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I. Separation Research

Calcium Chemical Exchange

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INTRODUCTION

The enrichment of calcium isotopes by chemical exchange relies on the tendency of the heavy calcium isotopes to preferentially occupy one of the phases of a two-phase system at equilibrium. This enrichment is described by the equilibrium single-stage separation factor, α, which is defined as:

$$\alpha = \frac{\frac{n_A}{1 - n_A}}{\frac{n_B}{1 - n_B}} \qquad (1)$$

where n represents the atom fraction of a particular isotope and
A and B identify the phase in which these atom fractions occur.

Since single-stage isotope enrichments for calcium are always small, it is convenient to introduce the separation coefficient, ϵ, which is defined as:

$$\epsilon = \alpha - 1 \qquad (2)$$

The magnitude of the separation coefficient is directly related to the magnitude of the enrichment occurring between the two phases.

METHODS FOR DETERMINING ϵ

Three methods are commonly employed to experimentally determine the separation coefficient for a variety of calcium exchange systems. These are two-phase equilibration, elution band chromatography, and

displacement band chromatography. The first method is attractive because of its apparent simplicity. However, in the case of calcium, isotope effects are usually small and high-precision mass ratio measurements are required. Thermal ionization mass spectrometry is the only known method capable of providing the required precision. However, calcium is one of the more difficult elements to analyze.

The introduction of experimental error in the form of undesirable kinetic isotope effects presents the greatest hazard when using this method. It is not difficult to observe the kinetics of exchange using tracers in the actual two-phase equilibration and eliminate these by equilibrating for a sufficient length of time. However, kinetic effects during the processing of samples for mass spectrometric analyses are more subtle and may be larger than the equilibrium isotope effect being sought.

In addition, the calcium samples obtained from the two-phase equilibration are chemically "dirty" and must be thoroughly processed in a multistep procedure to attain the purity required for isotope ratio analyses. A 100% recovery of the calcium sample in all steps is the only certain way to prevent unwanted enrichments, but this is also exceedingly difficult. This is a possible source of error when ϵ determinations are not found to be reproducible in different laboratories. Multistaging a separation may reduce the above problems, but it will not eliminate them. Two-phase equilibration has been successfully used for calcium liquid-liquid exchange systems.

Chromatographic techniques offer advantages for solid-liquid exchange systems in that a larger number of stages of separation may be achieved experimentally, thereby alleviating the problems associated with two-phase equilibration. The second method, elution chromatography, has been used frequently for calcium isotope separation coefficient measurements. In this technique, a quantity of calcium is injected into a column and eluted through the column with an acid (or

in some cases, another cation less strongly bound to the resin than calcium). The driving force for moving the calcium band is the distribution between calcium ions or complexes and the fluid phase eluting cations. As a consequence, the shape of the calcium band changes in its traverse of the column, with the band lengthening and calcium concentrations becoming smaller. The assumption is made that ϵ is not a function of concentration.

Elution chromatography requires that the isotopic enrichment profile reach a steady state (equilibrium). The total amount of calcium charged to the column must be sufficiently small relative to the column capacity that equilibrium is attainable within the length of the column. When a steady state is reached, the net transport of the enriched isotope through the band becomes zero. If these conditions are satisfied, both ϵ and the height equivalent to a theoretical plate (HETP) can be obtained. Because of the band lengthening and concentration reductions, this technique has little practical utility for adaptation to an enrichment process.

The third technique, displacement band chromatography, provides a reliable method for separation coefficient measurement and, at the same time, has the potential for application in a practical enrichment process. In this method, a calcium band is moved through the column by a displacing cation. The important distinction between elution and displacement chromatography is that the rate of movement of the band in the latter technique is determined solely by the rate of introduction of the displacing ion into the column. During displacement, the calcium concentration in the band remains at a constant value (except at the far front and rear of the band) and the band length does not change during passage through the column.

An important subcategory of this method is the breakthrough technique. In this case, the calcium in the column is continually displaced not by a different cation, but by calcium itself. Isotopic

enrichment occurs only at the front of the calcium band. Following the isotopically enriched band front is a region in which calcium concentrations are constant, no isotope enrichment has occurred, and net transport of the isotope being enriched is at a maximum. The following derivation illustrates the breakthrough technique for determining the separation coefficient.

INITIAL TRANSPORT EQUATION

The breakthrough technique for determining the separation coefficient is also referred to as the initial transport method for reasons that will become apparent from the following abbreviated derivation. A segment of arbitrary length 1 in a region in which the isotope concentration gradient is zero is specified, as illustrated in Figure I-1. Atom fractions n_A and n_B are as previously defined, and $dn/dl = 0$ for both phases. A frame of reference is also specified in which the interstage flow, L, in moles/time is of the same magnitude

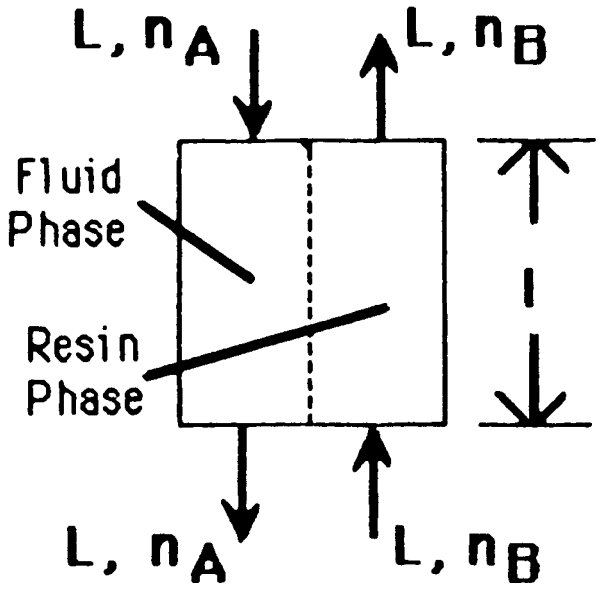


FIGURE I-1 - Flow in maximum net transport region.

in each phase but in opposite directions. Since the solid phase in a chromatography column is stationary, the segment shown in Figure I-1 moves downward through the column. It is evident that the velocity of this movement is equal to the velocity of the band front. The distance of the segment from the band front is not relevant to this derivation.

A material balance may be applied across the segment to obtain

$$\tau = L(n_A - n_B) \tag{3}$$

where τ represents the net transport of isotope n downward through the segment.

Equations (1) and (2) may be rearranged to yield

$$n_A - n_B = \epsilon n_B(1 - n_A) \tag{4}$$

Equation (4) combined with Equation (3) yields

$$\tau = \epsilon L n_B(1 - n_A) \tag{5}$$

This is the initial transport equation. A second term normally appearing in the complete transport equation representing diffusional and convectional back-mixing does not appear here since the concentration gradient, dn/dl, is zero. This equation describes the transport in any two-phase column operation (e.g., chemical exchange or distillation) at time zero. Conceptually, the isotopically enriched portion of the band preceding the maximum transport section may be regarded simply as a reservoir to contain the isotopes transported to the front of the band. The region following this segment may be regarded as an infinite reservoir supplying new material and receiving old material without changing in composition.

In practice, the initial transport equation is modified for application to breakthrough chromatography. If time t represents the total time for the band segment to traverse the column, then $L \cdot t = Q$, where Q is simply the total capacity of the solid phase in moles. Also, n_B, the atom fraction of isotope n on the solid, is not conveniently measured. By convention, the term n_o to represent the fluid phase is substituted for n_A and n_B. This introduces a small error since $n_B \doteq n_A/\alpha$. However, this error is insignificant compared to the experimental error in measuring transport.

Equation (5) now becomes

$$\tau_o = \epsilon Q n_o (1 - n_o) \tag{6}$$

where τ_o represents the total net transport of isotope n, in moles, during the course of the entire column run.

Since Q and n_o are known, the observed transport may be calculated by Equation (7).

$$\tau_o = \sum_i q_i (n_i - n_o) \tag{7}$$

where q_i is moles of calcium in sample i and
n_i is the atom fraction of isotope n in sample i.

Finally,

$$\epsilon = \frac{\sum_i q_i (n_i - n_o)}{Q n_o (1 - n_o)} \tag{8}$$

This is a remarkably simple expression compared to the outcome of the theoretical treatment for the isotope enrichment in elution chromatography. Q is accurately obtained by two independent procedures: computation of the total quantity of calcium metered into the column up to

the time of the breakthrough and total quantitative recovery of the calcium on the solid phase after completion of the run. The remaining measurements are equally straightforward.

A few comments on kinetics and theoretical stage heights are appropriate at this point. An approximate value of the height of an equivalent theoretical stage, or HETP, may be estimated from the front of the isotopic enrichment curve. (The more precise measurement methods of HETP are not relevant to this discussion.) Resistances to the exchange rate, both mass transfer and reaction rate, are encompassed within the theoretical stage definition. If the heterogeneous exchange rates are slow enough that the HETP becomes a length on the order of the column length, Equation (6) becomes invalid.

The breakthrough technique is probably the most reliable and unequivocal method for measuring ϵ in calcium chromatographic systems. The theoretical basis is exceedingly simple and straightforward compared with the elution technique. Enriched samples are more numerous and larger. Multistage separations can be achieved, thus minimizing the effects of unwanted fractionations in sample preparation.

CRYPTAND - CALCIUM EXCHANGE

Much of the work discussed below involves investigation of calcium exchange with resin-bound cryptands. Mound has only recently begun to acquire the capability to obtain reliable and sufficiently numerous isotope ratio analyses; thus this report is of necessity incomplete. The series of runs involved varying cryptands (2B21 and 2B22), varying temperatures (25 and 40°C), and varying anions (Cl^- and I^-).

The designation screening run is applied to runs done with small, short columns primarily to evaluate column capacity, packing behavior

(expansion, contraction, $\Delta\rho$), and the general shape of the breakthrough calcium concentration curve (frontal analysis is used in all cases). Full-scale isotopic enrichment runs are then made with systems that show promise for enrichment. Heumann and Schiefer have reported separation factors in the range of 1.0026 to 1.0057 for the $^{44}Ca/^{40}Ca$ pair in liquid-solid systems using cryptand (2B22) [1]. This substantial equilibrium isotope effect has prompted a continuing investigation of cryptand resins for use in calcium isotope separation.

Cryptand 2B21 Resin Experiments

Two column experiments have now been completed using a resin-bound 2B21 cryptand solid phase and a calcium chloride fluid phase. These experiments were performed at 25 and 40°C to assess the effect of temperature on the isotopic separation factor (ϵ) for this system.

Both experiments were done with the same standard 6.3-mm i.d., 109-cm long column packed with Kryptofix® 2B21 polymer* to yield a nominal resin bed depth of 75 cm. Both experiments also used the displacement band chromatography breakthrough technique. The experiment conducted at 40°C was completed during the first half of 1987 and was discussed in a previous report in this series [2].

The resin-bound calcium remaining from the 40°C experiment was eluted from the column with deionized water, using the low stability of the calcium-cryptand complex in aqueous solutions to effect removal. Elution was continued until the calcium content of the effluent was reduced to a constant 0.1 μg/mL as measured by inductively coupled plasma (ICP) spectroscopy. The column was then preconditioned at a flow rate of 0.100 mL/min with a series of

*E. Merck product consisting of insoluble Kryptofix 2B21 bound to Merrifield resin via an ether linkage.

