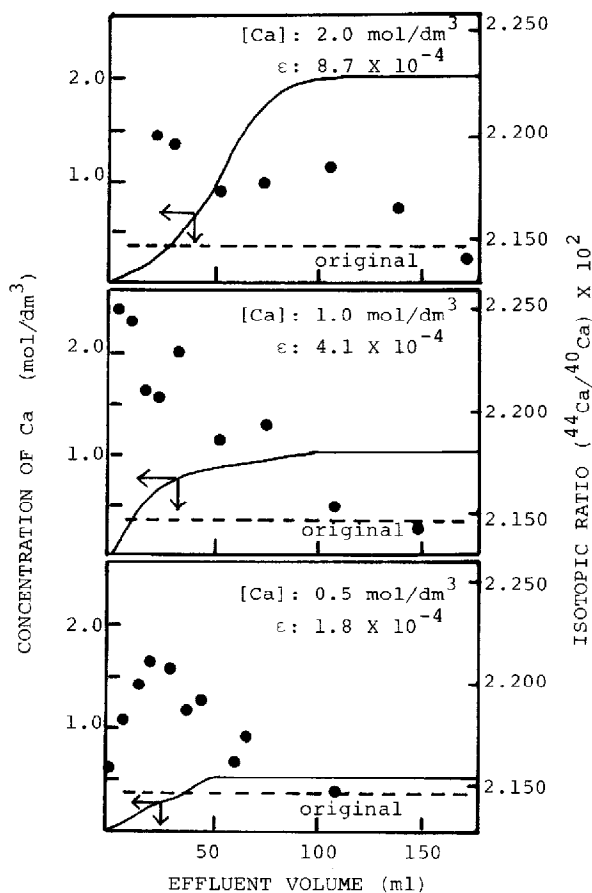

Fig. 7. Influence of feed solution concentration on the chromatogram and isotopic ratio (runs 9, 8 and 1).

However, from the viewpoint of calcium isotope enrichment, the highest concentration (2.0 mol/dm^3) seems to be less suitable than the case of 1.0 mol/dm^3, because the gradient of both the elution curve and the profile of the isotopic ratios are smaller. The separation coefficient obtained in run 9 is the largest among those reported for an aqueous medium.

The mass effect on the separation of calcium isotopes

In order to confirm the mass effect that occurred in the present isotope separation process, we measured the isotopic ratios for four calcium isotopes (^{48}Ca, ^{44}Ca, ^{43}Ca and ^{42}Ca) relative to ^{40}Ca in each experiment. In Fig. 8 a typical mass effect is illustrated by local enrichment factors, R_i/R_0, of each fraction for four isotopes obtained in run 6. The graphs shows that the enrichment factors are nearly proportional to the magnitudes of the mass differences, which indicates that the present separation process, although having some imperfections, accomplished a steady accumulation of the elemental isotope effect. The mass effect was evaluated as $3.5 \cdot 10^{-2}$ ($-\mu^+$). The largest enrichment factor obtained in the present work is 1.22, which means that ^{48}Ca was enriched to 0.225% from its original value of 0.185% during 5 weeks of migration and yielded 144 mg of the enriched calcium sample.
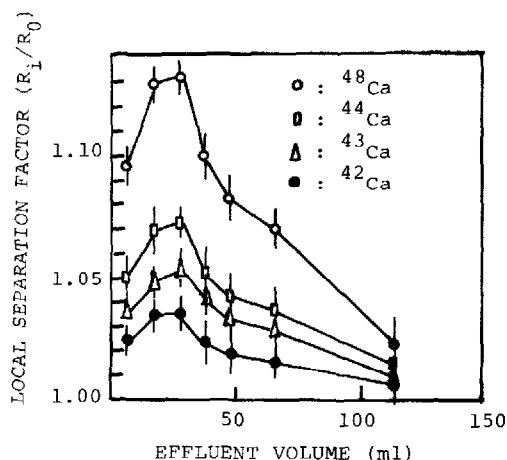

Fig. 8. Local separation factor for each isotope (run 6).

CONCLUSIONS

The partial separation of calcium isotopes was carried out by means of a counter-current electromigration using a cation-exchange resin as migration medium with Li$^+$ as supporting ion for the calcium migration band. Using the present apparatus, calcium band movement was easily controlled by balancing the hydraulic flow and the flow of electric current.

Comparing the results obtained from nine separation experiments, it can be concluded that: (1) the apparatus was stable and the isotope effect was accumulated with increasing migration distance; (2) the mass effect was observed and the value was found to be $3.5 \cdot 10^{-2}$ (very close to the largest value $5.1 \cdot 10^{-2}$ obtained in a molten

salt medium); (3) optimum operation conditions seem to be 1.0 mol/dm^3 CaCl$_2$, 80°C and a current density of 109 mA/cm^2; (4) the largest separation coefficient was obtained under the conditions of 2.0 mol/dm^3, 82°C and 109 mA/cm^2, however, these conditions were not best for the production system; (5) using the present process, the atomic fraction of ^{48}Ca was increased from its original value of 0.158 % to 0.226 %, and the amount of this enriched calcium sample produced was 144 mg.

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