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A NOVEL STRONTIUM-SELECTIVE EXTRACTION CHROMATOGRAPHIC RESIN*

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ABSTRACT

The effect of nitric acid concentration on the selectivity of a novel extraction chromatographic resin consisting of an octanol solution of 4,4'(5')-bis(t-butyl-cyclohexano)-18-crown-6 sorbed on an inert polymeric support for strontium over a number of alkali, alkaline earth, and other metal cations was evaluated. The effect of macro quantities of selected elements on strontium retention by the resin was also examined. The resin is shown to exhibit excellent selectivity for strontium over nearly all of the test elements; only lead and tetravalent neptunium, polonium, and plutonium show significant affinity for the material. In addition, concentrations of calcium or sodium ion up to ~0.1 $\underline{M}$ are shown not to diminish the sorption of strontium appreciably. Several useful radiochemical separation schemes devised on the basis of the results obtained are described.

INTRODUCTION

The radiometric determination of strontium-90 in environmental and biological samples requires its separation from large quantities of inactive matrix constituents and from a number of interfering radionuclides (1-12). Similarly, the preparation of various high purity radionuclides, for example, rubidium-82 for

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positron emission tomography (13), requires the isolation of radiostrontium from numerous other ions. In recent years, a variety of methods have been described for effecting the necessary separations, among them procedures based upon precipitation (1,11), liquid-liquid extraction (4-12), ion-exchange (8,9), and chromatography (14-16). All of these procedures, however, suffer from various limitations. Precipitation, for example, is tedious and must often be repeated several times to obtain adequate recoveries of strontium (1,11). Liquid-liquid extraction is too cumbersome for use with large numbers of samples and often requires the use of toxic solvents such as dichloroethane (12). Ion-exchange procedures typically require careful pH control, because satisfactory separations (particularly from calcium) are achieved only within a narrow pH range. Moreover, this range is affected by the amount of calcium present (9). Most importantly, ion exchange, like most of the other methods, is not suitable for samples containing high concentrations of acid. For the same reason, none of the various extraction chromatographic methods proposed (14-16) has proven entirely satisfactory. In addition, despite the use of selective crown ethers in the preparation of many of these materials, strontium/calcium or strontium/barium resolution is typically unsatisfactory.

Earlier work in this laboratory (17-19) has shown that strontium may be efficiently extracted from aqueous solutions containing high concentrations (1-7 $\underline{M}$) of nitric acid by solutions of various crown ethers dissolved in any of a number of aliphatic alcohols and ketones. Recently, we have demonstrated that this chemistry can be adapted to produce a novel extraction chromatographic resin by sorbing a solution of 4,4'(5')-bis(t-butylcyclohexano)-18-crown-6 (abbreviated DtBuCH18C6) in 1-octanol on an inert polymeric substrate (20). The resultant material provides a simple and effective means of overcoming many of the limitations associated with other methods of isolating radiostrontium. In a previous report (20), we presented preliminary data regarding appropriate loading and elution conditions, resin selectivity, and possible applications of the material in environmental analyses and bioassays. In this report, we present more detailed information on the performance of the resin, in particular, a systematic examination of its selectivity for strontium over alkali, alkaline earth, and other selected elements and of the effect of macro concentrations of various cations upon strontium

retention. In addition, we examine the elution behavior of a variety of metal ions on a column of the resin and describe several radiochemical separation schemes devised on the basis of the results obtained.

EXPERIMENTAL

Reagents

The 4,4'(5')-bis-t-butylcyclohexano-18-crown-6 (DtBuCH18C6) was obtained from Parish Chemical Co. (Orem, Utah) and purified via recrystallization from acetone. The 1-octanol (99 + %) was obtained from Aldrich Chemical Co. (Milwaukee, WI). Nitric acid was Ultrex II grade (J. T. Baker, Phillipsburg, NJ). All water was obtained from a Milli-Q2 system. All other materials were ACS reagent grade and were used as received.

Preparation of Strontium Selective Extraction Chromatographic Resin

The extraction chromatographic resins were prepared by impregnating Amberchrom™ CG-71md (80% within 50-100 μm), Amberchrom™ CG-71 cd (80% within 80-160 μm) or Amberlite® XAD-7 (100-125 μm) with a 1 $\underline{M}$ solution of DtBuCH18C6 in 1-octanol as detailed previously (20). Amberchrom™ CG resins (TosoHaas Corp., Montgomeryville, PA) and Amberlite® XAD-7 (Rohm and Haas, Philadelphia, PA) are basically the same material, however, the latter required treatment as previously described to remove traces of unreacted monomer (21). The resultant strontium-selective chromatographic resin is now commercially available under the name Sr•Spec™ (for strontium specific) from EIChroM Industries, Inc. (Darien, IL).

Radioactive Tracers

Radiochemical experiments were performed using ^{22}Na, ^{86}Rb, ^{137}Cs, ^{45}Ca, ^{85}Sr, ^{133}Ba, ^{224}Ra, ^{90}Y, ^{99}Tc, ^{201}Tl, ^{212}Pb, ^{210}Bi, ^{210}Po, ^{230}Th, ^{233}U, ^{239}Np, ^{239}Pu, and ^{241}Am. The ^{224}Ra was obtained from ^{228}Th using an extraction chromatographic column containing a quaternary ammonium nitrate (22). The ^{212}Pb, ^{210}Bi, ^{210}Po, and ^{90}Y were obtained from ^{224}Ra, ^{210}Pb, and ^{90}Sr,

respectively, using the strontium-selective resin as described below in the section on radiochemical separation schemes. The ^{239}Np was separated from ^{243}Am using BioRad™ anion exchange AG MP-1 column and 9 $\underline{M}$ HCl.

Radiometric Measurements

γ counting was performed in either a Beckman Biogamma counter or a Packard Cobra Autogamma counter. Alpha and β-counting were performed via liquid scintillation on a Packard Model 2000 CA counter. Standard radiometric assay and counting procedures were employed throughout.

Weight Distribution Ratio Determinations/Column Capacity Factors

The sorption of various radioisotopes from nitric acid solution by the resin was measured by contacting a known volume (typically 1.0 mL) of a spiked acid solution of appropriate concentration with a known weight of resin. The ratio of the aqueous phase volume (mL) to the weight of the chromatographic material (g) ranged from 70 to 180. (This ratio is determined primarily by the need to produce as easily measured decrease in the aqueous activity by contact with the resin.) Although equilibrium is generally reached in under 15 minutes, a 2 hour mixing time was normally employed.

The mixing of the solid and liquid phases was performed using small magnetic bars rotated at such a speed (about 200 rpm) that the resin was suspended in the aqueous phase. After equilibration, the phases were centrifuged and the aqueous phase withdrawn from the test tube. To ensure that the aqueous phase did not contain any dispersed resin, it was also filtered through Whatman #1 paper after centrifugation.