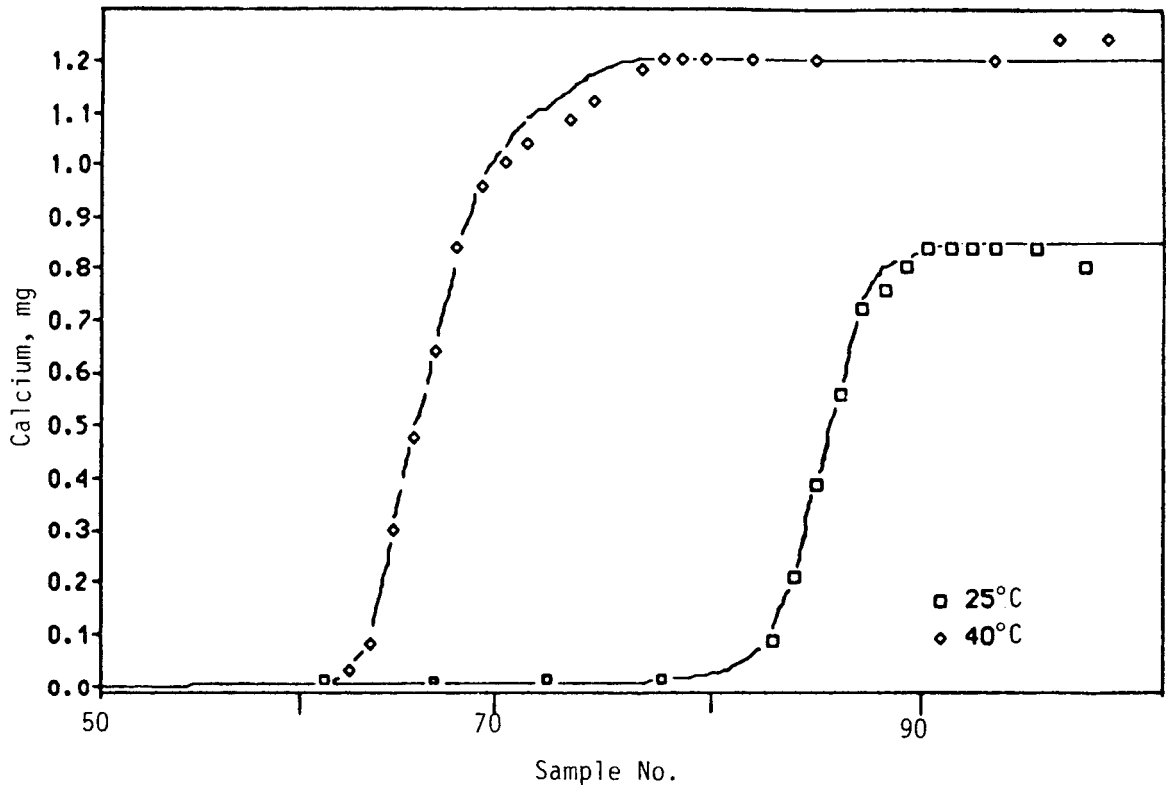
degassed MeOH:H_2O solutions, which increased in MeOH content from 25% to 90% (by volume).

A feed solution (1000 mL) was prepared to target conditions of 0.01 M $CaCl_2$ in 99:1 MeOH:H_2O. Purified CaO (556.16 mg, 9.92 mmole, corrected for CO_2 and H_2O absorption) was slowly titrated with a total of 2.48 mL concentrated ultrapure HCl (JTBaker "Ultrex" grade). Deionized H_2O was added to facilitate mixing during this step, but the volume added was kept below 1% of the final volume. The calcium concentration after complete dissolution was measured by ICP spectroscopy as 1.75 M before dilution to the desired feed value.

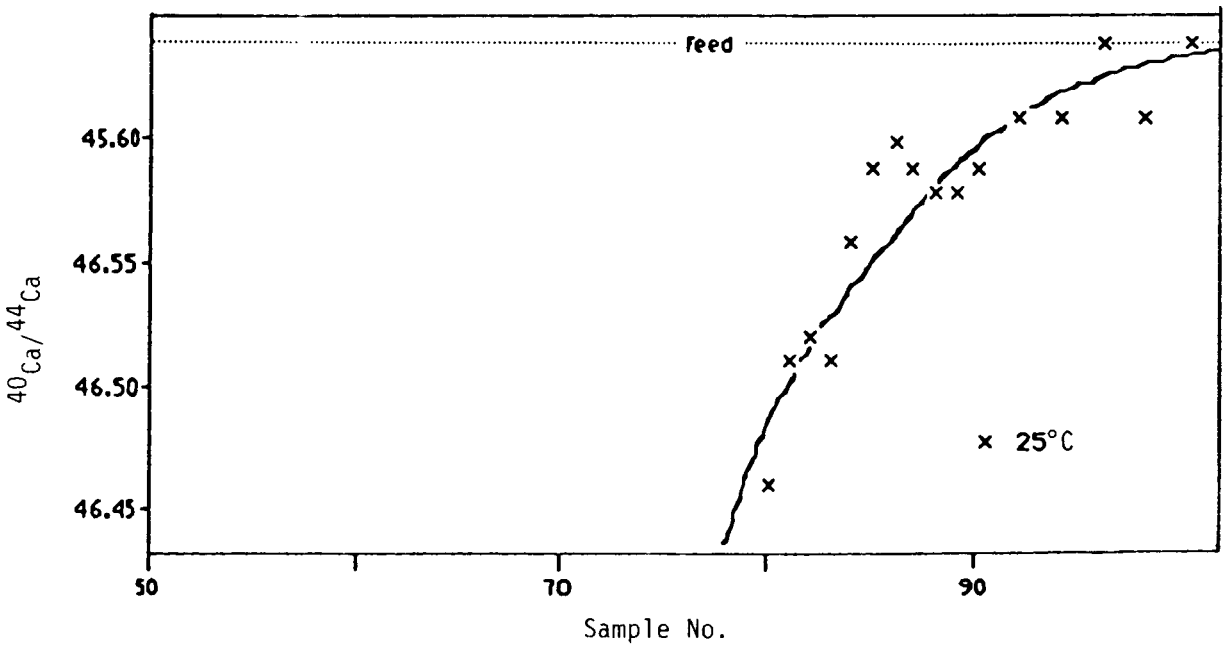
An appropriate quantity of this "prefeed" was transferred to a clean volumetric flask and enough degassed, deionized H_2O was added to yield 1% of the final volume (including the H_2O contribution from the titration). Degassed MeOH was then added to give a final volume of 1000 mL. The density of this solution was measured as 0.80 g/mL, and an aliquot (5.08 mL) was removed for determination of the final calcium concentration.

The $CaCl_2$ solution was pumped through the column (bottom to top) at a flow rate of 0.075 mL/min. The initial resin bed depth of 74.6 cm remained unchanged throughout the experiment. During the 112 hr of column operation, 224 samples (0.9 mg of calcium in a 2.25-mL volume) were collected.

Samples were evaporated to dryness and redissolved in a measured volume of 0.1 M HNO_3. Calcium, sodium, and potassium concentrations were determined by ICP spectroscopy, and the remaining sample was purified by cation exchange chromatography prior to isotope ratio measurements. Calcium concentration and isotopic enrichment profiles for this experiment are shown in Figure I-2, along with the calcium breakthrough curve from the 40°C experiment.



(a)



(b)

FIGURE I-2 - Calcium breakthrough curves at 25 and 40°C (a) and isotopic profile at 25°C (b) for $CaCl_2$-2B21 resin experiments.

The separation coefficient for the $CaCl_2$-2B21 cryptand resin (25°C) experiment was computed on a sample-by-sample basis from Equation (8) and yielded a value of $\epsilon = 0.00022$. The solid curve shown in the isotopic enrichment plot in Figure I-2(b) is an illustrative fit only.

Because of problems with the mass spectrometer, isotope ratio measurements for the 40°C experiment were too erratic to allow calculation of a separation coefficient. These samples will be reanalyzed, but there is no evidence that the separation coefficient will be significantly larger than that found for this system at 25°C.

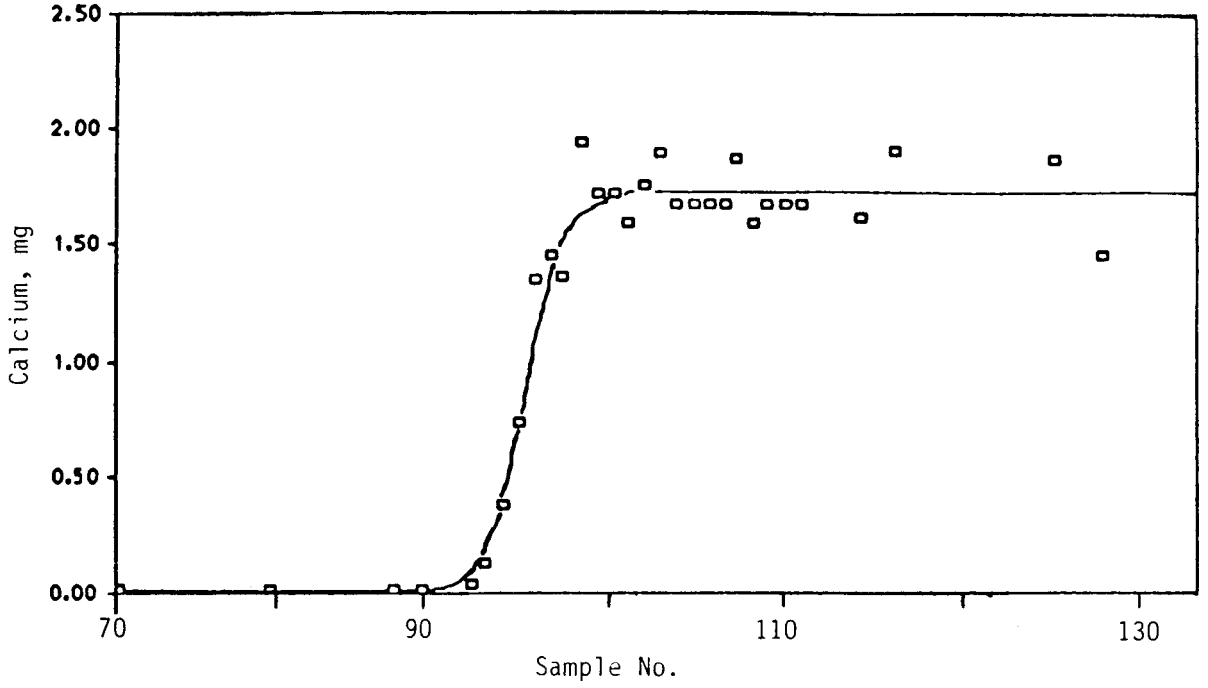
Cryptand 2B22 Resin Experiments

Three column experiments using the resin-bound cryptand Kryptofix® 2B22 polymer* have been completed. These experiments were designed to determine the anion- and solvent-dependent behavior of the isotopic separation factor for a given metal-resin system. The latest data from these experiments are presented below.

