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CHROMATOGRAPHIC SEPARATION OF CALCIUM ISOTOPES WITH POLYMER-BOUND LIGANDS

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ABSTRACT

Calcium isotopes were enriched in chromatography columns containing the polymer-bound ligands cryptand [2_B22], cryptand [2_B21], and 18-Crown-6. The largest equilibrium single stage separation factor, 1.0039 ± 0.0002 for the calcium 40/44 isotope pair, was found in calcium exchange with cryptand [2_B22]. The largest separation factor found for 18-Crown-6 was 1.0025 ± 0.0003 for the 40/44 isotope pair. The size of the isotope effect was found to be highly dependent on the solvent composition. An iminodiacetate resin ion exchange column yielded small enrichments of calcium isotopes. Calcium 40/44 exchange with the chelating functional group iminodiacetate yielded a small equilibrium separation factor of 1.00011 ± 0.00003, which was more typical of calcium ion exchange isotope effects.

Comparisons of the above chemical systems based on separative power showed crown chemical exchange to be an improvement over cryptand and iminodiacetate exchange. The cryptand system was rendered impractical as a consequence of a slow exchange rate and a resulting large stage residence time contribution to the separative power, on the order of 45 min. The separation factor for the iminodiacetate system was too small for practical applicability.

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INTRODUCTION

Chromatographic techniques for enriching isotopes have been undergoing a gradual development for several decades. The chromatographic enrichment of metal isotopes was first reported in 1938 (1). High enrichments of nitrogen isotopes were first achieved in the early fifties using displacement band chromatography (2). Recent studies with modern column packings have demonstrated substantial increases in separative power for the same nitrogen process (3). Uranium isotope enrichment by redox displacement band chromatography has reached an advanced stage of development (4) and is seriously being considered for a commercial process. Thus, chromatography, as a technique for separating isotopes, is steadily approaching practicality.

There is a continuing interest in finding a practical chemical method for separating stable calcium isotopes for use as tracers in biomedical research. The present method of separating calcium isotopes with electromagnetic separators (calutrons) is costly. Chemical exchange can be effected in an inherently less costly, reversible process if certain fundamental requirements relating to the isotope effect and stage hold-up times can be met. A chemical exchange reaction must possess a useful equilibrium single stage separation factor and be applicable to a process with short theoretical stage heights.

First, consider separation factors. Calcium ion exchange separation factors tend to be very small (5-12). One notable exception to this according to literature reports is iminodiacetate exchange with calcium (13). Liquid-liquid chemical exchange exhibits larger separation factors for the calcium amalgam exchange system (14, 15) and the calcium crown exchange system (16). However, liquid-liquid extraction systems tend to have long theoretical stage heights along with complicated column operation and reflux processes. An alternative approach is to adapt the larger liquid-liquid isotope effects to a chromatographic process. Chromatography columns characteristically exhibit the short theoretical stage heights necessary for a process requiring a large number of stages. Further, the technology required for passing a displacement band continuously through a cyclic arrangement of columns has been demonstrated (4).

Horwitz and co-workers were the first to enrich calcium isotopes by extraction chromatography (17). That work involved immobilizing an organic soluble extractant on bonded phase silica gel. Heumann and Schiefer reported the largest isotope effect found for calcium in column studies utilizing polymer-bound cryptands (18). The authors of this paper investigated calcium ion exchange in conjunction with unbound crown in an attempt to utilize the large macrocycle isotope effect in a chromatography column (19). Other investigators have reported on sodium (20) and potassium (21) isotope effects using a macrocyclic compound in conjunction with ion exchange chromatography. Further information on isotope separations with macrocyclic compounds can be found in

an extensive review by Heumann (22). Work with the amalgam system has been extended by Klinskii and Knyazev with the adaptation of calcium amalgam exchange to a chromatographic method (23).

In the work described below, the iminodiacetate and cryptand chemical exchange systems were reexamined using the initial transport method (breakthrough technique). The intent was to obtain precise separation coefficients in column experiments and to make a preliminary assessment of the practical applicability of these systems to an enrichment process. Further, work was started on calcium exchange with polymer-bound 18-Crown-6 for the same purposes.

EXPERIMENTAL

Materials and Columns

Chelex-100 (sodium iminodiacetate) and Kryptofix 2_B22 (cryptand) were obtained from Bio-Rad and Merck, respectively. The structures of these materials along with the polymer-bound 18-Crown-6 packings are shown in Figure 1. Compound III, a polymer-bound 18-Crown-6 with a $-CH_2OCH_2-$ tether, was obtained from Professor R. A. Bartsch of Texas Tech University. This material was originally synthesized for use in organic catalysis studies (24). Compound IV, 18-Crown-6 with a $-CH_2O(CH_2)_9-$ tether, was synthesized at Mound according to the synthesis developed by Anelli et al. (25). The solid supports for compounds III and IV were 200-400 mesh chloromethylated (4.2 meq/g) polystyrenedivinylbenzene from Fluka and Bio-Rad, respectively.