Weight distribution ratios were calculated from the following equation:

$$D_W = \left(\frac{A_0 - A_s}{W}\right) / \left(\frac{A_s}{V}\right)$$

where A_0 and A_s are the aqueous phase activities (cpm) before and after equilibration, respectively, W is the weight of resin (g) and V is the aqueous phase volume (mL). The D_W values may be converted to the number of free column

volumes to peak maximum (i.e., the resin capacity factor), k', by dividing by 2.19. This factor includes the conversion of D_W to D (a volume distribution ratio) and the value of the ratio of the volume of stationary phase to the volume of mobile phase, v_s/v_m, typically observed for chromatographic columns packed with the strontium-selective resin. (See section on column characterization.)

Effect of Matrix Constituents

The effect of the presence of macro quantities of various cations and anions upon the capacity factor of the resin for strontium was evaluated by measuring the uptake by the resin of ^{85}Sr from 3 $\underline{M}$ nitric acid containing increasing amounts of calcium, sodium, ammonium, or potassium nitrate, potassium chloride or increasing amounts of oxalic, phosphoric, sulfuric, or hydrochloric acid. From the measured activities, D_W and k' values were calculated as described above.

Column Preparation and Characterization

Columns were packed as described previously (20). The selectivity and radiochemical separation experiments were performed using either disposable glass BioRad Econocolumns (5.0mm i.d. by 10cm length) or disposable plastic column from Isolab Inc., Akron, OH (7.9mm i.d. × by 6.2cm in length).

The bed density (weight in grams of column material per ml of bed), the volume of stationary phase (v_s) and the volume of mobile phase or free column volume (v_m) were measured using a precision bore column of known cross-sectional area. (The term stationary phase refers to the volume of liquid extractant solution contained in the pores of the support.) To calculate the bed density, the weight of chromatographic material required to fill a column to a known bed volume was determined. This was accomplished by quantitatively transferring a portion of resin from a bottle containing a known weight of resin to the calibrated column. After the resin had completely settled, the height of bed was measured. The bed density was then calculated from the weight of resin and the volume of bed.

The density of the extractant loaded beads was obtained by two different methods. In the first, the weight of water displaced by a known weight of extractant loaded resin suspended in water in a calibrated volumetric flask was

measured. (Care must be taken to allow time for the resin to wet completely so that all air is excluded.) In the other method, a portion of chromatographic material was added to solutions of varying nitric acid concentration until a concentration was found in which the resin remained suspended after centrifugation. At this point, the density of the chromatographic material is the same as the density of the nitric acid solution. Because the chromatographic resin extracts HNO_3 and because the isopycnic condition involved ~5 $\underline{M}$ HNO_3, the density measured in HNO_3 solution was slightly higher than the density measured in water. Therefore, the average of the two values was used in all calculations. (See Results and Discussion.)

The volume of mobile phase (v_m) (same as the free column volume) was calculated from the difference in the bed volume and the volume of resin in the bed, the latter quantity being the weight of chromatographic material in the bed divided by its density. The free column volume was also obtained by measuring the volume of effluent preceding breakthrough of ^{137}Cs or ^{22}Na. The breakthrough technique sometimes gave a somewhat lower value, e.g., 0.63. The volume of liquid stationary phase, v_s, was determined from the weight of extraction chromatographic material in the column, the resin loading (i.e., the weight percent of extractant solution comprising the resin) and the density of the extractant solution.

The capacity of a calibrated column packed with Sr-selective resin was measured by saturating the column with 0.1 $\underline{M}$ $Sr(NO_3)_2$ in 3 $\underline{M}$ HNO_3. A few drops of 3 $\underline{M}$ HNO_3 followed by N_2 pressure was used to force the $Sr(NO_3)_2$ solution from the interstatial volume of the bed. The column was then eluted with 20 free column volumes (F.C.V.) of H_2O to remove the Sr. The resultant elutrient was analyzed for Sr by ICP/AES.

Elution Curves for Sr

The concentration profiles for the elution of Sr with 3 $\underline{M}$ HNO_3 and stripping with H_2O were measured with the same calibrated column used for v_m and v_s measurements. The bottom of the column, including bed support and Cheminert™ end fittings, was the same as described in (23). This design reduces the dead space below the bed to a few microliters. A small (~10 μl) aliquot of ^{85}Sr in 4 $\underline{M}$ HNO_3 was introduced at the top of the bed and then eluted with 3.2 $\underline{M}$

HNO_3. The effluent was sampled at intervals and γ counted. A flow rate of ~2 ml/cm^2 min was employed throughout. All runs were carried out at ambient temperature (23-25 °C). In a separate column run, the elution of Sr was carried out to near breakthrough and then H_2O was introduced into the reservoir. The run was continued with more frequent assaying of the effluent to better define the Sr elution curve.

The latter procedure was also carried out for Pb. Approximately 60 free column volumes (F.C.V.) of 0.1 $\underline{M}$ HNO_3 were passed through the column before crossing over to 0.1 $\underline{M}$ $(NH_4)_2C_2O_4$.

Elution Behavior of Selected Cations

A 600 μL portion of a multi-element stock solution containing strontium and more than thirty other metal cations (selected either because of their presence in a variety of environmental, biological, or nuclear waste samples or because of literature reports indicating some interaction with 18-crown-6 based macrocycles) was introduced to a column of the strontium-selective resin (bed volume = 1.00 mL; bed height = 5.0 cm) and eluted with 3 $\underline{M}$ nitric acid. In no case did any of the constituents exceed more than 10% of the capacity of the column. The eluate was collected in a series of 3.00 mL aliquots until 18 mL (~30 F.C.V.) had been collected. The elutriant was then changed to 0.05 $\underline{M}$ nitric acid to strip sorbed strontium from the column. A total of 6.00 mL (~10 F.C.V.) were collected and a portion subjected to analysis by ICP-AES (24) or atomic absorption (AA). The elution behavior of several of the elements (e.g., Na) was also checked radiometrically using an appropriate tracer. Flow rates were maintained at 1-2 mL cm^{-2} min^{-1} throughout.