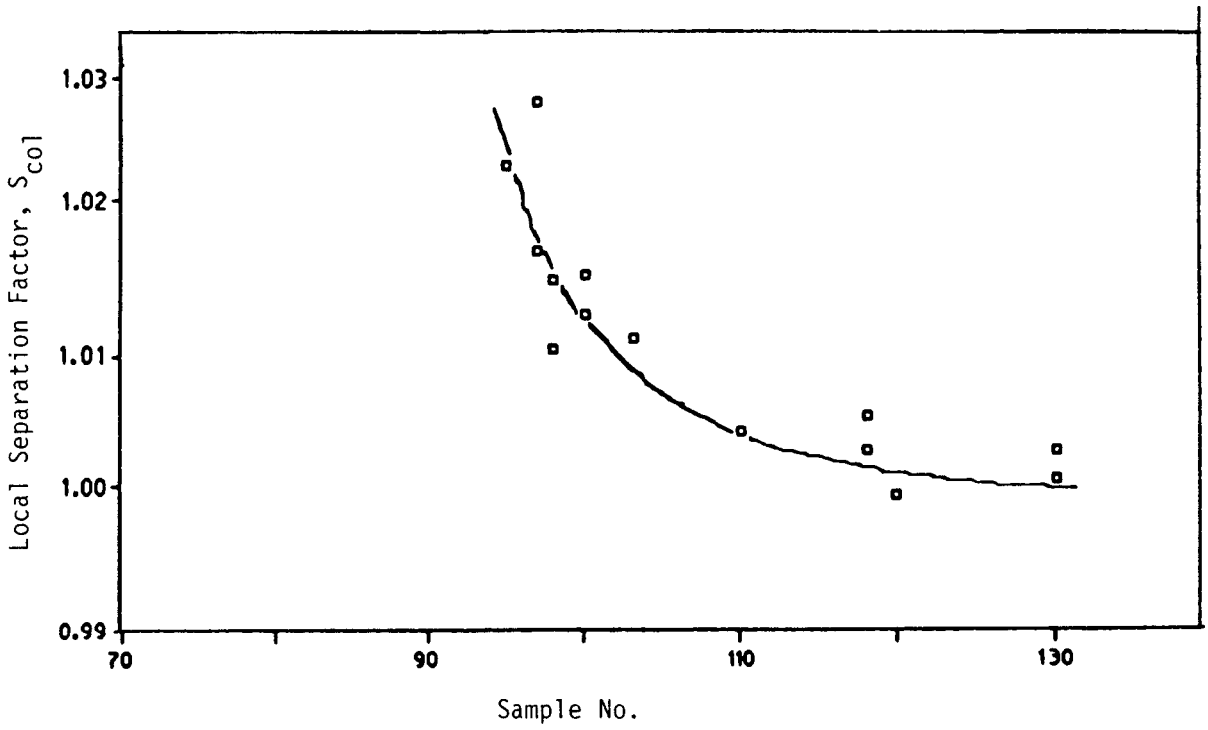
$CaCl_2$-2B22 Cryptand Resin Column Experiment (25°C). The baseline experiment for this series used $CaCl_2$ dissolved in 99:1 MeOH:H_2O (by volume) as the fluid phase and was described in a previous report in this series [3]. Isotope ratio measurements have now been obtained to provide the data necessary for calculating the isotopic separation factor for this system.

The calcium breakthrough curve is reproduced in Figure I-3, along with a local column separation factor curve. The local column separation factor is defined here as:

*E. Merck product consisting of insoluble Kryptofix 2B22 bound to Merrifield resin via an ether linkage.



(a)



(b)

FIGURE I-3 - Calcium breakthrough curve (a) and isotopic profile (b) for $CaCl_2$-2B22 resin experiment.

$$S_{col} = R_s/R_f \quad (9)$$

where R_s is the $^{44}Ca/^{40}Ca$ ratio of the sample and
R_f is the $^{44}Ca/^{40}Ca$ ratio of the feed.

The isotope ratio measurements for this experiment were performed on three different mass spectrometers and are shown as local column separation factors since the natural abundance feed isotopic ratios varied slightly among the three instruments. It should be emphasized that the separation factor, S_{col}, is a ratio of two ratios and that slight differences in absolute values from different mass spectrometers cancel. The separation coefficient obtained for this system was 0.0017.

CaI_2-2B22 Cryptand Resin Column Experiment. The second experiment in this series used CaI_2 dissolved in 99:1 MeOH:H_2O (by volume) as the fluid phase and, hence, duplicated the $CaCl_2$-2B22 experiment except for substitution of the anion. The 2B22 cryptand column used for the chloride experiment was prepared for this experi ent by eluting the calcium with deionized H_2O. As before, elution was continued until the calcium content of the effluent was reduced to 0.1 μg/mL or less as measured by ICP spectroscopy. The column was then preconditioned at a flow rate of 0.100 mL/min with a series of degassed MeOH:H_2O solutions.

A feed solution (1000 mL) was prepared to target conditions of 0.01 M CaI_2 in 99:1 MeOH:H_2O. Purified CaO (568.00 mg, 10.13 mmole) was slowly titrated with a total of 2.15 mL 57.3% HI (Aldrich "Gold Label" grade). Deionized H_2O was added to facilitate mixing, but the volume was kept below 1% of the final volume. Enough degassed, deionized H_2O was added to the resultant CaI_2 to total 1% of the target volume, including the water contributed during titration. Degassed MeOH was added to yield a final volume of 1000 mL. The density of this solution was measured as 0.79 g/mL, and the excess H^+ ion concentration was calculated as 1.5×10^{-4} M

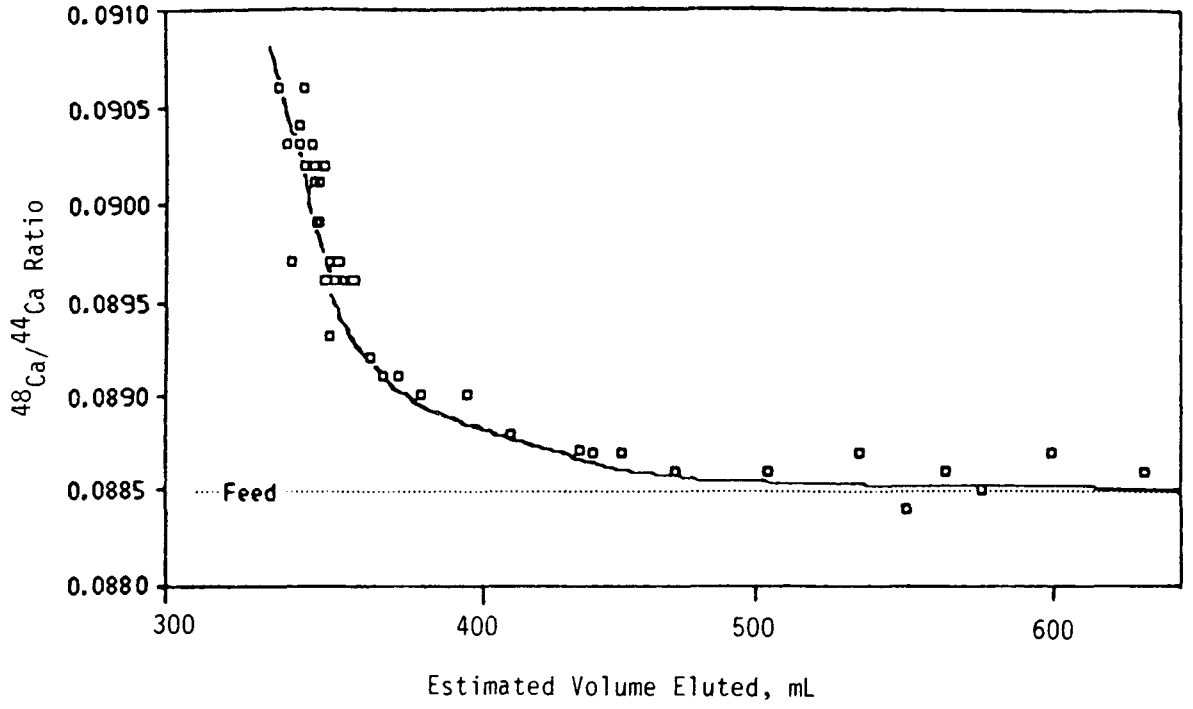
(3.4% of the estimated column capacity). A 5.94-mL aliquot was removed and analyzed by ICP spectroscopy to give a measured feed calcium concentration of 7.39×10^{-3} M.

The CaI_2 solution was pumped through the column (top to bottom) at an initial flow rate of 0.100 mL/min. A leaking piston seal on the pump caused depletion of the feed reservoir before the calcium breakthrough was reached. A second batch of CaI_2 solution (measured $Ca^{++} = 7.45 \times 10^{-3}$ M; estimated excess $H^+ = 4 \times 10^{-3}$ M) was used to continue the experiment. The resin bed depth remained constant at 99.5 cm throughout the test.

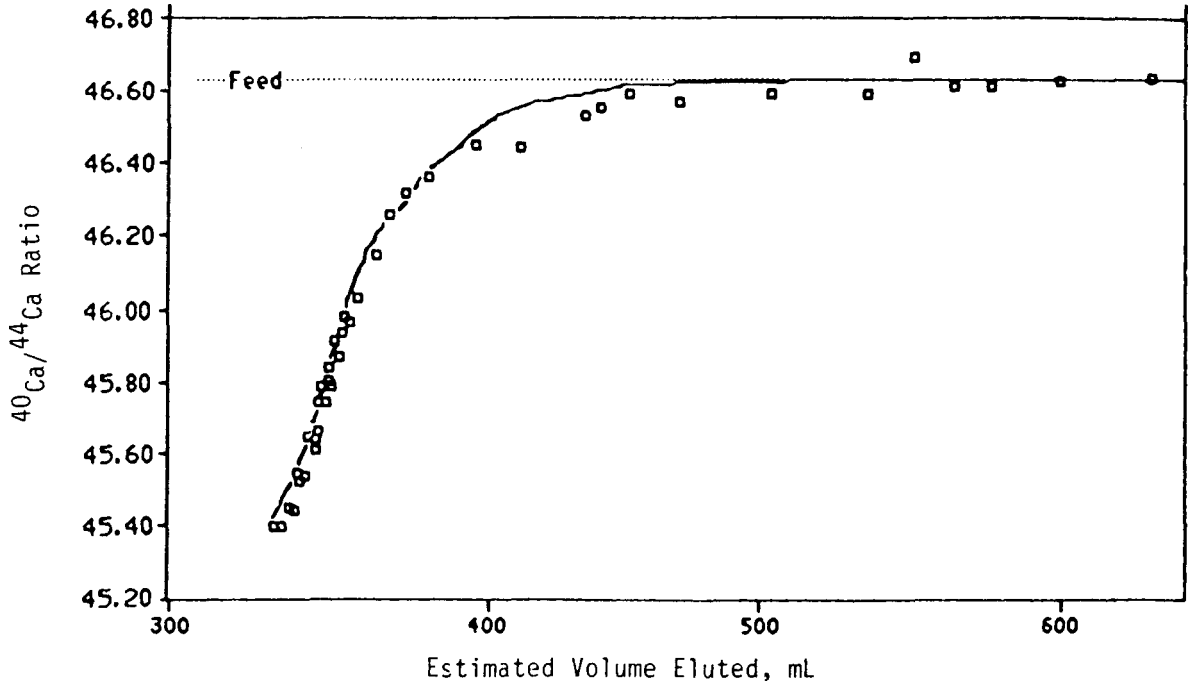
During the course of the experiment, two colored bands developed and progressed down the column. A dark brown band at the head of the column was preceded by a light yellow, more rapidly moving band. The light yellow band emerged from the column between samples 697 and 708. The bands were attributed to excess iodide species originating from the reagent HI. Since the calcium band front preceded these impurities through the column, they are not expected to affect the isotopic exchange process.

In all, 797 samples were collected during the cumulative 68.76 hr of column operation. Samples were processed as described for the $CaCl_2$-2B21 cryptand resin column experiment. A meaningful, complete calcium breakthrough curve for this experiment could not be obtained because of flow rate variations caused by the pump failure. Consequently, the total column capacity could not be measured directly from the calcium flow rate. Instead, the calcium was eluted from the column and measured by ICP spectroscopy to give a total column capacity of 157.7 mg.