Column runs were performed in jacketed glass columns maintained at constant temperatures of 20.0°C, except for the Chelex run, which was maintained at 25.0°C. Two 1-m long, 6.3-mm i.d. columns connected in series were used for the Chelex run. These columns were conditioned with 1-N aqueous NaCl, Baker analyzed, to remove any excess calcium or potassium impurities. The feed solution was aqueous 0.95-M NaCl, 0.05-M $CaCl_2$ corresponding to conditions in Reference 12.

The cryptand runs were made in 1-m, 6.3-mm i.d. columns. The solvent medium for the cryptand runs was a 70/30 mixture of methanol/chloroform by volume to which 1.65 vol % water was added in accordance with Reference 18. The feed solutions contained 0.01-M $CaCl_2$. The column sizes with the polymer-bound crown materials varied according to the available material. For compound III, run PMOC-1 was made in a 3.0-mm i.d. column with a packed length of 18.7 cm in a solvent of methanol with 0.5% water by volume; run PMOC-4 was made in a 6.5-mm i.d. column with a packed length of 4.3 cm in 70/30 $MeOH/CHCl_3$ plus 0.5% water. The larger diameter column was used to avoid column plugging caused by packing expansion. The water content of the crown column runs was reduced to improve the stability of the calcium-crown complex. These columns were cleaned with approximately a hundredfold column volume of 50/50 methanol/water before preconditioning. Compound IV, run

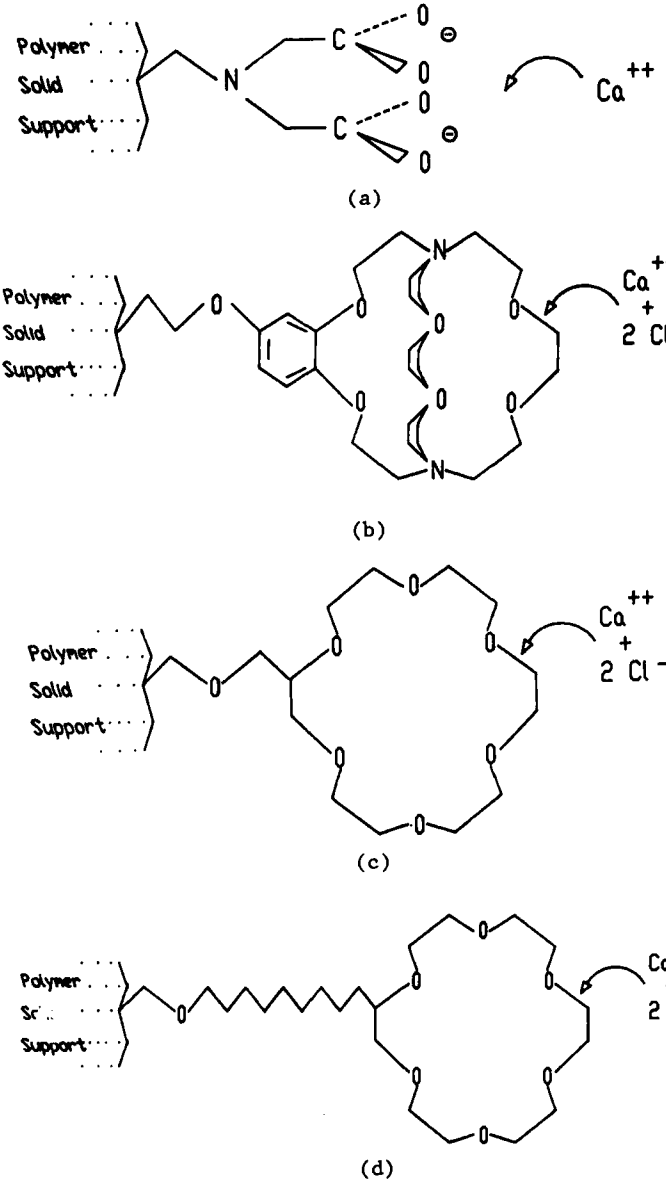


Fig. 1. Structures of polymer-bound ligands. 1a shows compound I, Chelex-100 from Bio-Rad; 1b shows compound II, Kryptofix 2_B22 from EM Industries; 1c shows compound III, polymer-bound 18-Crown-6 with a $-CH_2OCH_2-$ tether from Texas Tech University; and 1d shows compound IV, polymer-bound 18-Crown-6 with a $-CH_2O(CH_2)_9-$ tether synthesized at Mound.

MONC-1, was made in a 3.0-mm i.d. column with a packed length of 15.4 cm in 70/30 MeOH/$CHCl_3$ plus 0.5% water by volume. This column was washed with a hundredfold column volume of methanol. This material was unwettable with water, and the 50/50 mix of water/methanol appeared to be ineffective. Additional details about these runs may be found in several Mound reports (26, 27, 28).