RESULTS AND DISCUSSION

Column Characteristics

One of our objectives was to design columns of 1-2 mL bed volume that gave flow rates under gravity of 1-2 mL/cm^2/min at room temperature. These

specifications were selected for convenience of operation in the separation of either radiostrontium or inert strontium. At the same time, we wished to achieve sufficient chromatographic performance in terms of minimal band spreading and tailing to provide good decontamination factors and good overall recoveries of Sr. To meet these specifications, we selected two particle size ranges: 50-100 μm and 80-160 μm. (Some batches of the large particle size material were 100-125 μm.) Table 1 summarizes the characteristics of the bulk material and packed beds. Note that the value of the fractional free column shown, 0.69-0.71, was calculated from the weight of column material and the density of the extractant loaded beads.

k' vs. HNO₃ Concentration

The strontium-selective chromatographic material was characterized by measuring the capacity factor, k' (the number of free column volumes to peak maximum) versus the HNO₃ concentration for a wide range of metal ions. (k' is related to the liquid-liquid distribution ratio (D) by the equation $k' = D \cdot v_s/v_m$.) Figures 1 and 2 summarize the results of this study. (Preliminary data of this type is presented in one of our earlier publications (25).) The k'_{Sr} data are shown in each plot for ease of comparison. Several features of these data are noteworthy. First, as can be seen in Fig. 1, k'_{Sr} exceeds that of each alkali metal by a wide margin over virtually the entire range of acidities considered. The excellent selectivity of the resin over sodium is particularly important, given the ubiquitous nature of this element. Interestingly, k' for strontium rises steadily with increasing nitric acid concentration (although some decrease in the slope of the line is observed at high acidities where the nitric acid can compete with strontium for oxygen atoms in the crown ether), while for each of the other elements, it reaches a maximum at ~1-2 M, then gradually declines. (The shape of the k' acid dependency plots is the subject of another study (26).) Note that with the exception of potassium, each of the alkali metal ions is essentially unretained (k' ≤ 2) under typical loading conditions (e.g. ~3 M HNO₃).

The shape of k'_{Sr} versus HNO₃ plot is similar to that observed for the corresponding liquid-liquid extraction system using 0.2 M and 0.4 M DtBuCH18C6 in 1-octanol (18). However, D_{Sr} calculated from k' and v_s/v_m is a

factor of two higher than D_{Sr} predicted from the liquid-liquid extraction data assuming a first power extractant dependency. This disparity in D between the two systems may be due to the nature of the liquid phase in porous supports, where extremely small volumes of solution are in contact with a large polar surface area.

Figure 1 also shows that k' for strontium greatly exceeds that of each alkaline earth cation except Ba, which is fairly well retained at high (> 1 $\underline{M}$) nitric acid concentrations. The low capacity factor of the resin for calcium is especially significant, as many environmental and biological samples contain large quantities of this element. Moreover, its complete separation from strontium with traditional, ion exchange techniques has often proven difficult. The data in Fig. 1 show clearly the conditions that may be used for maximum retention of Sr as well as maximizing the selectivity for Sr over K, Ba, and Ra.

Figure 2 summarizes the behavior of several other elements of interest either because of their possible presence in nuclear waste samples (e.g., Am, U) or because of literature (27-29) suggesting the possibility of their interaction with 18-crown-6 based macrocycles (e.g., Pb). As can be seen, lead is retained by the resin even more strongly than is strontium over a wide range of nitric acid concentrations. Similarly, tetravalent plutonium, neptunium, and polonium are retained at least as well as strontium over certain ranges of acidities. The behavior of Np(IV) and Pu(IV) is consistent with work reported in (27-29). The data in Figs. 1 and 2 suggest a number of radiochemical separations that can be performed on the strontium-selective resin and clearly show, in most cases, the appropriate acidities for loading and stripping. Specific applications of the resin are described below.

Elution Curves for Sr^{2+}

Figure 3 shows a comparison of the elution curves for Sr^{2+} obtained with a pair of identical columns packed with the two different particle size resins (16). The k's obtained from the elution curves (V_{max} -1) are 81 and 88 for the small and large particle sizes, respectively, which is in good agreement with k' = 80 at 3.2 $\underline{M}$ HNO_3 from the batch uptake measurements (Fig. 1). The difference in k' between the two particle sizes is probably due to the slightly higher packing density obtained with the larger size resin.

The elution curves show fairly good symmetry, but the superiority of the 50-100 μm particle size material is obvious. Breakthrough occurs 25 free column volumes sooner with the coarser material, although the holdup of Sr is quite good for both materials. Note that k' can be increased somewhat by increasing the HNO3 concentration (Fig. 1).

The number of theoretical plates (N) calculated from the elution curves (30) for the small and large diameter resin is 93 and 19, respectively. From N, the height equivalent of a theoretical plate (HETP) and the reduced plate height (h) are obtained from the following equations:

$$HETP = \frac{L}{N}$$

$$h = \frac{HETP}{dp}$$

where L is the length of column and dp is the particle diameter. (L and dp must have the same units (e.g., cm) as HETP.) The values of HETP and h are 0.11 cm and 15 for fine material and 0.53 cm and 48 for the coarse material. The HETP for the small particle size resin is consistent with plate heights reported for 75 μm Celite (27). No valid comparisons can be made with the larger particle size resin. However, the reduced plate height, h, for the two different particle sizes should be the same if the homogeneity of packing of the two columns was similar (23,30). The large difference in h, 15 vs. 48, indicates that the column containing the small particle size resin has a more uniformly packed bed. This difference, however, may be due to the fact that a 2.7 mm i.d. column is too narrow for resin particles with diameters in the 100-125 μm range.

Elution Behavior of Selected Cations

Table 2 shows the elution behavior of thirty-four different elements on a 1.0 cm³ bed volume column packed with the 50-100 μm strontium-selective chromatographic resin. All constituents except Rb, Cs, Ra, and Tc were present in the same solution. Rubidium and cesium were run together and analyzed by AA. Radium and technetium were run separately because of their radioactivity. A small

concentration of oxalic acid was used in the 3 $\underline{M}$ HNO$_3$ elutrient to help solubilize Zr and Mo. The data in Table 2 show that the extraction chromatographic resin is highly selective for Sr. Only Ba and Hg show any significant retention. The behavior of Ba and K is consistent with the k' data in Fig. 1. The stripping of Sr from the column with 0.05 $\underline{M}$ HNO$_3$ is also consistent with data in Fig. 1, that gives a $k'_{Sr} = 1$ at 0.05 $\underline{M}$ HNO$_3$. The broad peak for Hg indicates not only a significant retention, although less than that of Sr, but also perhaps a kinetics problem.

Effect of Matrix Constituents

The nitric acid dependency data shown in Figs. 1 and 2 are important not only because they clearly delineate the conditions for the separation of Sr from different metal ions but also because they indicate which elements may cause a significant diminution in k'_{Sr} if present in concentration exceeding the capacity of a given column. Sodium, potassium, calcium, iron, and aluminum are the major constituents of many soils, minerals, and groundwaters. Similarly, sodium, potassium and ammonium ion are frequently present in high concentrations in bioassay samples, e.g., urine. The effect of increasing concentrations of several of these matrix constituents on k'_{Sr} was therefore measured. In this way, the concentration of a particular matrix constituent at which strontium retention is significantly decreased could be determined. Figure 4 shows the effect of sodium, potassium, calcium and ammonium nitrates in 3 $\underline{M}$ HNO$_3$ and potassium chloride in 3 $\underline{M}$ HNO$_3$ on k'_{Sr}. Iron(III) and aluminum were not included in the study because their extractability by DtBuCH18C6 is less than that of sodium and calcium (19). The data show that Na$^+$ and Ca^{2+} have very little effect on k'_{Sr} until their concentrations exceed 0.4 $\underline{M}$. However, K$^+$, as expected from the data in Fig. 1, has a significant suppressing effect on k'_{Sr} above 0.03 $\underline{M}$. There is no difference in KNO$_3$ and KCl when present in 3 $\underline{M}$ HNO$_3$. The effect of NH$_4^+$ is less than that of K$^+$ but greater than that of Na$^+$. The ionic radius of NH$_4^+$ (1.42 Å) is slightly larger than the ionic radius of K$^+$ (1.33 Å), but sufficiently small to fit into the 18-crown-6 cavity.