The isotopic enrichment profiles are shown in Figure I-4. This chemical system appears to show more promise than those reported above, at least in terms of enrichment. This was the only experiment for which the ^{48}Ca enrichment was significantly larger than the



(a)



(b)

FIGURE I-4 - Isotope enrichment profiles for CaI_2 system.

error limits on the mass spectrometric data. The volume eluted coordinate of these plots represents only a rough approximation as a consequence of the erratic pump performance. Volumes were estimated by summing individual sample volumes after completion of the experiment. However, the extent of methanol evaporation while the samples were residing in the fraction collector could not be determined. Further work must be done with this system before a separation coefficient can be reported.

$CaCl_2$/Methanol:Chloroform-2B22 Cryptand Resin Column Experiment. Most of the column experiments with the 2B22 and 2B21 cryptand resins have used a mobile phase of $CaCl_2$ dissolved in 99% methanol-1% water. Heumann has reported a relatively large separation factor ($^{44}Ca/^{40}Ca$) of 0.0057 at 20°C on a 2B22 cryptand resin using a mobile phase of methanol/chloroform/water (70:30 by volume + 1.65% H_2O) [1]. An experiment was conducted to determine the effect of chloroform on the separation factor as determined by the breakthrough technique.

The column used for this experiment was the same 6.3-mm diameter by 109-cm long column used previously for the 2B22 cryptand experiments. As before, the column contained Kryptofix® 2B22 polymer packed to a depth of 99.5 cm. Again, calcium was eluted from the packing with deionized H_2O, and the column was preconditioned with methanol/water solutions followed by a methanol/chloroform/water phase.

The feed solution for this experiment was prepared by dissolving 1.046 g (9.42 mmole) $CaCl_2$ in 16.6 mL H_2O and diluting to 1000 mL with MeOH:$CHCl_3$ (70:30 by volume). This solution was pumped to the column at a flow rate of 0.100 mL/min (6.0 mL/hr). Samples were collected at 12-min intervals to yield 1.2 mL per sample. Sample analysis is under way, but a discussion of results will be deferred until the next report in this series.

FREE CRYPTAND 222 EXPERIMENTS

In all of the preceding work, the cryptand functional group was chemically bound to the resin. Binding the cryptand to the resin substantially alters its complexing characteristics with calcium ions. For example, calcium cryptates (not bound to a resin) are exceedingly stable in aqueous solutions, with values for the log of the stability constant of 4.40 (cryptand 222) and 6.95 (cryptand 221) [4]. However, the distribution of calcium onto resin-bound cryptands from aqueous solutions is negligible. Thus, a methanolic fluid phase was used in the resin-bound cryptand experiments to achieve a suitable calcium distribution. The inability of resin-bound cryptands to complex with aqueous calcium is presumed to be a consequence of steric restrictions imposed by the resin binding and, possibly, a result of the hydrophobicity of the Merrifield resin used.

Work described below has shown that calcium may be effectively separated from the 222 cryptand with which it is complexed by gradient elution chromatography. This separation was accomplished in a packed bed 5 cm deep and 3 cm in diameter composed of 200 to 400 mesh Bio•Rad AG 50 W-X4 sulfonate resin preloaded with calcium chloride cryptate. In a gradient elution with hydrochloric acid, calcium was obtained first from the column, followed by acid-complexed cryptand. Results of this elution are shown in Table I-1. It is evident from these data that calcium cryptate ions are initially absorbed onto the resin and that these are displaced by the more strongly bound acid cryptate ions.

This is an exceedingly complicated system since it involves a basic ligand with a zero formal charge. Further work to describe the observed behavior in more detail was beyond the scope of this project. However, this behavior did suggest the feasibility of the use of free cryptands in ion exchange columns for calcium isotope enrichment. Such a free cryptand chemical system permits the use of conventional column packings along with aqueous fluid phases.

Table I-1 - GRADIENT ELUTION OF CALCIUM CRYPTATE

Elution Step	Eluent Volume (cm^3)	Eluent HCl (M)	Total Calcium (mg)	Total Cryptand (mg)
1	50	0(H_2O)	0.1	--
2	53	0.1	85	--
3	50	0.5	260	--
4	50	1.0	220	--
5	53	2.0	148	27
6	50	4.0	20	590
7	56	6.0	0.6	228

Screening Experiments

Two column screening experiments were performed to determine whether the previously expected large calcium-cryptand isotope effect could be utilized in an aqueous system. These runs were designated as free cryptand runs and relied on the distribution of cryptand between the two phases to obtain an isotopic enrichment.

Two exchange reactions can be written for the first of these experiments:

$$^{44}Ca^{++}_{aq} + {}^{40}Ca[222]^{++}_{res} \rightleftharpoons {}^{40}Ca^{++}_{aq} + {}^{44}Ca[222]^{++}_{res} \qquad (a)$$

$$^{*}Ca[222]^{++}_{aq} + Ca[222]^{++}_{res} \rightleftharpoons Ca[222]^{++}_{aq} + {}^{*}Ca[222]^{++}_{res} \qquad (b)$$

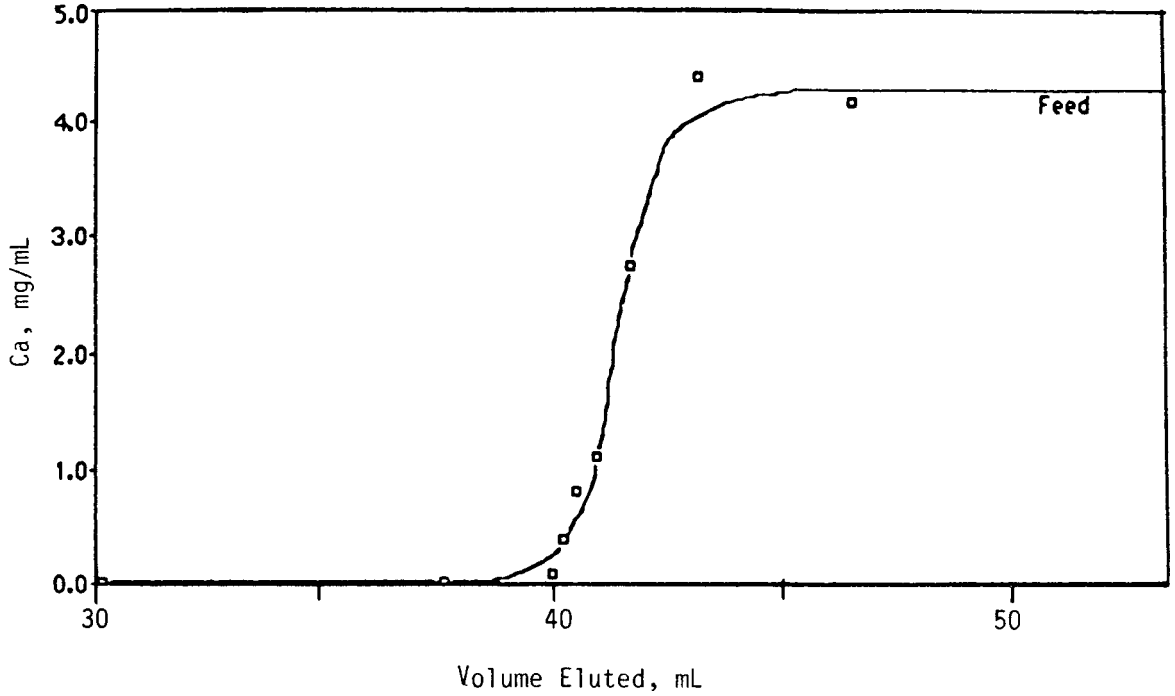
These are parallel reactions and the observed separation coefficient represents a composite of the two reactions. Reaction (b) is expected to exhibit a small isotope effect since the coordination sphere of calcium is relatively unchanged whether it is on the resin or in the aqueous phase. Thus, the mole fraction of the aqueous calcium

cryptate species must be kept small if a large separation coefficient is to be realized.

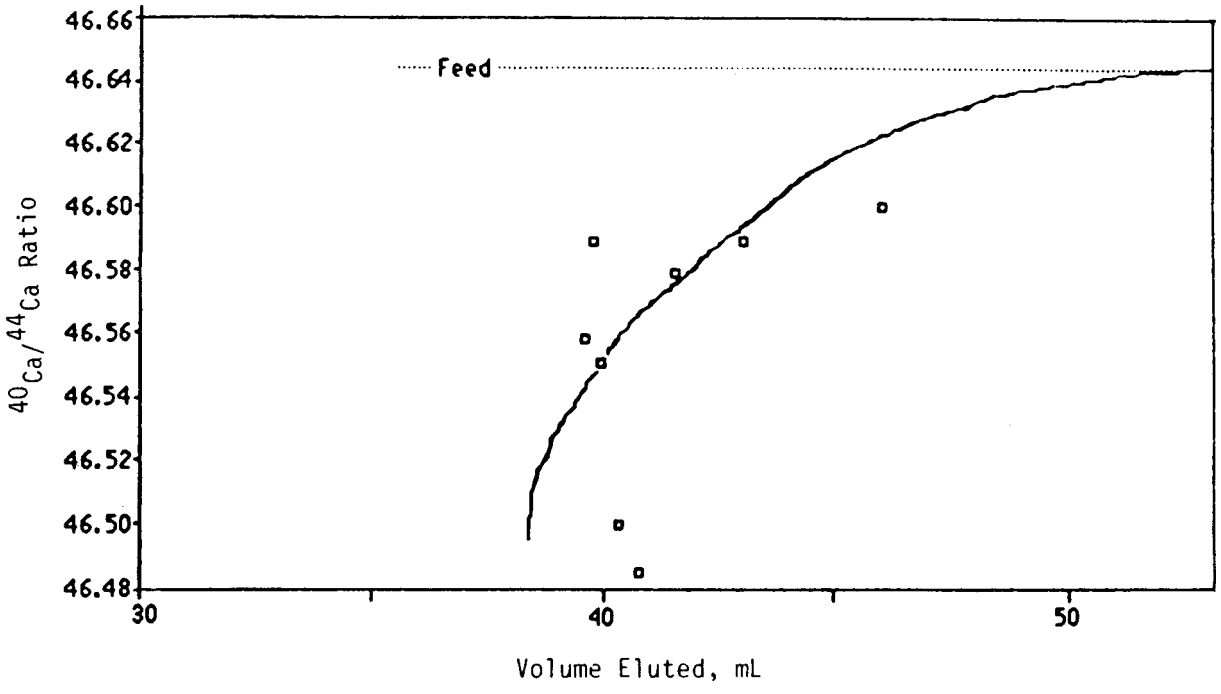
A column 6 mm in diameter and 22 cm long was packed with 200 to 400 mesh Bio•Rad AG 50 W-X4 resin containing 0.90 g 222 cryptand. The resin was mixed with aqueous cryptand before the column was filled. The column was then packed by recycling the equilibrated supernatent solution to prevent cryptand losses. The pH of the supernatent was 2.22, indicating that no significant quantities of the strongly basic cryptand remained in the fluid. The pH of a blank mixture of resin plus water (without cryptand) in equivalent quantities was 2.20. An aqueous feed solution of 0.10 M $CaCl_2$ and 0.022 M cryptand 222 was prepared. The calcium capacity of the column was 160 mg. In this experiment, large samples were collected until trace quantities of calcium were detected by atomic absorption spectrophotometry. The sample size was then reduced to 0.25 mL and gradually increased to 4.0 mL.