Procedure and Sample Preparation

The breakthrough technique (also referred to as frontal analysis) was used for all column experiments. Figure 2 shows a schematic of this type of operation. A feed solution containing natural abundance calcium chloride was passed continuously through the columns, initially free of calcium, while effluent samples were collected in a fraction collector. Upon reaching steady state, the calcium concentration and isotopic composition in the samples were equal to those of the feed. The isotopic composition in the solid phase at steady state differed from that of the fluid phase by one equilibrium stage. The amount of heavy isotope transported from the solid phase to reach equilibrium conditions was then present in the samples, and a simple material balance yielded the separation coefficients.

Samples were dried, redissolved in 0.1-N HNO_3, and split in half for concentration analysis by inductively coupled plasma (ICP) and mass ratio analysis. The Chelex and cryptand samples were purified in small ion exchange columns. This step was eliminated as unnecessary in all of the crown runs. An atomic absorption spectrophotometer was used to spot check for possible contaminations throughout the experimental procedures. After completion of each enrichment run, all of the calcium was recovered from the

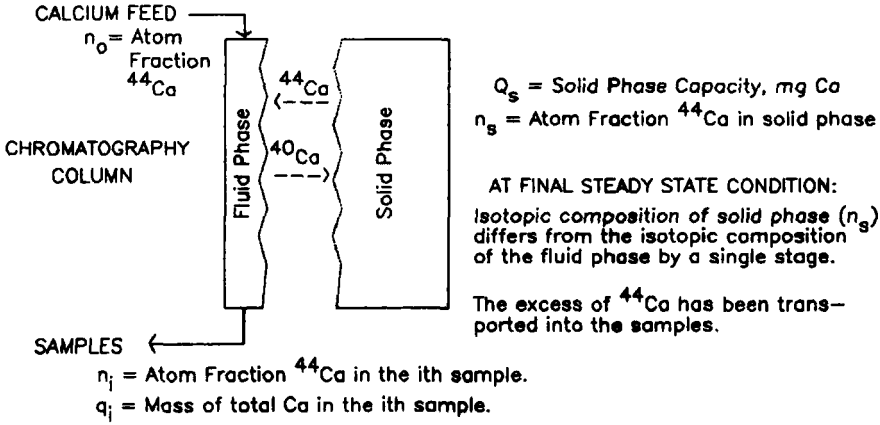


Fig. 2. Breakthrough technique. At final steady state condition, $n_i = n_o$ and net transport of calcium isotopes across the solid-fluid interface becomes zero.

column. This recovery was accomplished by eluting the calcium from the column into a fraction collector until calcium could no longer be detected in the samples. The eluting solvents were 8-N HCl (Chelex run), water (cryptand and compound III runs), and methanol (compound IV run). The recovered $CaCl_2$ was dried to remove solvents, consolidated, and redissolved in dilute nitric acid and water to a known volume, then analyzed in triplicate by ICP.

Mass Spectrometry

The calcium isotope ratio measurements for this work were made with a Finnegan MAT 261 thermal ionization mass spectrometer (TIMS). This instrument has a 90°, 23-cm radius magnetic field which, through its ion optic design, produces a mass dispersion that is comparable to a 46-cm conventional magnetic field. Other features are a variable multicollector design, multiple sample turret, and capability for complete computer control. The latter two features allow analysis of up to 13 samples without operator intervention. The multicollector permitted simultaneous collection of the ion beams for the masses 40, 42, 43, and 44.

A calcium working reference solution was analyzed along with the samples to assess instrument performance over time. Process blanks were also performed to rule out the possibility of unwanted isotope fractionation during sample processing, especially for the samples undergoing ion exchange purification. The calcium 40/44 ratio in the reference material was 46.384 ± 0.006 (2 sigma(mean)) for 33 samples. The ratio for process blanks was 46.385 ± 0.006 (2 sigma(mean)) for four samples, indicating that fractionation was not occurring in the sample processing steps.

RESULTS AND DISCUSSION

The emphasis of this work was to establish calcium isotope separation coefficients for promising chromatographic systems including iminodiacetate, cryptand, and crown systems and to assess practical applicability by comparing the separative power of these systems in actual column performance. Isotope enrichment profiles for these three systems are shown in Figures 3 through 6. The curves were fitted to polynomials by the method of least squares. Horizontal lines on the isotope profiles show natural abundance feed isotope ratios. Table 1 lists the column parameters and run conditions along with the separation coefficients obtained from these column runs.

Separation Coefficients

Isotopic enrichment of calcium proceeds according to the chemical exchange reaction:

$$^{40}Ca^{2+}_{fluid} + {}^{44}CaL^{2+}_{solid} = {}^{44}Ca^{2+}_{fluid} + {}^{40}CaL^{2+}_{solid} \qquad (1)$$