The effect of increasing concentrations of $H_2C_2O_4$, H_3PO_4, H_2SO_4, and HCl in 3 $\underline{M}$ HNO$_3$ on k'_{Sr} was also studied. No significant reduction in k'_{Sr} occurs up to 0.5 $\underline{M}$ concentration of these acids except in the case of oxalic acid. Even here, however, k'_{Sr} from 3 $\underline{M}$ HNO$_3$ is reduced by only 10% by the addition of 0.5 $\underline{M}$ $H_2C_2O_4$.

<u>Radiochemical Separations</u>

The data in Figs. 1, 2 and 4 and Table 2 suggest a number of highly efficient separations of Sr (and Pb) from a wide range of metal ions that can be performed using the strontium-selective chromatographic resin. In every case, the Sr-containing solution is loaded onto the column in 2-8 $\underline{M}$ HNO$_3$. After loading, the column is generally rinsed with 10 F.C.V. of, for example, 3 $\underline{M}$ HNO$_3$ or 3 M HNO$_3$/0.01 - 0.05 $\underline{M}$ oxalic acid, to achieve additional decontamination of unretained or weakly retained constituents. The Sr is then eluted from the column with either H$_2$O or dilute (0.01 to 0.05 $\underline{M}$) HNO$_3$. Figure 5 shows the elution curve for Sr stripped with H$_2$O at room temperature from a column packed with 50-100 μm particle size resin. As can be seen from the data, 10 F.C.V. is sufficient to remove > 99% of the Sr.

<u>Separation of Sr from HLW</u>

Foremost among the possible radiochemical separations is the removal of ^{90}Sr from acidic high-level liquid waste (HLW). HLW is an extremely complex mixture of fission products, inert constituents, and actinides (31,32). The data in Table 2 show that Sr is retained, while fission products Rb, Y, Zr, Mo, Tc, Ru, Rh, Pd, Cs, and lanthanides, together with commonly occurring inert constituents in waste, e.g., Na, Al, Cr, Fe, Ni, are either not retained or only slightly retained. Only Ba shows any appreciable retention. However, Np(IV) and Pu(IV) are significantly retained by the resin from 3 to 6 $\underline{M}$ HNO$_3$, whereas U(VI) and Am(III) show only negligible retention. The retention of Np and Pu can be readily reduced using oxalic acid as a hold back reagent. Loading a HLW solution in 3 $\underline{M}$ HNO$_3$ - 0.05 $\underline{M}$ $H_2C_2O_4$ prevents the retention of Np and Pu and at the same time

is beneficial in solubilizing Zr and Mo. As discussed above, oxalic acid has very little effect on k_{Sr}'.

An example of the separation of Sr from a synthetic dissolved sludge waste (supposedly representative of sludge from a HLW storage tank (31)) using the Sr selective resin is described in (25).

The strontium-selective resin can also be used as a Np-Pu selective resin by eliminating or sequestering complexing anions such as oxalate, phosphate, and fluoride in the load and rinse. Separation of Np and Pu from Sr is readily achieved by eluting the two actinides with 20 F.C.V. of 2 $\underline{M}$ HNO_3. However, as will be shown in a future publication, there are much more effective methods for separating the tetravalent actinides.

Separation of Sr from Environmental and Bioassay Samples

The strontium-selective resin is ideally suited for the separation of Sr from a wide range of environmental and biological samples, e.g., soil, groundwater, and bioassay samples, because of its high selectivity for Sr in 2-6 $\underline{M}$ HNO_3 over the major constituents of many such samples (Na, Mg, Ca, Al and Fe). Only K requires special consideration. The data in Fig. 4 show the levels of K that can be tolerated in 3 $\underline{M}$ HNO_3 without significantly reducing the retention of Sr. Two approaches can be taken in reducing the interference from K. First, Sr can be coprecipitated from dissolved samples. Calcium phosphate and carbonate have been found to be effective for this purpose (33). Alternatively, the column can be loaded in 6 $\underline{M}$ HNO_3. The selectivity of Sr over K(k_{Sr}'/k_K') from 6 $\underline{M}$ HNO_3 is 110 compared to 25 from 3 $\underline{M}$ HNO_3. Moreover, k_K' from 6 $\underline{M}$ HNO_3 is < 1, (See Fig. 1) which means that concentrations of potassium of the order of 6 mg per ml of load solution would have minimal effect on Sr retention. In general, the retention of Sr in the presence of 0.1 to 0.5 $\underline{M}$ K^+ is calculated to be twice as high in 6 $\underline{M}$ HNO_3 as in 3 $\underline{M}$ HNO_3 (26).

The separation of Sr from Ba and Ra can also be maximized by elution with high nitric acid concentrations or $LiNO_3$ (33). For example, k_{Sr}'/k_{Ba}' and k_{Sr}'/k_{Ra}' are 12 and 170, respectively, from 7 $\underline{M}$ HNO_3 vs. 4.4 and 38 from 3 $\underline{M}$ HNO_3. (See Fig. 1).

The separation of Sr from bioassay samples is particularly convenient when the analysis involves the initial removal of all actinides using an extraction chromatographic column containing CMPO in TBP as the stationary phase (21). The effluent containing the load and rinse from CMPO-TBP column is the feed for the column packed with the Sr selective resin.

^{90}Sr-^{90}Y Separation

The separation of ^{90}Y from its parent ^{90}Sr is extremely rapid and efficient because ^{90}Y has no measurable retention. Furthermore, each time the separation is carried out, the purity of ^{90}Y with respect to other fission products and commonly occurring impurities such as Na, Ca, Al and Fe, improves because only ^{90}Sr is retained on the column. The use of the strontium-selective resin for the ^{90}Y-^{90}Sr separation is one of the key features of a new process for the isolation of multicurie quantities of high purity ^{90}Y (34).

Separation of Pb from Environmental Samples

The strontium-selective resin is also ideally suited for the separation of Pb from a wide range of environmental samples such as soil and groundwater, and from minerals for geochemical purposes. The data in Figs. 1 and 2 show that lead is strongly retained from not only high nitric acid concentrations but even from dilute (e.g., 10^{-2} $\underline{M}$) nitric acid. This feature makes separation of Pb from all constituents found in soil and groundwater extremely simple. Lead can be stripped from the resin by a variety of reagents. Table 3 lists k'_{Pb} for several complexing reagents and acids. Figure 6 shows the elution curve for Pb stripped with 0.1 $\underline{M}$ $(NH_4)_2C_2O_4$ at room temperature from a column packed with 50-100 μm particle size resin. The data show that 10 F.C.V. is sufficient to remove > 99% of the Pb. The resultant effluent can be readily destroyed by evaporation of the water and sublimation of the ammonium oxalate. The remaining residue, including any char, is readily soluble in nitric acid for loading on mass spectrometer filaments.