The breakthrough curve and isotope enrichment profile for this experiment are shown in Figure I-5. Based on the work with resin-bound cryptands discussed above, there is evidence that the expectation of a large calcium-cryptand equilibrium isotope effect may be unfounded. Isotope profiles in screening runs are not usually measured since it is preferable to obtain larger enrichments from 1-m long columns. However, because further work on free cryptand systems will probably be delayed until the upper limit of the cryptand effect is determined, the isotope profiles were measured. The separation coefficient calculated from the preliminary and incomplete data shown in Figure I-5 is 0.0007 for the 44/40 isotope pair. This is about 50% of that found for the $CaCl_2$/2B22/25°C resin-bound system and three times that found for the $CaCl_2$/2B21/25°C system.

A second screening experiment was conducted to test the feasibility of displacing a magnesium-cryptate complex from a cation exchange



(a)



(b)

FIGURE I-5 - Calcium breakthrough curve (a) and ^{44}Ca enrichment curve (b) for free cryptand 222 experiment.

resin using calcium. The proposed displacement reaction is given by Reaction (c) and the proposed isotopic enrichment reaction is given by Reaction (d).

$$Ca^{++}_{aq} + Mg[222]^{++}_{res} \rightleftharpoons Ca[222]^{++}_{res} + Mg^{++}_{aq} \qquad (c)$$

$$^{40}Ca^{++}_{aq} + {}^{48}Ca^{++}_{res} \rightleftharpoons {}^{48}Ca^{++}_{aq} + {}^{40}Ca^{++}_{res} \qquad (d)$$

Magnesium-loaded Dowex 50-X4 (200 to 400 mesh) was prepared by adding 0.93 g $Mg(OH)_2$ to 1.5 g resin slurried in water. The pH of the resulting slurry was 8. After 0.55 g (0.0015 mole) of cryptand 222 was added and mixed, the slurry pH rose to 11.8. The loaded resin was then packed into a 5.8-cm diameter by 8.7-cm long column.

A feed solution containing 0.039 M $CaCl_2$ and 0.0075 M cryptand 222 was passed through the column, and a series of samples was collected. The results of the calcium and magnesium concentration measurements are shown in Figure I-6. The calcium curve shows a typical

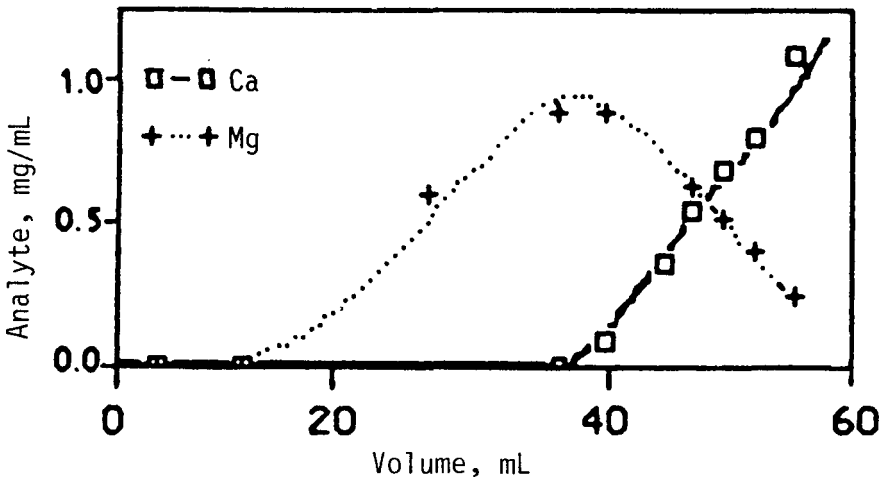


FIGURE I-6 - Calcium and magnesium concentration profiles for magnesium-cryptand experiment.

breakthrough curve approaching, but not reaching, the feed concentration because of premature termination of the experiment. The magnesium curve shows the expected displacement, but this also was not completed. Samples were examined by ultraviolet spectrophotometry to assess the behavior of the cryptate. Quantitative analyses were not possible, but the spectra showed incomplete absorption of the cryptate during loading of the resin and subsequent "leakage" throughout the experiment. No attempt was made to determine calcium isotopic ratios for this experiment because of the lack of a suitable procedure for separating the magnesium contaminant from the calcium in the samples.

ADDITIONAL INFORMATION

Isotope ratios were obtained for the natural abundance calcium feed material at intervals during the sample analysis period. The $^{40}Ca/^{44}Ca$ ratios are shown in Figure I-7, along with the average of 46.64 ± 0.03. The $^{48}Ca/^{44}Ca$ ratio average was 0.0885 ± 0.00014. The instrument used was a 15-in. 90° gas mass spectrometer modified for thermal ionization of solids.

An ion exchange purification procedure has been adopted for preparing calcium samples to be analyzed by mass spectrometry. Calcium samples were pretreated prior to this ion exchange purification in several ways. Samples from column experiments using nonaqueous solvents (e.g. methanol) were evaporated to dryness and redissolved in dilute HCl or HNO_3. Nonvolatile organic components such as complexants were destroyed by heating the sample to 750°C for 4 hr, after which the residue was redissolved in acid. Known aliquots were removed for calcium concentration analyses by ICP spectroscopy or ion chromatography.

Following the appropriate pretreatment, small ion exchange columns were prepared in disposable pipette tips using a plug of glass wool

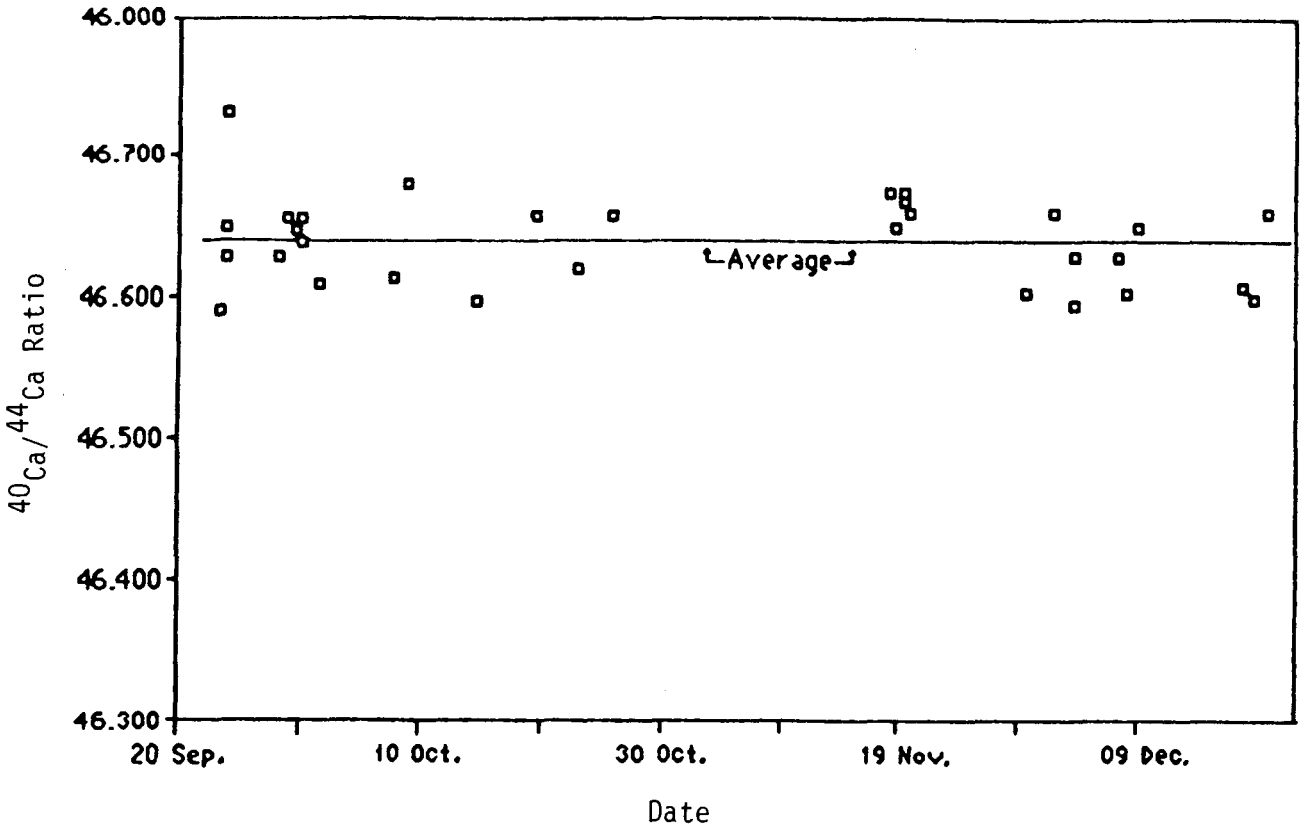


FIGURE I-7 - Feed sample isotope ratio analyses.

and 0.4 to 0.5 mL 200 to 400 mesh Dowex 50W-X4 cation exchange resin. These columns were washed with 3 M HNO_3 to remove impurities, particularly sodium. Sodium contamination levels were traced in a semiquantitative fashion with an atomic absorption spectrophotometer (Buck Scientific Model 200).

Aliquots containing 0.05 to 0.2 mg of calcium were loaded on the ion exchange column from dilute (0.2 M or less) HCl or HNO_3 and washed with 0.2 M HNO_3 until the sodium content of the effluents was reduced to background levels. The calcium was quantitatively eluted into a clean glass vial with 2 M HNO_3, evaporated, digested in concentrated HNO_3, and evaporated to dryness again. Just prior to mass spectrometric analysis, the samples were dissolved in 0.1 M HNO_3 and adjusted to a calcium concentration of 0.2 mg/mL.

Liquid Phase Thermal Diffusion

W. M. Rutherford

ISOTOPIC THERMAL DIFFUSION OF THE LOWER ALKYL BROMIDES

Previous research has shown that the isotopic thermal diffusion factor in substituted benzenes and in carbon disulfide is dependent on relative differences in mass between diffusing molecules and also on differences in the distribution of mass within the molecules [5,6]. The effect of mass distribution is related to relative differences in the second moment. The thermal diffusion factor for these systems is well-represented by an equation of the form:

$$\alpha_T = c_1(m_1-m_2)/(m_1+m_2)+c_2(I_1-I_2)/(I_1+I_2) \qquad (1)$$

where α_T is the isotopic thermal diffusion factor,
m_1 and m_2 are the molecular masses, and
I_1 and I_2 are second moments about some suitable axis of rotation.

The results of more recent experiments indicate that the coefficient of the second term of Equation (1) is zero for systems in which molecular rotation is hindered [7]. Thus, only the first order mass difference term is required to correlate isotopic thermal diffusion effects in the lower alkyl chlorides [7].

The current series of experiments was extended to include measurements of the thermal diffusion separation of isotopically substituted bromine in several of the lower alkyl bromides. As was the case in previous experiments, the thermal diffusion factor was determined from the results of measuring separation as a function of time in a short, precisely constructed thermal diffusion column.

The thermal diffusion column was the same one that was used for the earlier experiments with alkyl chlorides. It was 46 cm long with an average annular diameter of 1.9 cm and a hot-to-cold wall spacing of 266 μm. Hot wall temperatures ranged from 98 to 100°C, depending on the compound. The cold wall temperature was 23°C.

The purity of methyl bromide purchased from the Matheson Company was stated as 99.5%. 1-bromopropane purchased from MCB Manufacturing was found by gas chromatographic analysis to contain 99.6% 1-bromopropane. Ethyl bromide from Fisher Scientific, purified by liquid phase thermal diffusion, contained no detectable impurities at an analytical sensitivity of 0.01%. All materials were degassed and dried over molecular sieve 4A prior to use.