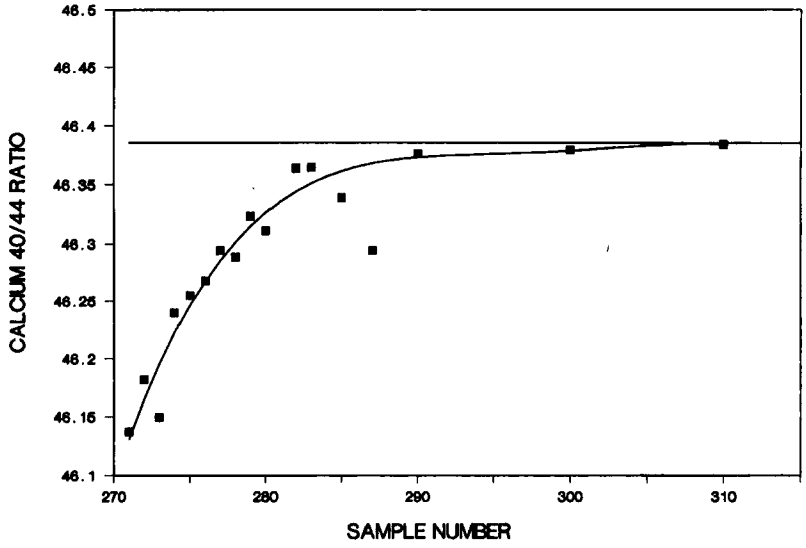
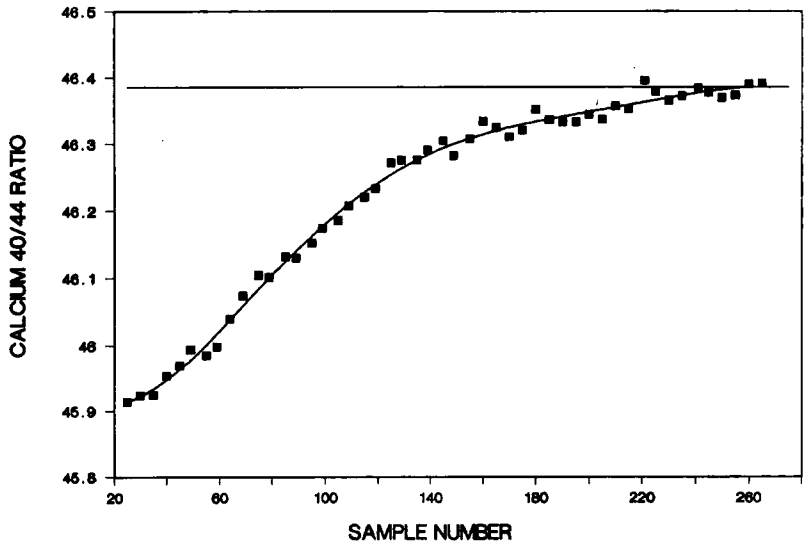
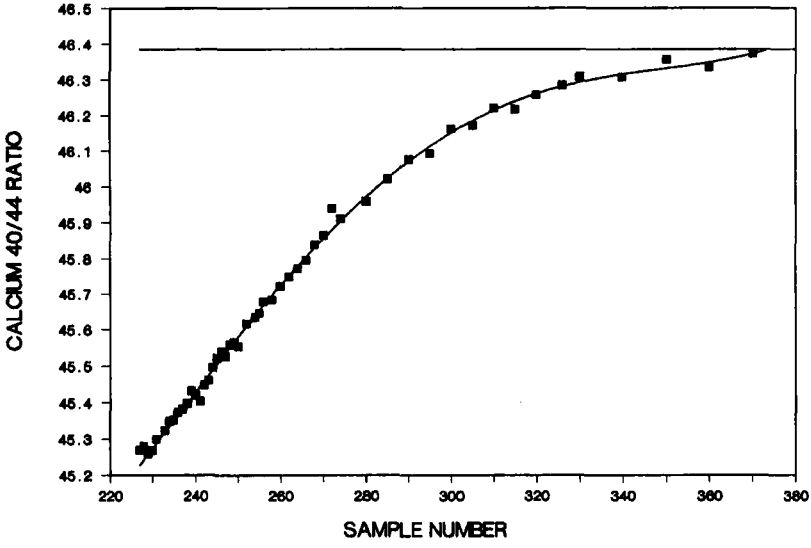


Fig. 3. Calcium-44 enrichment profile for compound I, iminodiacetate. The horizontal line indicates the natural abundance feed isotope ratio. The curve is a least squares polynomial fit of the data.

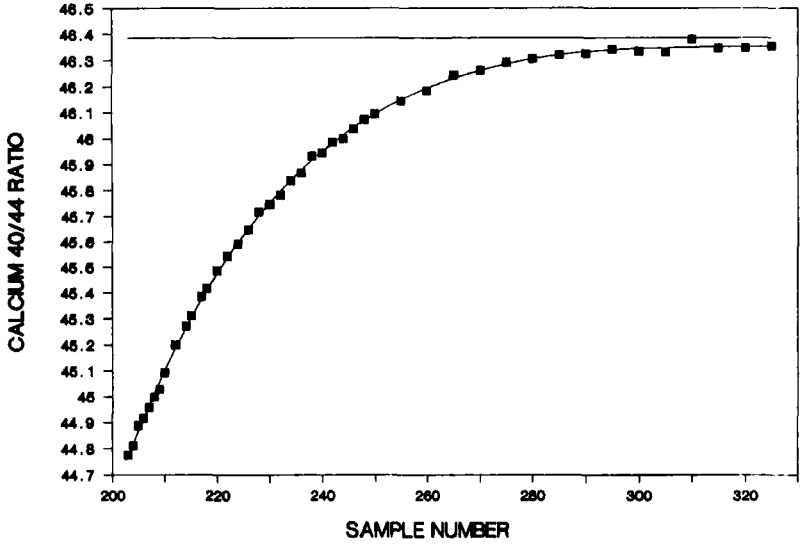


(a)