Although the k'_{Pb} for ammonium carbonate is greater than the k'_{Pb} for ammonium oxalate, its use as a stripping agent is worthy of consideration because the carbonate is more easily sublimed. Both the oxalate and carbonate can only be

used for trace amounts of Pb because of the low solubility of lead carbonate and oxalate. If macro quantities of lead are loaded onto the resin, e.g., from a lead bearing waste solution, then a complexing agent such as N-hydroxyethylethylene-diaminetriacetate (pH = 6.5) can be used to strip the Pb. Note that in each case, best results are obtained when stripping is preceded by a column rinse with a few F.C.V. of deionized water.

Isolation of ^{212}Pb and the Separation of ^{210}Po-^{210}Bi-^{210}Pb

Lead-212 is a very useful isotope to study the partitioning behavior of Pb. Its half-live is sufficiently long to enable one to carry out a number of experiments and its daughters approach secular equilibrium within a few hours. Its isolation from either ^{238}Th (1.91 y) or ^{224}Ra (3.64 d) is easily carried out with the strontium-selective resin. Loading and rinsing can be carried out from a wide range of nitric acid concentration as explained above. Neither parent nor ^{212}Bi is retained by the resin. Polonium-216 and 212 are of no consequence because of their short half-lives. Stripping ^{212}Pb from the column can be accomplished as described above. (See Fig. 6 and Table 3).

The strontium-selective resin can also be used to separate polonium and bismuth daughters from lead parents, e.g, lead-210. For example, if a ^{210}Pb-^{210}Bi-^{210}Po mixture is loaded onto the resin from 1 $\underline{M}$ HNO$_3$, the Pb and Po will be retained while Bi will break through in the first few free column volumes. Polonium can then be eluted with 0.1 $\underline{M}$ or 6 $\underline{M}$ HNO$_3$. Finally, lead can be stripped as described above.

Separation of Pb from Tl

A method for measuring the flux of solar neutrinos involving the separation of minute quantities of ^{205}Pb from kilograms of ^{205}Tl has been reported (35). A reduction of the Tl content of the Pb of nearly 17 orders of magnitude may be required. The strontium-selective resin is ideally suited to the separation of Pb from Tl. (See Fig. 2). Loading from ~ 0.5 $\underline{M}$ HNO$_3$ - 0.15 $\underline{M}$ Tl^{1+} solution would effectively remove the Pb from the mass of Tl. Additional decontamination of Pb from Tl can be achieved by acidifying the strip solution, e.g., (NH$_4$)$_2$H Citrate, to 3 - 4 $\underline{M}$ HNO$_3$ and loading on a second column. Exhaustive rinsing of the resin

with 0.5 $\underline{M}$ HNO$_3$ will achieve at least 10^4 decontamination of Tl from Pb. The influence of macroquantities of Tl on Pb retention is discussed in (26).

CONCLUSIONS

The results of this study demonstrate that an extraction chromatographic material comprised of an octanol solution of 4,4'(5') bis(t-butylcyclohexano)-18-crown-6 sorbed on an inert polymeric support provides a simple and efficient method for the separation of strontium from a wide variety of metal ions in nitric acid media. Under appropriate conditions, the resin can also function as either a lead-selective or tetravalent actinide (i.e., Pu(IV), Np(IV))-selective material. This versatility, together with the minimal impact of macro concentrations of many commonly encountered elements upon the resin performance, suggest that the material is likely to find numerous applications beyond those described here.

TABLE 1.

CHARACTERISTICS OF STRONTIUM-SELECTIVE EXTRACTION
CHROMATOGRAPHIC MATERIAL AND PACKED COLUMNS

BULK MATERIAL	
Stationary Phase	1.0 $\underline{M}$ DtBuCH18C6 in 1-octanol[a] (ρ = 0.912 g/mL)
Support	Amberchrom™ CG-71 or Amberlite™ XAD-7
Particle Sizes (diam.)	50-100 µm; 80-160 µm; 100-125 µm
Extractant Loading	40 weight percent
Average Density of Extractant-Loaded Beads[b]	1.12 g/ml

PACKED COLUMN	Particle Size	
	50-100 µm	80-160 µm
v_s, ml/ml of Bed[c]	0.146±0.004	0.152±0.004
Bed Density (g/ml)	0.33	0.35
v_m (Also F.C.V.), ml/ml of Bed[c]	0.71±0.01	0.69±0.01
v_s/v_m[c]	0.21±0.01	0.22±0.01
Capacity:		
Calc. mg Sr/ml of Bed	12.8	13.3
Exp. mg Sr/ml of Bed	10.6	—

[a] 1 $\underline{M}$ concentration of DtBuCH18C6 in 1-octanol is close to a saturated solution; therefore, the Sr retention from nitric acid is close to the maximum that can be achieved with this system.

[b] Picnometric density and flotation density values were 1.079 and 1.157 g/ml, respectively, using the 50-100 µm particle size resin. The calculated density is 1.094 g/ml, assuming 100% pore filling and no swelling.

[c] Average of five measurements: error is one σ.

TABLE 2.

ELUTION BEHAVIOR OF COMMON ELEMENTS AND FISSION
PRODUCTS ON THE STRONTIUM-SELECTIVE RESIN

PERCENT OF ELEMENT FOUND IN F.C.V. #

Element	3 M HNO$_3$ - 0.01 M Oxalic Acid						0.05 M HNO$_3$	
	1-5	6-10	11-15	16-20	21-25	26-30	31-40	F.C.V.
Li	100	—	—	—	—	—	—	
Na	100	—	—	—	—	—	—	
K	66	35	—	—	—	—	—	
Rb	100	—	—	—	—	—	—	
Cs	100	—	—	—	—	—	—	
Mg	100	—	—	—	—	—	—	
Ca	100	—	—	—	—	—	—	
Sr	—	—	—	—	—	—	99	
Ba	—	—	53	42	6	0.7	—	
Ra	——99——		1	—	—	—	—	
Al	100	—	—	—	—	—	—	
Cr	100	—	—	—	—	—	—	
Mn	100	—	—	—	—	—	—	
Fe	99	0.6	0.2	0.4	—	—	—	
Co	100	—	—	—	—	—	—	
Ni	100	—	—	—	—	—	—	
Cu	100	0.2	—	—	—	—	—	
Zn	100	0.2	—	—	—	—	—	
Y	100	0.1	—	—	—	—	—	
Zr	91	0.4	0.2	—	—	—	—	
Mo	——84——			——16——		—	—	
Tc	57	43	—	—	—	—	—	
Ru	100	—	—	—	—	—	—	
Rh	100	—	—	—	—	—	—	
Pd	100	—	—	—	—	—	—	
Ag	15	88	2	—	—	—	—	
Cd	100	0.1	—	—	—	—	—	
La-Eu	100	0.1	—	—	—	—	—	
Hg	5	5	19	40	19	10	5	

Column parameters: Particle size = 50-100 μm, Bed Volume = 1.0 cm^3, Bed height = 5.0 cm, and 1 F.C.V. = 0.60 mL.