Results of the transient separation measurements of the ^{79}Br-^{81}Br substituted pairs are presented in Figure I-8, which is a plot of the logarithm of the separation factor as a function of time. The method used for reduction of these data to obtain experimental thermal diffusion factors was described in a previous report [8]. It involves fitting the experimental transient data by adjusting column parameters H and Y to fit the data. These parameters are the initial transport coefficent and the natural logarithm of the equilibrium separation factor, respectively. The thermal diffusion factor is directly proportional to the initial transport coefficient.

The performance of thermal diffusion columns may deviate significantly from theory as the result of nonideal experimental conditions. This can adversely affect the accuracy of thermal diffusion factors derived from measured separation data. A useful test of the validity of the theory in an experiment is provided by calculating a factor, F, which is an approximate measure of the ratio of the internal circulation rate to that calculated from theory. F is given by

$$F = (K_{exptl}/K_{theory})^{1/2} \qquad (2)$$

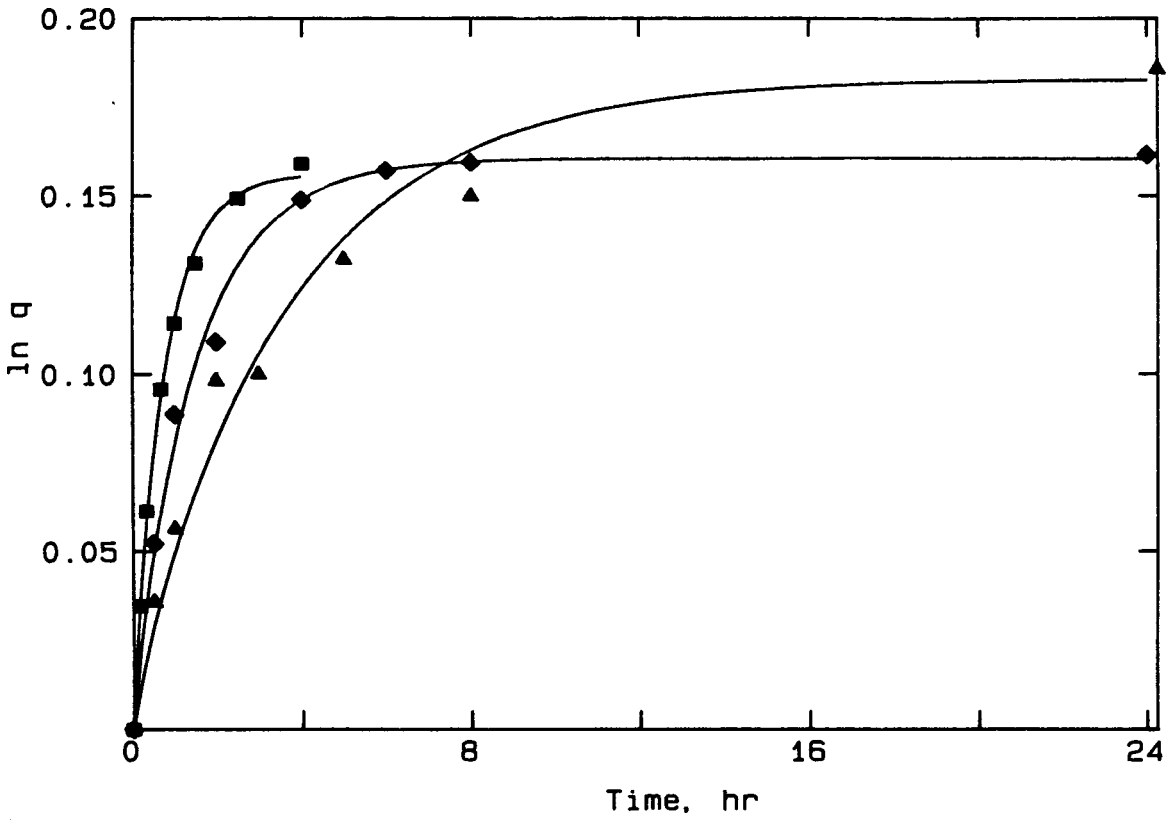


FIGURE I-8 - Separation of ^{81}Br-^{79}Br as a function of time for three alkyl bromides. The squares are data for methyl bromide, the diamonds are data for ethyl bromide, and the triangles are data for 1-bromopropane.

where K_{exptl} is the experimental remixing coefficient and
K_{theory} is the corresponding coefficient calculated from the theory of the thermal diffusion column.

K_{exptl} is derived from the experimental results by

$$K_{exptl}=HL/Y \qquad (3)$$

where L is the length of the column and

$Y = \ln q_e$, where q_e is the equilibrium separation factor.

Ideally, F should equal unity.

Thermal diffusion factors derived from the experimental data are given in Table I-2, along with the F factor calculated for each experiment. The thermal diffusion factors are plotted as a function of carbon number in Figure I-9. Also plotted in Figure I-9 are the thermal diffusion results obtained earlier for some of the lower alkyl chlorides. The average temperature for the experiments was 60 ± 1°C.

The results obtained in this investigation are substantially more accurate than those obtained earlier for some of the same compounds [9,10]. There are several reasons for the improvement: (1) significant improvements have been made in the construction and operation of the experimental columns; (2) the hot wall temperature has been reduced to a point where there is little corrosion of the column by the liquid halogen compound, a problem encountered in earlier work; and (3) the data were reduced using accurate experimental values of viscosity and density that were recently measured at Mound [11].

Table I-2 - ^{81}Br-^{79}Br THERMAL DIFFUSION FACTORS FOR THE LOWER ALKYL BROMIDES

Compound	Thermal Diffusion Factor, α_T	F Factor
Methyl bromide	0.0219	1.04
Ethyl bromide	0.0189	1.14
1-bromopropane	0.0154	1.03

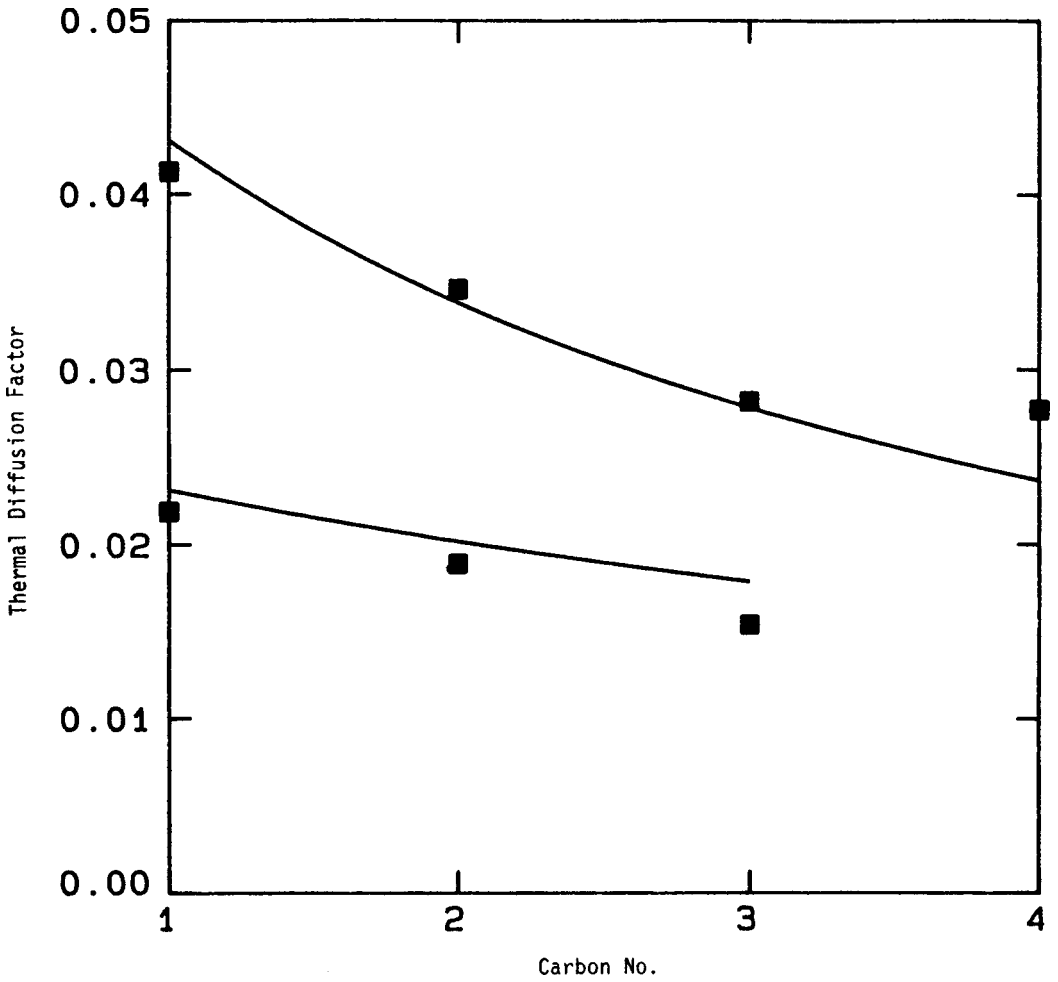


FIGURE I-9 - Bromine isotopic thermal diffusion factors for the lower alkyl chlorides and bromides. The upper curve represents the chlorides and the lower curve represents the bromides.

In previous work with carbon disulfide and with substituted benzenes, c_1, the coefficient of the first term in Equation (1), was found to be approximately equal to 2 (1.97 for benzene, 2.20 for carbon disulfide). In more recent work, this value, with $c_2 = 0$, was found to correlate thermal diffusion data for the alkyl chlorides. Thus, for the alkyl chlorides, it was found that

$$\alpha_T = 2.2(m_1 - m_2)/(m_1 + m_2) \quad (4)$$

This is Equation (1) where $c_1 = 2.2$ and $c_2 = 0$.

The two smooth curves in Figure I-9 represent the values predicted by Equation (4) for the alkyl chlorides and the alkyl bromides. Equation (4) fits the two sets of experimental data reasonably well, considering that the accuracy of the measurements is on the order of ±15%. These results appear to support the conjecture that, when molecular rotation is hindered, isotopic thermal diffusion in liquids depends only on the relative difference in mass between the diffusing species.

SEPARATION OF SILICON ISOTOPES BY THERMAL DIFFUSION

Silicon isotopes can be separated by liquid phase thermal diffusion of organosilicon compounds. In earlier experiments, the thermal diffusion factor for the ^{30}Si-^{28}Si pair in tetramethylsilane was found to be large enough to support practical scale experiments, and the fluid was found to be chemically stable for extended periods at normal operating temperatures [12]. The practicality of the process was later demonstrated by the operation of an experimental nine-column cascade designed for the separation of ^{30}Si from a natural abundance material containing 3.1% ^{30}Si [13]. After an extended startup period, the enrichment of ^{30}Si at the bottom of that system reached 42%.

At that time, theoretical calculations showed that the nine-column system could not yield reasonable rates of production of enriched material at concentrations much above 20% ^{30}Si. The system was gradually expanded, therefore, as additional equipment was constructed, tested, and made available.

Following the first expansion, from 9 to 10 columns, it was possible to sustain a low production rate of material enriched to approximately 50% ^{30}Si. A total of 6.2 g of tetramethylsilane was accumulated at this isotopic concentration during a 63-day production period. Figure I-10 is a plot of product concentration as a function of time beginning at an arbitrary zero point when the system was nine columns long.