Fig. 4. Calcium-44 enrichment profiles for compound II, Cryptand $[2_B22]$ at high (a), intermediate (b), and low (c) flow rates. The horizontal lines indicate the natural abundance feed isotope ratios. The curves are least squares polynomial fits of the data.

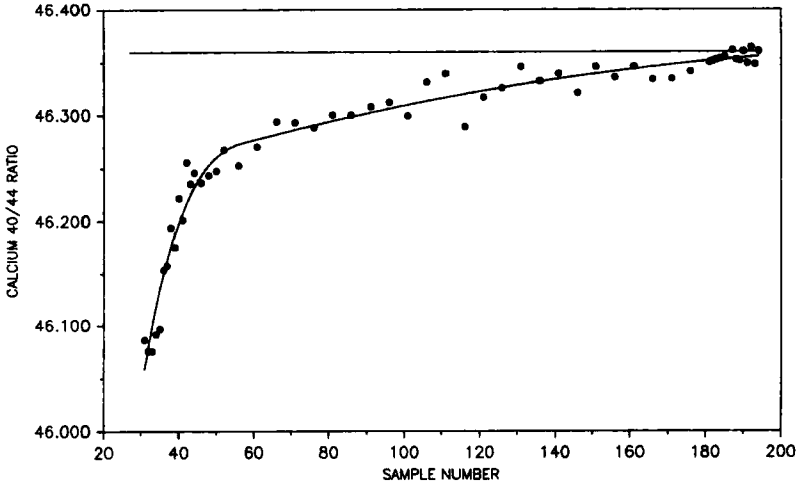


(b)

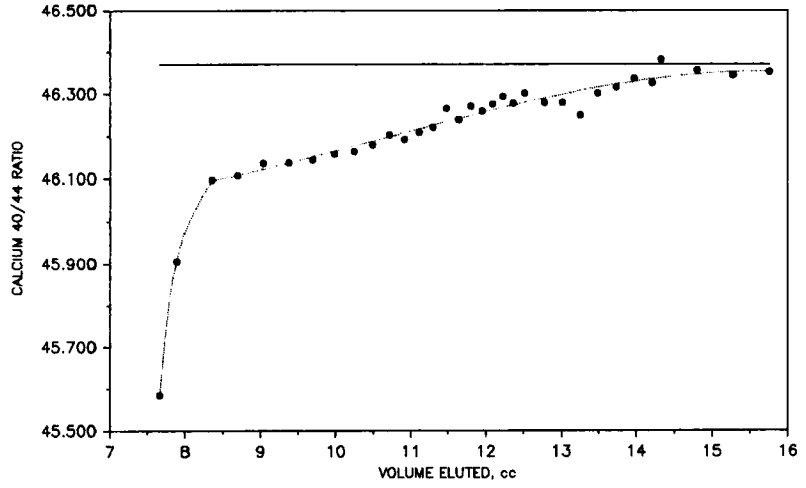


(c)

Fig. 4. (continued)



(a)



(b)

Fig. 5. Calcium enrichment profiles for compound III, 18-Crown-6, runs PMOC-1 (a) and PMOC-4 (b). The horizontal lines indicate the natural abundance feed isotope ratios. The curves are least squares polynomial fits of the data. The dotted curve (run PMOC-4) was not used in separation coefficient computation (see text).

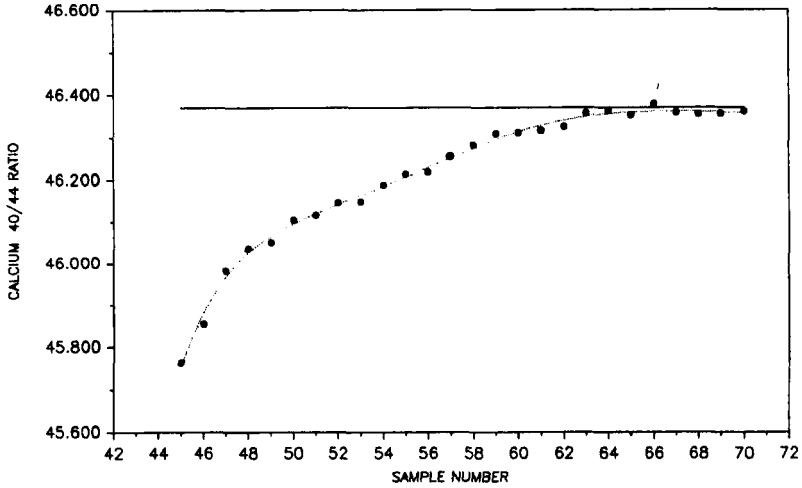


Fig. 6. Calcium enrichment profile for compound IV, 18-Crown-6, run MONC-1. The horizontal line indicates the natural abundance feed isotope ratio. The dotted curve is a least squares polynomial fit of the data and was not used in separation coefficient computations (see text).