TABLE 3.

RETENTION OF Pb IN THE PRESENCE OF VARIOUS REAGENTS 23-25 °C

Reagent	k_{Pb}
0.1 $\underline{M}$ H_2SO_4	4.4
0.1 $\underline{M}$ $(NH_4)_2$ Sulfate (pH 6.0)	3.3
1 $\underline{M}$ Acetic Acid	48
0.1 $\underline{M}$ (NH_4) Acetate (pH 7.0)	75
2 $\underline{M}$ HCl	163
0.1 $\underline{M}$ $(NH_4)_2$ Tartrate (pH 6.7)	0.55
0.1 $\underline{M}$ $(NH_4)_2H$ Citrate (pH 5.1)	1.05
0.1 $\underline{M}$ $(NH_4)_2$ C_2O_4 (pH 6.4)	1.5
0.1 $\underline{M}$ $NH_4HC_2O_4$ (pH 3.2)	4.0
0.1 $\underline{M}$ $(NH_4)_2$ CO_3 (pH 9.1)	6.4

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FIGURE CAPTIONS

Figure 1. Acid dependency of k' for alkali and alkaline earth metal ions at
23-25 °C. Particle size of loaded resin: 50-100 μm.

Figure 2. Acid dependency of k' for the actinides and other selected ions at
23-25 °C. Particle size of loaded resin: 50-100 μm.

Figure 3. Comparison of elution curves for Sr from 50-100 μm and
100-125 μm particle size strontium-selective resin. Bed volume =
0.59 ml, L = 10.1 cm. Bed density = 0.33 g/ml for 50-100 μm and
0.35 g/ml for 100-125 μm. Elutrient = 3.2 $\underline{M}$ HNO_3,
Temp. 23-25 °C; Flow rate = 1-2 ml/cm^2/min.

Figure 4. The effect of matrix constituents on k'_{Sr}. T = 23-25 °C. Particle size
of loaded resin = 50-100 μm.

Figure 5. Stripping of ^{85}Sr from strontium-selective chromatographic resin.
Column dimensions, bed volume and conditions are the same as in
Fig. 3.