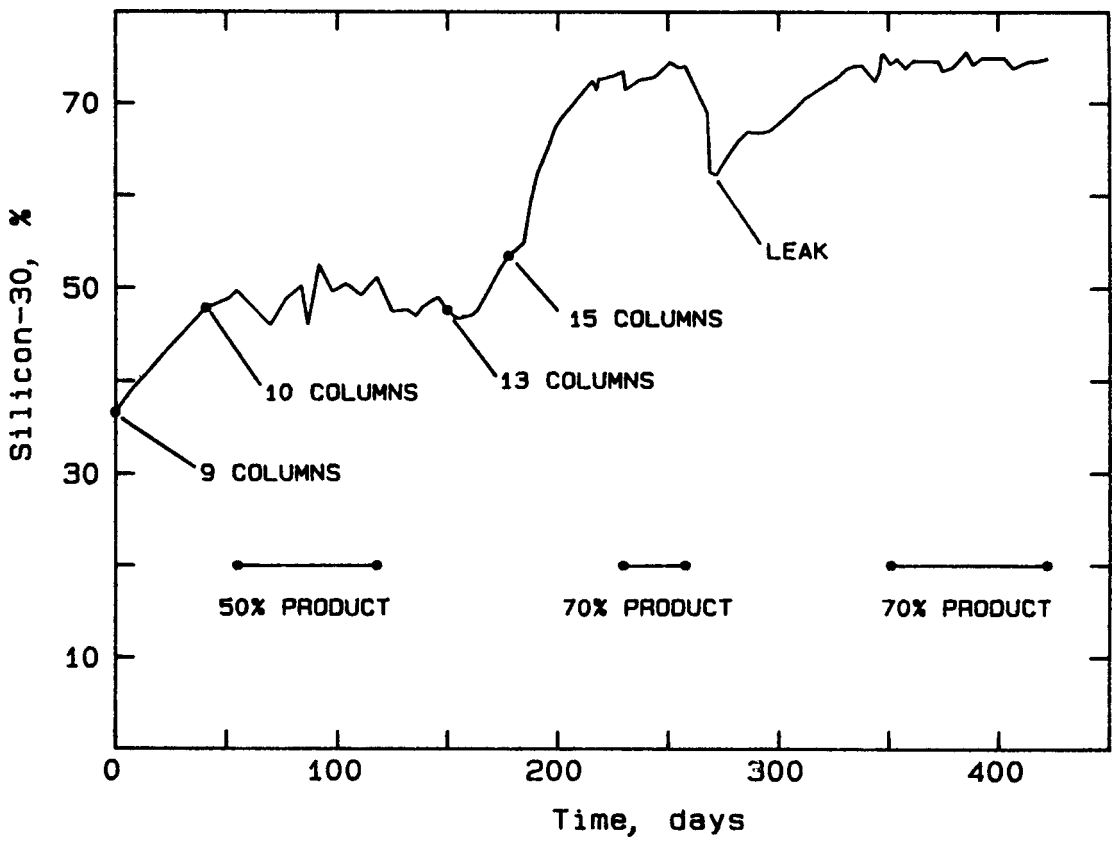


Figure I-10 - Separation of ^{30}Si by thermal diffusion of tetramethylsilane.

Extension of the cascade to 13, then 15 columns resulted in a rapid increase of the product enrichment to greater than 70% ^{30}Si. Additional product was removed from the cascade at that concentration in two sustained runs of 28 and 71 days, respectively. The experiments were interrupted for a time by a utility failure and an associated large loss of partially enriched tetramethylsilane.

The average production rate of tetramethylsilane during the 71-day run was 0.25 g/day. This result is in good agreement with the value of 0.25 g/day predicted from theory using the cascade parameters given in Table I-3. In Table I-3, the column parameters H and Y are the initial transport coefficient and the natural logarithm of the equilibrium separation factor, respectively, for unit difference in molecular mass.

Table I-3 - COLUMN PARAMETERS FOR THE TETRAMETHYLSILANE CASCADE

Column	Length (m)	Spacing (μm)	10^5H (g/s)	Y
1	2.44	305	7.02	0.32
2	1.11	305	7.02	0.15
3	1.10	305	7.02	0.15
4	1.14	305	7.02	0.15
5	1.14	305	7.02	0.15
6	1.17	254	3.76	0.32
7	1.17	254	3.76	0.32
8	1.16	254	3.76	0.32
9	1.14	254	3.76	0.32
10	0.61	254	3.76	0.17
11	0.76	254	3.76	0.21
12	0.76	254	3.76	0.21
13	0.76	229	2.62	0.32
14	0.76	203	1.74	0.51
15	0.76	203	1.74	0.51

II. Calculations in Plutonium Chemistry

Determination of Plutonium Oxidation State Distributions

G. L. Silver

Volume 1 of The Chemistry of the Actinide Elements edited by Katz, Seaborg, and Morss contains a method for determining plutonium oxidation state distributions [1]. These distributions are calculated as a function of the plutonium oxidation number (N) and the acidity of the solution in which the plutonium is dissolved. Briefly, the method requires solving a cubic equation (Equation (7.25) in the cited work) for the ratio of uncomplexed hexavalent plutonium to uncomplexed pentavalent plutonium. This ratio is denoted by an italic capital M. The value of this ratio is substituted into the right-hand sides of Equations (7.21) to (7.24). The right-hand side of each of these equations is then divided by the sum of the right-hand sides. In this division, the term $[PuO_2^+]$ disappears by cancellation. Each of the four divisions produces a quotient that represents the fraction of one of the four plutonium oxidation states.

Equation (7.25) (the plutonium "characteristic equation") on page 825 of the Actinide Elements book may be solved with great accuracy by a number of the standard root-finding procedures. This author's preference of procedures is the bisection method. This method was used many years ago on a modified form of the characteristic equation to determine oxidation state distributions as well as the solution acidity induced by rearrangement of the initial distribution [2]. The original program was prepared in FOCAL language, a product of the Digital Equipment Corporation. FOCAL is now a dead language.

Appendix II-A presents an alternative method for determining equilibrium oxidation state distributions for plutonium. It is written in version 1.1 of BETTERBASIC language, a product of Summit Software Technology of Norwood, MA. This language accesses the 8087 math coprocessing chip. The basis of the program is a uniplex routine. The virtues of the program are that it is easy to write and

that it works for most situations that typically arise in the laboratory. Convergence is not guaranteed, however. Therefore, purists may prefer to use the characteristic equation to prepare programs using algorithms they consider to be more reliable.

The program begins by asking the user for values of the equilibrium constants for two chemical reactions that are specified in the prompts. These equilibrium constants are denoted K_1 and K_2, and the chemical reactions are given as Equations (7.1) and (7.2) on pages 820 and 821 in the Actinide Elements book. After the numerical values of K_1 and K_2 are entered, the value of the first hydrolysis constant of the tetravalent plutonium cation is solicited. This constant may be given as zero if hydrolysis is to be neglected in determining the final acidity and oxidation state distribution.

Next, the limit of accuracy on the calcuations is requested. In the example in Appendix II-A, the entry is 1E-07. This number is the absolute value of the logarithm of the most recently calculated ratio Q_1/K_1. K_1 is the equilibrium constant previously entered, and Q_1 is the concentration quotient $[Pu^{3+}][PuO_2^{+}][H^{+}]^4/[Pu^{4+}]^2$. For most purposes, 1E-07 will provide more than enough accuracy. In problems where convergence of the routine is not obtained, the entry may sometimes be relaxed to 1E-06 or 1E-05 for satisfactory execution of the program.

The alpha coefficients of the four plutonium oxidation states are requested next. If no complexation is desired, unity may be entered for all four values. AX, the alpha coefficient for the tetravalent plutonium cation, is taken in the program as the entered value of AX plus the term $KH/[H^{+}]$. (KH is the constant for the first hydrolysis reaction of the tetravalent cation.) Thus, the term AX solicited is the alpha coefficient that arises from all other complexation reactions, except complexation by hydrolysis of Pu^{4+} to $PuOH^{3+}$. If unity is entered as the value of AX, the alpha coefficient for tetravalent plutonium will ultimately be assigned the value $1 + KH/[H^{+}]$.

An alpha coefficient is the ratio of the concentration of total soluble oxidation state to the concentration of uncomplexed oxidation state. For tetravalent plutonium, this ratio is $([Pu^{4+}]+[PuOH^{3+}])/[Pu^{4+}]$ if hydrolysis is the sole form of complexation. An alpha coefficient may be calculated if the concentrations of unbound complexing agents and their appropriate formation constants are known.

The initial fractions of dissolved plutonium oxidation states are requested next. These numbers should sum to unity. In the example in the appendix, a solution initially containing 50% trivalent and 50% hexavalent plutonium is examined. The oxidation number (N) of such a solution is 4.5.

Next, the initial solution acidity in molar units is requested. A 1 M acid solution is considered in the example. The total concentration of soluble plutonium is next requested. The most common response to this prompt will be zero. Zero concentration is entered to allow the solution to be studied at constant acidity, historically the most frequently considered case.

At this point, the program gives the user an option. The final solution conditions may be approached through use of the ratio of unsequestered hexavalent to pentavalent plutonium (method No. 1) or through use of the ratio of unsequestered trivalent to pentavalent plutonium (method No. 2). A general rule of thumb regarding selection of the appropriate method is to use method No. 1 for oxidation numbers of four or greater and to use method No. 2 for oxidation numbers less than four. If the wrong method is selected, as will be indicated by failure of the program to converge, the user should break into the program at the computer keyboard and restart at line 270.

The uniplex routine needs two reasonable guesses for the true hexavalent/pentavalent or trivalent/pentavalent ratio. Extreme guesses such as 1E30 and 1E32 or 1E-30 and 1E-32 usually work, but are

often so distant from the true value that convergence is slow. Sometimes these guesses are too extreme, and "ordinary" numbers such as 1 and 100 are better. Experience will suggest what values usually work for what circumstances. The example in the appendix uses 100 and 200 as the first guesses because it was known that the ratio of uncomplexed hexavalent/pentavalent plutonium for N=5 and H^+=1 M is approximately 150. Numbers such as 10 and 12 would also work in this example. The routine is sufficiently flexible to accommodate most reasonable guesses.

Bad guesses occur most frequently between oxidation numbers 3 and 4 or between 5 and 6. This results because some values of the aforementioned ratios are forbidden in these ranges of N. (Forbidden variable combinations are discussed elsewhere [3].) If the user supplies the routine with forbidden values of *M* for the given value of N, the routine falters. Failure to start satisfactorily is indicated by failure of the displayed numbers to progress "downward" to the accuracy limit. The routine must now be interrupted from the computer keyboard, and either the guesses or the method must be changed.

This author has found few problems that cannot be solved by method No. 1 or method No. 2 using one of the sets of suggested guesses. If alpha coefficients are large (such as 1E20), these guesses may be inadequate and can be revised to even more extreme values such as 1E50 and 1E52 or 1E-50 and 1E-52. Experimenting with the method often works and is encouraged. (Note added in proof: at line 570, set G(A) = 1E50.)

Large values of the alpha coefficients or extreme values of N (close to 3.0 or 6.0) cause another kind of convergence problem: the accuracy of the routine becomes the limiting factor. For example, suppose the true value of the equilibrium ratio Pu^{3+}/PuO_2^+ is 6.999999999999992345. Because the 8087 chip has a limit of 14 digits,

the true ratio cannot be obtained, and the user must be satisfied with 6.9999999999999, a number that may be too far from the correct ratio to allow the desired accuracy to be obtained. In this case, the diminishing numbers will reach a limit and then repeat endlessly. The best possible solution is to break out of the program from the computer keyboard and go to line 680.

The program yields the equilibrium fractions of the four oxidation states. Precipitation of insoluble phases is not considered; therefore, the distribution refers only to soluble oxidation states. "Tetravalent-OH" represents $PuOH^{3+}$; the fraction of this species is also included in the fraction of total tetravalent plutonium. The final acidity is printed. The last piece of information is the value of K_1 computed using the calculated valence state distribution. This value should closely match the entered value of K_1. In the example in the appendix, agreement is close. If the agreement is not close, the problem was not satisfactorily solved by the routine. The user may then wish to revert to a more conventional method using a standard root-solving procedure, such as the bisection method. When calculation is finished, another problem may be solved by starting the routine at any of three locations, as indicated.