Table 1. Column Parameters, Run Conditions, and Separation Coefficients

Run Name	Column[a] Packing	Feed Rate (cm^3/hr)	Feed, Ca Conc. (M)	Qs (mg Ca)	Column Length (cm)	Separation $\epsilon \times 10^4$	Coefficient Error
IMDA	I	5.7	0.053	642	188.1	1.1	0.3
IFR[c]	II	6.0	0.0094	104	99.5	38[d]	3
HFR[e]	II	90.0	0.0107	95	99.5	39[d]	3
LFR[f]	II	3.0	0.0103	99	99.5	41	2
PMOC1	III[g]	0.69	0.104	10.5	18.7	17	3
PMOC4	III	0.69[h]	0.086	27.8	4.3	25	3
MONC1	IV	0.69	0.110	7.24[i]	15.4	25	3

[a]See Figure 1.

[b]95% C.L.

[c]Intermediate flow rate.

[d]Composite value $39 \times 10^4 \pm 2 \times 10^4$.

[e]High flow rate.

[f]Low flow rate.

[g]Methanol/0.5% water solvent.

[h]Flow rate dropped after breakthrough because of overpressure.

[i]Low capacity because of poor calcium complex stability.

where L represents a polymer-bound cryptand or 18-Crown-6. To represent the iminodiacetate reaction, the solid phase species is shown as CaL_{solid} without the divalent charge. In all cases, the heavy isotopes were enriched in the fluid phase. The structures of the four ligands used in this study are shown in Figure 1. The equilibrium single stage separation factor for the ^{40}Ca-^{44}Ca isotope pair is defined as:

$$\alpha = \frac{\left[\frac{n_o}{1 - n_o}\right]_{fluid}}{\left[\frac{n_s}{1 - n_s}\right]_{solid}} \qquad (2)$$

where n_o and n_s are atom fractions of ^{44}Ca in the fluid and solid phases, respectively. For the chemical systems investigated in this report, the equilibrium single stage separation factor is the same as the equilibrium coefficient of the chemical exchange reaction. The separation coefficient is defined as:

$$\epsilon = \alpha - 1 \qquad (3)$$

Unless otherwise specified, all separation coefficients in this report refer to the ^{40}Ca-^{44}Ca isotope pair.

The separation coefficients were calculated from the expression:

$$\epsilon = \frac{\Sigma q_i (n_i - n_o)}{Q_s n_o (1 - n_o)} \qquad (4)$$

where n_i is the atom fraction ^{44}Ca in the i^{th} fluid sample, q_i is the total calcium in the i^{th} fluid sample, and Q_s is the total calcium capacity of the solid phase. The separation coefficients were obtained from a summation of these values over the full range of enriched samples according to Equation 4.

In several of the column runs, the number of isotopically enriched samples obtained was quite large, exceeding 200 in two of the runs. It was impractical and unnecessary to analyze every sample in these runs. In these cases, the values used in the summation term in Equation 4 were computed values from the fitted curves. The fitted curves are shown as solid lines in Figures 3, 4, and 5(a). For the column runs shown in Figures 5(b) and 6, every enriched sample was analyzed and the measured values were used in the summation term of Equation 4. These curves are shown as dotted lines to indicate that the fitted values were not used in the separation coefficient computation.

Table 1 lists the separation coefficients obtained. The three cryptand [2_B22] runs were performed at widely varying flow rates, primarily as a test of the reliability of the breakthrough technique. Although the breakthrough curves and isotope enrichment profiles

varied considerably from run to run, the separation coefficients remained the same within experimental error. This replicability demonstrated the efficacy of the method and indicated that no untoward kinetic effects were influencing the results.

The largest separation coefficients obtained, as shown in Table 1, were 0.0039 for the cryptand [2_B22] system and 0.0025 for both of the crown systems. These are larger than the 10^{-4} and 10^{-5} range found for calcium ion exchange without complexing ligands (5-12) and are of the same order of magnitude as the largest isotope effects reported in the literature.

Only three types of calcium chemical exchange systems have been reported as having unusually large separation coefficients: the amalgam, chelating ion exchange, and various macrocyclic polyether systems. Drury reported a single stage separation factor of 1.0013 per mass unit for calcium amalgam chemical exchange (14). This corresponds to a separation coefficient of 0.0052 for the 40/44 isotope pair. While this isotope effect is sufficiently large for a process, the undesirability of operating a process with mercury as a working fluid weighs heavily against it. Gutsykov et al. found a separation coefficient of 0.0041 using an iminodiacetate chelating resin in a multistage two-phase equilibration determination (12). The value obtained from the breakthrough technique shown in Table 1 did not replicate that value.