Figure 6. Stripping of ^{212}Pb from strontium-selective chromatographic resin.
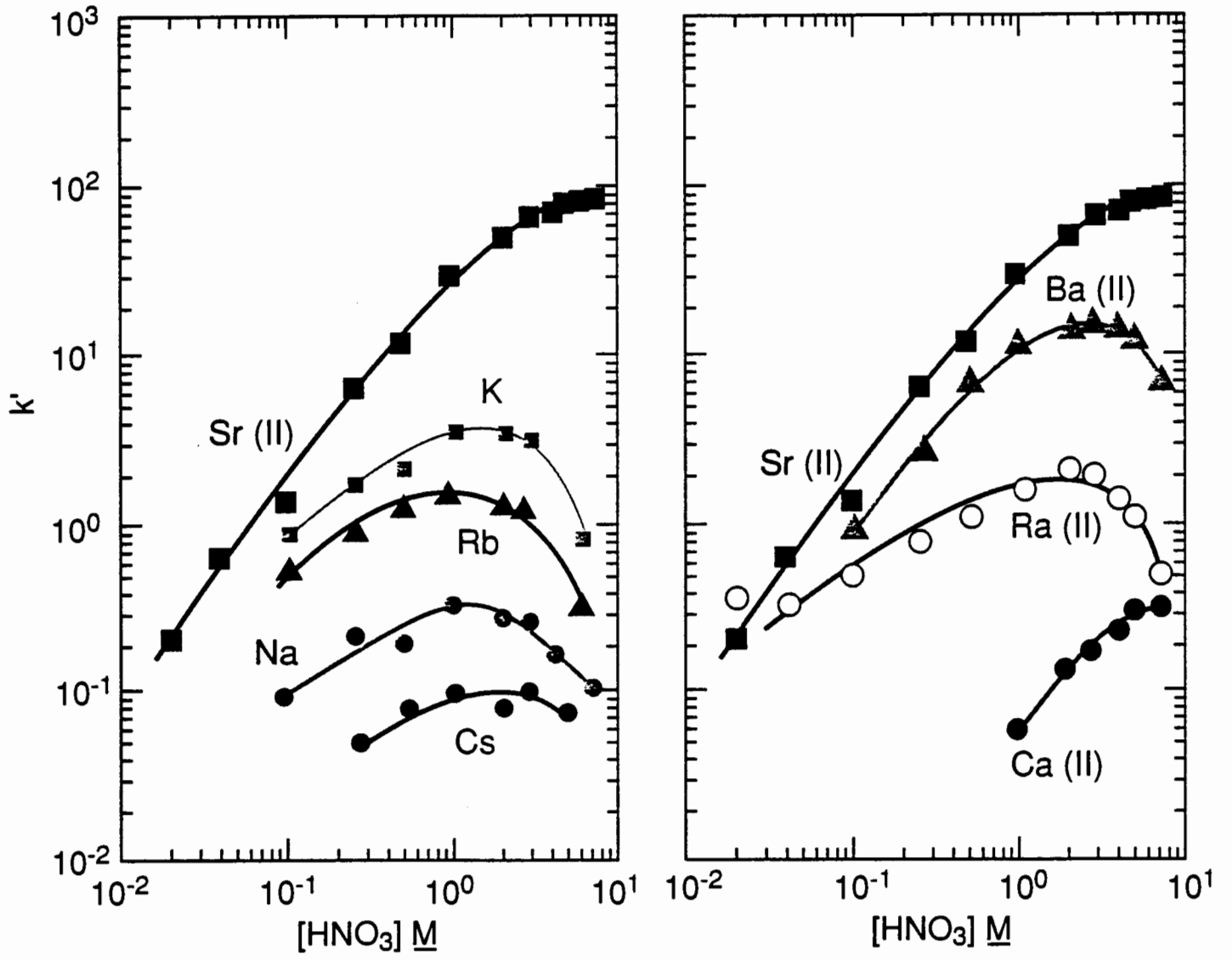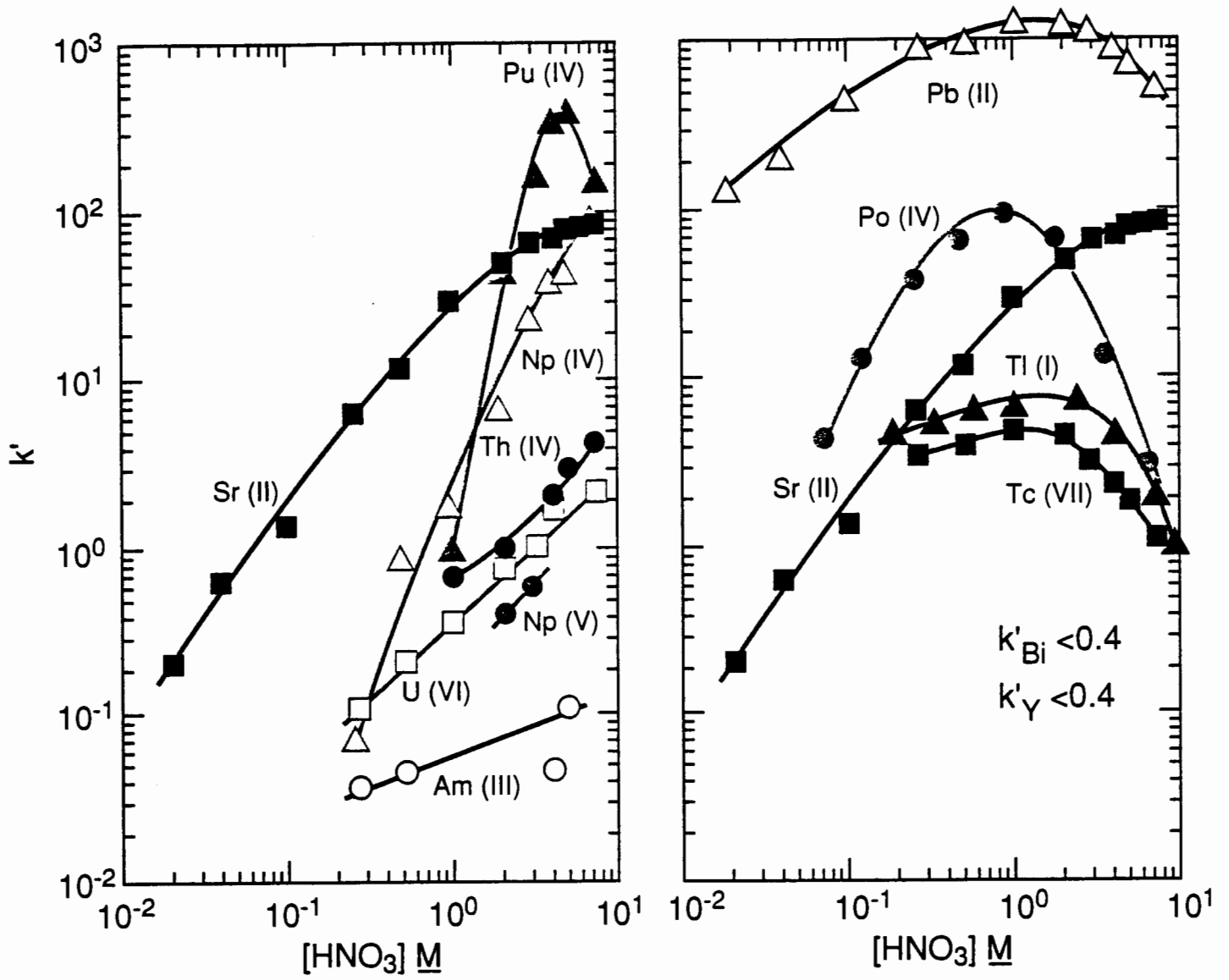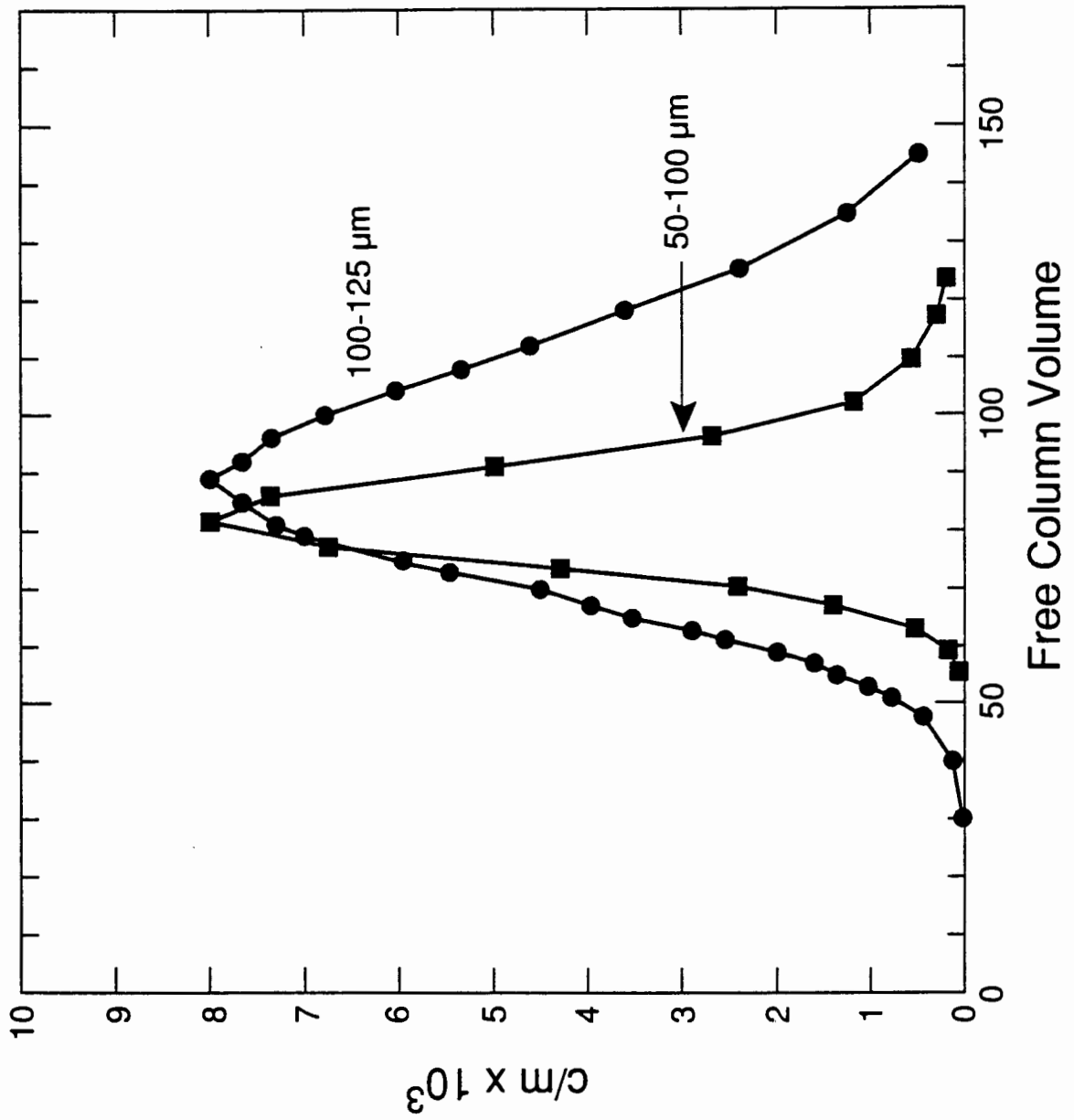Column