Suggesting so many possible causes of failure gives the impression that the routine has limited use. However, this author has not experienced failure when the plutonium concentration is zero unless the oxidation number is close to 3.00 or 6.00. Failure is usually not observed if the plutonium concentration is typical of that observed in laboratory situations; that is, 0.2 M or less. Failure can be induced by higher concentrations of plutonium or by unusual circumstances: for example, 1 M plutonium, all pentavalent, initially in 1 L of 0.10 M acid. Success is sometimes achieved in unusual circumstances if the hydrolysis constant is initially set equal to zero, then reset to its value of approximately 0.03 in a new problem that takes the initial conditions as the final conditions obtained with the KH=0 assignment.

Appendix II–A

BETTERBASIC Program for Determining Plutonium Oxidation State Distributions

```
SOURCE
PROCS=0
INTEGER: A
REAL ARRAY(5): J
REAL ARRAY(5): G
REAL: R,E,CR,CW,K1,K2,KH,AW
REAL: A4,AY,AZ,AX,WI,XI,XHI,YI
REAL: ZI,HO,HN,T,ZU,WU,N,XU
REAL: WR,XR,YR,ZR,XHR,PUT,WF,XF
REAL: YF,ZF,XHF,Q1,AL,MT,OP
   10 PRINT "                  UNIPLEX ROUTINE FOR STUDYING PU SOLUTIONS": PRINT
   20 PRINT "THE VALUE OF THE OBJECTIVE FUNCTION IS CONTINUOUSLY PRINTED."
   30 PRINT "THIS VALUE MUST (!) DIMINISH TOWARD ZERO TO SOLVE THE PROBLEM."
   40 PRINT "IF THE OBJECTIVE FUNCTION FAILS TO DECREASE, THE INITIAL GUESSES"
   50 PRINT "FOR THE PU(6)/PU(5) RATIO (METHOD #1) OR THE PU(3)/PU(5) RATIO"
   60 PRINT "(METHOD #2) ARE UNACCEPTABLE.  TRY OTHER VALUES.  THE TWO METHODS"
   70 PRINT "REQUIRE DIFFERENT STARTING VALUES.":  PRINT
   80 INPUT "GIVE 2PU(4) = PU(3) + PU(5) CONSTANT           ", K1
   90 INPUT "GIVE PU(4) + PU(5) = PU(3)+ PU(6) CONSTANT     ", K2
  100 INPUT "GIVE PU(4) + HOH = PU(4)OH  + H CONSTANT       ", KH: PRINT
  110 INPUT "GIVE ACCURACY LIMIT, A NUMBER LIKE 1E-07    ", AL: PRINT
  120 PRINT "GIVE ALPHA COEFFICIENTS FOR PU(3), PU(4), PU(5), PU(6)"
  130 PRINT "BUT DO NOT INCLUDE HYDROLYSIS OF PU(4) TO PU(4)OH"
  140 INPUT "AW =                ", AW
  150 INPUT "AX =                ", A4
  160 INPUT "AY =                ", AY
  170 INPUT "AZ =                ", AZ: PRINT
  180 PRINT "GIVE INITIAL VALENCE STATE DISTRIBUTION"
  190 INPUT "PU(3) =          ", WI
  200 INPUT "PU(4) =          ", XI
  210 INPUT "PU(4)OH =        ", XHI
  220 INPUT "PU(5) =          ", YI
  230 INPUT "PU(6) =          ", ZI
  240 N=3*WI+4*(XI+XHI)+5*YI+6*ZI: PRINT
  250 INPUT "GIVE INITIAL ACIDITY          ", HO: HN=HO
  260 INPUT "GIVE PU MOLARITY              ", T: PRINT
  270 PRINT: INPUT "USE METHOD #1 OR METHOD #2?      ", MT
  280 PRINT "TO CHANGE METHODS, TYPE 'GOTO 270'": PRINT
  290 PRINT "GIVE TWO DISTINCT GUESSES FOR THE OXIDATION STATE RATIO"
  300 PRINT "1E30, 1E31 OR 1E-30, 1E-31 USUALLY WORK, BUT ARE EXTREME"
  310 PRINT "TO OBTAIN A DISTRIBUTION WITH LIMITED ACCURACY, TYPE 'GOTO 680'"
  320 INPUT "FIRST GUESS IS      ", J(1)
  330 INPUT "SECOND GUESS IS     ", J(2)
  340 FOR A=1 TO 2: GOSUB 500: NEXT A
  350 IF G(1)<G(2) THEN GOTO 370
  360 SWAP G(1),G(2): SWAP J(1),J(2)
  370 R=2*J(1)-J(2): A=3: J(A)=R: GOSUB 500
  380 PRINT G(1)
  390 IF G(3)<G(1) THEN GOTO 400 ELSE GOTO 440
  400 E=3*J(1)-2*J(2): A=4: J(A)=E: GOSUB 500
  410 IF G(4)<G(1) THEN GOTO 420 ELSE GOTO 430
  420 G(2)=G(1): G(1)=G(4): J(2)=J(1): J(1)=J(4): GOTO 370
  430 G(2)=G(1): G(1)=G(3): J(2)=J(1): J(1)=J(3): GOTO 370
  440 IF G(3)<G(2) THEN GOTO 450 ELSE GOTO 480
  450 CR=1.5*J(1)-J(2)/2: A=3: J(A)=CR: GOSUB 500
  460 IF G(2)<G(3) THEN GOTO 480
  470 SWAP G(3),G(2): SWAP J(3),J(2)
  480 CW=(J(1)+J(2))/2: A=3: J(A)=CW: GOSUB 500: J(2)=J(3): G(2)=G(3)
  485 GOTO 350
  490 SWAP G(3),G(2): SWAP J(3),J(2): GOTO 350
  500 IF MT<1.5 GOTO 510 ELSE GOTO 560
```

```
  510 ZU=J(A): IF ZU>0 THEN GOTO 530
  520 G(A)=1E50: RETURN
  530 WU=((N-5)*AY*K2+(N-6)*AZ*ZU*K2)/(AW*(3-N)*K2+AX*(4-N)*ZU)
  540 XU=WU*ZU/K2: IF WU>0 THEN GOTO 610
  550 G(A)=1E50: RETURN
  560 WU=J(A): IF WU>0 THEN GOTO 580
  570 G(A)=1E10: RETURN
  580 XU=WU*((3-N)*AW*WU+(5-N)*AY)/(AX*(N-4)*WU+AZ*K2*(N-6))
  590 ZU=XU*K2/WU: IF XU>0 THEN GOTO 610 ELSE GOTO 600
  600 G(A)=1E50: RETURN
  610 WR=WU*AW: XR=XU*AX: YR=AY: ZR=ZU*AZ: XHR=XU*KH/HN
  620 PUT=WR+XR+YR+ZR: WF=WR/PUT: XF=XR/PUT: YF=YR/PUT: ZF=ZR/PUT
  630 XHF=XHR/PUT: HN=HO+4*T*(ZF+YF-ZI-YI)+T*(XHF-XHI)
  640 IF HN>0 THEN GOTO 660
  650 G(A)=1E50: RETURN
  660 AX=A4+KH/HN: Q1=WU*HN^4/XU^2: R=Q1/K1: G(A)=ABS(LOG(R))
  670 IF (G(A)-AL)>0 THEN RETURN
  680 PRINT
  690 PRINT "TRIVALENT =                ", WF
  700 PRINT "TETRAVALENT =              ", XF
  710 PRINT "TETRAVALENT -OH =          ", XHF
  720 PRINT "PENTAVALENT =              ", YF
  730 PRINT "HEXAVALENT =               ", ZF
  740 PRINT "FINAL ACIDITY =            ", HN
  750 PRINT "COMPUTED K1 VALUE =        ", Q1: PRINT
  760 PRINT "DO YOU WANT TO START AT ALPHA COEFFICIENTS (OPTION #1)"
  770 PRINT "AT INITIAL VALENCE STATE DISTRIBTION INFORMATION (OPTION #2)"
  780 PRINT "OR AT ACIDITY AND MOLARITY INFORMATION? (OPTION #3)"
  790 PRINT: INPUT "GIVE OPTION NUMBER    ", OP
  800 IF OP<1.1 THEN GOTO 120
  810 IF OP<2.1 THEN GOTO 180
  820 GOTO 250
ENDFILE
```

UNIPLEX ROUTINE FOR STUDYING PU SOLUTIONS

```
THE VALUE OF THE OBJECTIVE FUNCTION IS CONTINUOUSLY PRINTED.
THIS VALUE MUST (!) DIMINISH TOWARD ZERO TO SOLVE THE PROBLEM.
IF THE OBJECTIVE FUNCTION FAILS TO DECREASE, THE INITIAL GUESSES
FOR THE PU(6)/PU(5) RATIO (METHOD #1) OR THE PU(3)/PU(5) RATIO
(METHOD #2) ARE UNACCEPTABLE.  TRY OTHER VALUES.  THE TWO METHODS
REQUIRE DIFFERENT STARTING VALUES.

GIVE 2PU(4) = PU(3) + PU(5) CONSTANT           6.97E-04
GIVE PU(4) + PU(5) = PU(3)+ PU(6) CONSTANT     13.2
GIVE PU(4) + HOH = PU(4)OH  + H CONSTANT       0.03

GIVE ACCURACY LIMIT, A NUMBER LIKE 1E-07    1E-07

GIVE ALPHA COEFFICIENTS FOR PU(3), PU(4), PU(5), PU(6)
BUT DO NOT INCLUDE HYDROLYSIS OF PU(4) TO PU(4)OH
AW =                1
AX =                1
AY =                1
AZ =                1
```

```
GIVE INITIAL VALENCE STATE DISTRIBUTION
PU(3) =          0.5
PU(4) =          0
PU(4)OH =        0
PU(5) =          0
PU(6) =          0.5

GIVE INITIAL ACIDITY          1
GIVE PU MOLARITY              0


USE METHOD #1 OR METHOD #2?       1
TO CHANGE METHODS, TYPE 'GOTO 270'

GIVE TWO DISTINCT GUESSES FOR THE OXIDATION STATE RATIO
1E30, 1E31 OR 1E-30, 1E-31 USUALLY WORK, BUT ARE EXTREME
TO OBTAIN A DISTRIBUTION WITH LIMITED ACCURACY, TYPE 'GOTO 680'
FIRST GUESS IS       100
SECOND GUESS IS      200
```

```
 6.8689381029680E-05
 4.4046512874537E-06
 4.4046512874537E-06
 4.4046512874537E-06
 4.4046512874537E-06
 1.6380030951990E-07
 1.6380030951990E-07
 1.6380030951990E-07
 1.6380030951990E-07
 1.2172762389933E-07

TRIVALENT =                    8.3718825524205E-02
TETRAVALENT =                  .62289931917816
TETRAVALENT -OH =              .01814269861684
PENTAVALENT =                  3.0448850710695E-03
HEXAVALENT =                   .29033697022657
FINAL ACIDITY =                1
COMPUTED K1 VALUE =            6.9699998533767E-04

DO YOU WANT TO START AT ALPHA COEFFICIENTS (OPTION #1)
AT INITIAL VALENCE STATE DISTRIBTION INFORMATION (OPTION #2)
OR AT ACIDITY AND MOLARITY INFORMATION? (OPTION #3)

GIVE OPTION NUMBER
```

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