Several studies have shown large calcium isotope effects with macrocyclic compounds in liquid-liquid extraction and chromatographic systems. Heumann used a specially designed liquid-liquid extraction apparatus to obtain a separation coefficient of 0.0080 with (unbound) cryptand [222] in a water chloroform system (29). The high water solubility of calcium cryptate precludes practical application of this effect. Work at Mound with dicyclohexano 18-Crown-6 and its isolated stereoisomers yielded a separation coefficient of 0.0040 in multistage solvent extraction separations (16). Long theoretical stage heights and a highly complex reflux are shortcomings of this system. Chromatography, with its potentially short stage heights in combination with the macrocycle isotope effect, offers process alternatives. Polymer-bound cryptand [2_B22] yielded a separation coefficient of 0.0039 in this work using the breakthrough technique. This compares to the range of values 0.0026 to 0.0057 at -21°C to 20°C, respectively, found by Heumann for the same system (18).

The separation coefficient of 0.0025 found for the polymer-bound 18-Crown-6 systems shown in Table 1, while smaller than the cryptand isotope effect, showed distinct advantages when theoretical stage heights of the column runs were considered.

Stage Heights

The height equivalent of a theoretical stage (HETP) in this work is defined as the length of band over which exactly one equilibrium stage of separation is achieved at steady state conditions. Steady state conditions are attained when a band has moved at total reflux

long enough that no additional isotope enrichment can occur. This usage is the convention for isotope separation; however, it is often defined differently for other chromatography work.

If a precise determination of HETP is not necessary, as was the case in this work, a close approximation can be obtained by noting the change in isotope enrichment as a function of column length in breakthrough experiments. The steady state (maximum enrichment per unit length) is most closely approached near the front of an enrichment band. Since the separation coefficient was independently determined from Equation 4, an estimate of HETP can be computed. It should be emphasized that stage heights are not involved with the computation of the separation coefficient in the breakthrough technique. The separation coefficient value is solely the result of a straightforward isotope material balance.

As can be seen in Table 2, all of the cryptand HETPs are inordinately long and vary by a factor of 30 over a flow rate range spanning a factor of 30. This suggests, but does not prove, that there is a reaction rate limitation. Other evidence also supports the possibility of a rate limitation. The rate constant for the calcium cryptate [222] decomplexation reaction in water is 0.26 s^{-1} (30), corresponding to a half-time of 2.7 s. Generally, for macrocyclic complexes in methanol, the rate is at least 100 times slower than that for water. The presence of chloroform and stereochemical restrictions of the binding tether in the polymer-bound material may restrict the rate even more. Thus, one expects to observe half-times on the order of 300 to 3000 s, which is consistent with the stage residence times.

Table 2. Separation Coefficients, Stage Heights, Residence Times, and Separative Powers for Selected Chemical Exchange Systems

	Chelex-100[a]	Cryptand [222B][b]	18-Crown-6[c]
Separation Coefficient (ϵ)	0.000011	0.0039	0.0025
Theoretical Stage Height (mm)	1.4	19 to 560[d]	0.15
Stage Residence Time (s)	73	2850	25
Separative Power (g/L-yr)[e]	0.007	0.066	21

[a]Iminodiacetate.

[b]Three runs, 70/30 $MeOH/CHCl_3$ % by vol.

[c]Run PMOC-4, 70/30 %.

[d]T_{res} and U are independent of flow rate.

[e]Calcium as calcium-44 with units gram/liter-year.

On the other hand, the equivalent rate constant for 18-Crown-6 is greater than 3.2×10^7 s^{-1} (31) and no reaction rate limitation is expected. None of the column packings used in this work are well suited for rapid mass transfer, and the long stage heights are more likely a consequence of mass transfer resistance. Synthesis of compounds III and IV with macroporous solid supports is presently being pursued.

Separative Power

Theoretical stage heights alone are not a good measure of the performance of a chemical system since short stage heights can often be achieved by using low band velocities. The stage residence time, T_{Res} = (1/2)(HETP/band velocity), gives a better indication of the column performance. The stage residence time is related to the time required to reach the desired level of enrichment in a cascade and must be on the order of several seconds or less for a process to be useful with the range of separation factors under study. Also, unit volume column capacity, $\bar{C}$ moles/unit volume, must be reasonably large to reduce the size of a separations system. A measure of overall performance of a chemical exchange system in a chromatography column is the separative power, δU, which is defined:

$$\delta U = \frac{\epsilon^2 \bar{C}}{8 T_{Res}} \qquad (5)$$

For a given enrichment and production rate, the size of a cascade is inversely proportional to the separative power. Thus, the larger the separative power, the more compact the working part of a production system. Separative powers for iminodiacetate, cryptand, and crown systems are shown in Table 2. The iminodiacetate system is unsuitable as a consequence of the small separation coefficient. The stage residence time for the cryptand system is far too long for practical application. An increase in temperature is unlikely to provide the three orders of magnitude increase in reaction rate necessary to permit stage residence times of a few seconds.