dimensions, bed volume, and conditions are the same as in
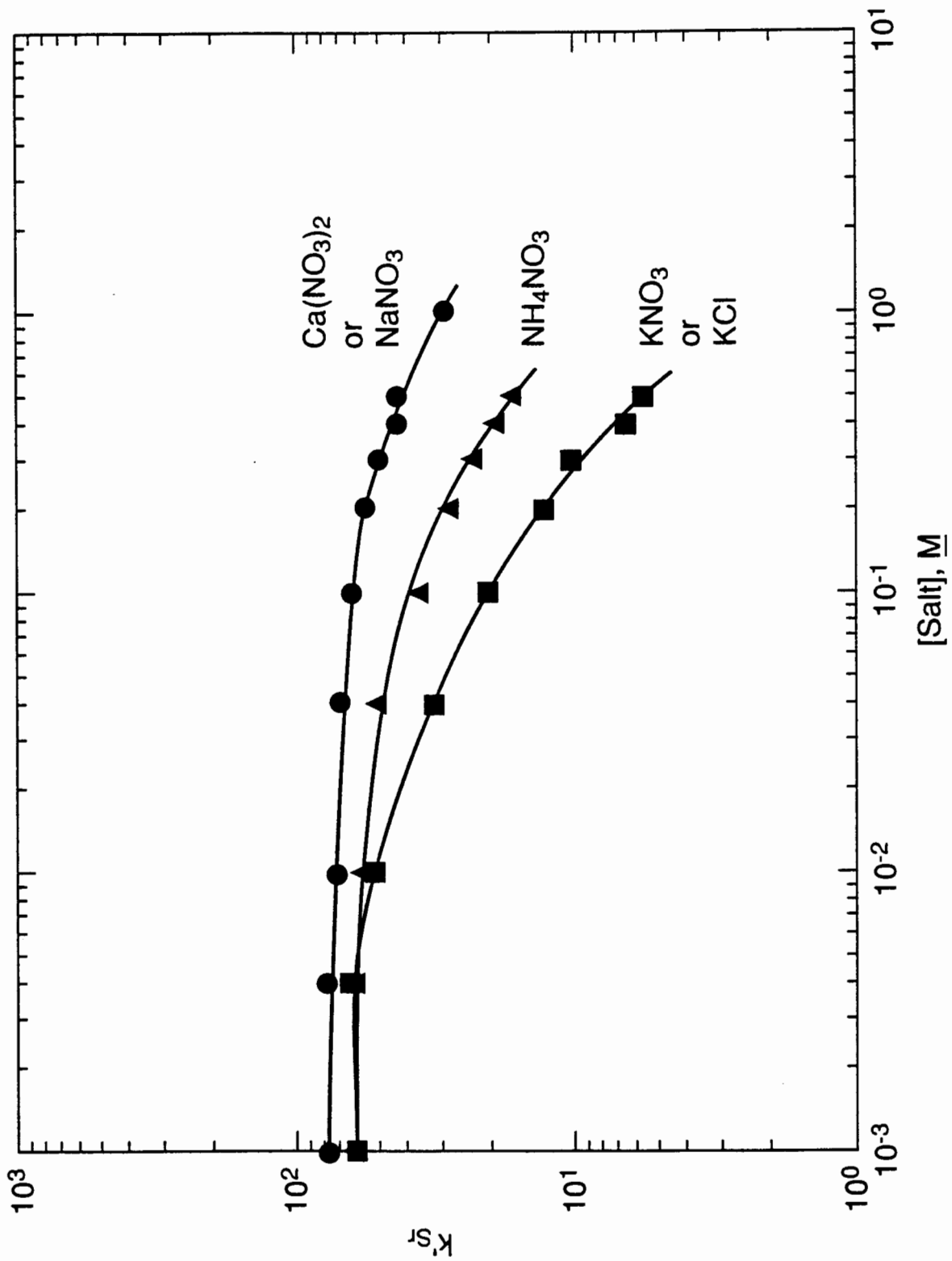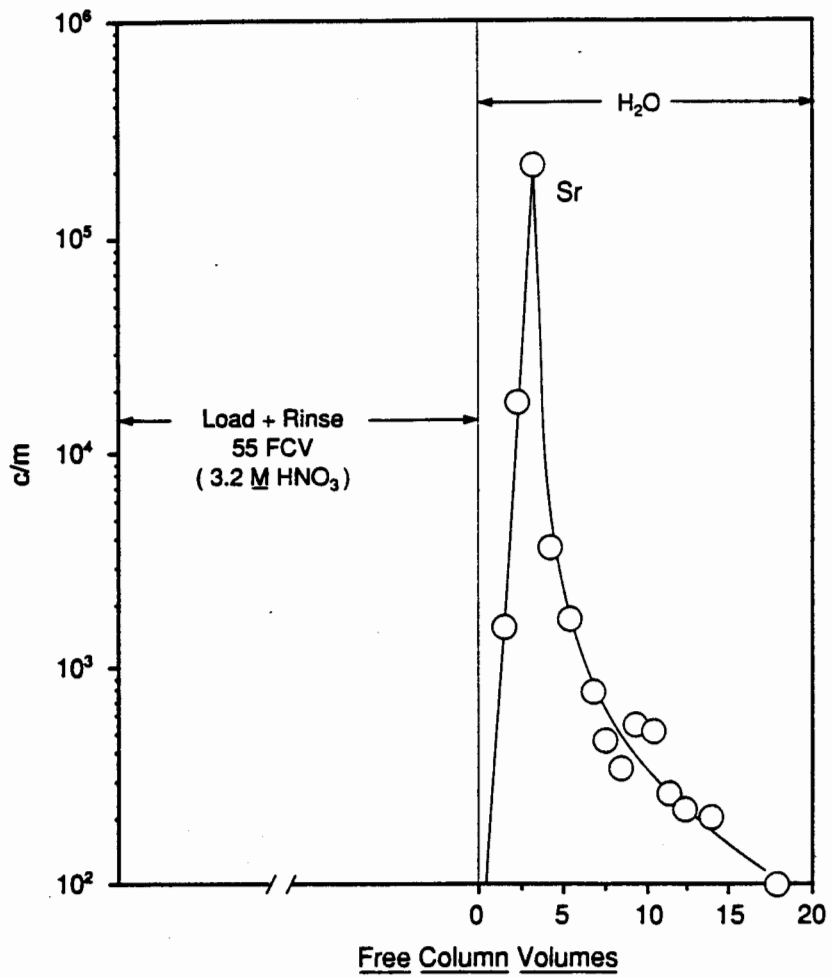Fig. 3.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.