The fundamental characteristics and separative power of the crown chemical exchange system listed in Table 2 do not eliminate this method as a potential separations process. Additional development work would be required, however, for an assessment of the system in a chromatographic enrichment process.

SUMMARY AND CONCLUSIONS

Calcium isotope enrichment by chemical exchange with polymer-bound ligands was investigated. The breakthrough technique of column chromatography was used to determine separation coefficients for three types of chemical systems: a chelating resin (iminodiacetate), cryptands, and 18-Crown-6. The first two systems lacked practical applicability as a consequence of a small separation coefficient and an exchange rate limitation, respectively. Separative power calculations showed the crown system to be a significant improvement over

these systems; however, further development work would be necessary to define the practical applicability of the system for a chromatographic enrichment process.

REFERENCES

1. Taylor, T. I., and H. C. Urey, *J. Chem. Phys.*, *6*, 429 (1938).

2. Spedding, F. H., J. E. Powell, and H. J. Svec, *J. Am. Chem. Soc.*, *77*, 6125 (1955).

3. Park, W. K., and E. D. Michaels, *Sep. Sci. Technol.*, *23(12&13)*, 1875 (1988).

4. Seko, M., T. Miyake, and H. Takeda, *AIChe Symp. Ser.*, *78*, 221(1982), p. 41-48.

5. Russell, W. A., and D. A. Papanastassiou, *Anal. Chem.*, *50*, 1151 (1978).

6. Lee, D. A., *J. Inorg. Nucl. Chem.*, *38*, 161 (1976).

7. Jepson, B. E., and G. C. Shockey, *Sep. Sci. Technol.*, *19(2&3)*, 173 (1984).

8. Kobayashi, N., Y. Fujii, M. Okamoto, and H. Kakihana, *Bull. Res. Lab. Nucl. React.*, *5*, 19 (1980).

9. Klinskii, G. D., D. A. Knyazev, and G. I. Vlasora, *Russ. J. Phys. Chem.*, *48(3)*, 380 (1974).

10. Heumann, K. G., *Z. Naturforsch.*, *27b*, 126&492 (1972).

11. Aaltonen, J., *Suomen Kemi.*, *B44*, 1 (1971).

12. Heumann, K. G., *Z. Naturforsch.*, *37b*, 786 (1982).

13. Gutsykov, V. V., E. S. Lobzhanidze, and M. R. Mirianashvili, *Russ. J. Phys. Chem.*, *55(11)*, 1667 (1981).

14. Zucker, D., and J. S. Drury, *J. Chem. Phys.*, *41*, 1678 (1964).

15. Klinskii, G. D., and D. A. Knyazev, *Russ. J. Phys. Chem.*, *48*, 6 (1974).

16. Jepson, B. E., and R. DeWitt, *J. Inorg. Nucl. Chem.*, *38*, 1175 (1976).

17. Horwitz, E. P., W. H. Delphin, C. A. Bloomquist, and G. F. Vandergrift, *J. Chromatogr.*, *125*, 203 (1976).

18. Heumann, K. G., and H. P. Schiefer, *Angew. Chem. Int. Ed. Engl.*, *19(5)*, 406 (1980).

19. Jepson, B. E., and W. F. Evans, *Sep. Sci. Technol., 22(2&3)*, 1029 (1987).

20. Delphin, W. H., and E. P. Horwitz, *Anal. Chem., 50(7)*, 843 (1978).

21. Schmidhalter, B., and E. Schumacher, *Helvetica Chemica Acta, 65(6)*, 1687 (1982).

22. Heumann, K. G., *Topics in Current Chemistry, Organic Chemistry* F. L. Boschke (ed.), Springer-Verlag, Berlin, 1985, pp. 77-132.

23. Klinskii, G. D., and D. A. Knyazev, *Tr. Inst. Mosk. Khim. Teknol. im. D. I. Mendeleeva, 130*, 90 (1984).

24. Pugia, M. J., A. Czech, B. P. Czech, and R. A. Bartsch, *J. Org. Chem., 51*, 2945 (1986).

25. Anelli, P. L., B. Czech, F. Montanari, and S. Quici, *J. Am. Chem. Soc., 106*, 861 (1984).

26. *Mound Activities in Chemical and Physical Research: July-December 1987*, MLM-3527, Monsanto Research Corporation (July 1988), 46 pp.

27. *Mound Activities in Chemical and Physical Research: January-June 1988*, MLM-3559, EG&G Mound Applied Technologies (December 1988), 27 pp.

28. *Mound Activities in Chemical and Physical Research: July-December 1988*, MLM-3594, EG&G Mound Applied Technologies (June 1989), 25 pp.

29. Heumann, K. G., and H. P. Schiefer, *Z. Naturforsch., 36b*, 566 (1981).

30. Loyola, V. M., R. G. Wilkins, and R. Pizer, *J. Am. Chem. Soc., 97*, 7382 (1975).

31. Izatt, R. M., J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen, and D. Sen, *Chem. Rev., 85*, 271 (1985).