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# Characterization of an Improved Extraction Chromatographic Material for the Separation and Preconcentration of Strontium from Acidic Media

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**Abstract:** The determination of radiostrontium in biological and environmental samples generally requires its preliminary separation and preconcentration, both to remove radionuclides that may interfere with subsequent $\beta$-counting and to free it from the large quantities of inactive substances present (e.g., calcium). Extraction chromatography employing an inert support impregnated with a solution of a crown ether in an oxygenated, aliphatic solvent (e.g., 1-octanol) has previously been demonstrated to provide a simple and effective method for the isolation of strontium from a variety of samples for subsequent determination. In this work, it is shown that a chromatographic resin capable of retaining strontium efficiently and selectively from acidic media can be prepared simply by dispersing a crown ether alone on an appropriate support. This "solventless" resin is demonstrated to offer several advantages over its conventional analog, in particular, good physical stability, higher capacity, and improved metal ion retention. In addition, extended X-ray absorption fine structure measurements are shown to provide insight into the coordination environment of metal ions sorbed by the resin.

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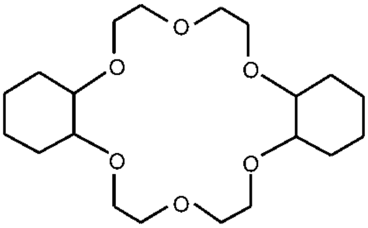
## INTRODUCTION

Radiostrontium is one of the major heat generators in high-level nuclear wastes. Because its presence greatly complicates their handling and long-term storage, there has been considerable interest in the development of solvent extraction (SX) processes for its removal from waste solutions (1, 2). Complicating the design of such processes are the substantial activity, the high acidity, and the complex and variable composition of the wastes. To be considered suitable for use in strontium recovery, an extractant must therefore exhibit good radiolytic stability, excellent selectivity, and tolerance for high-acid concentrations. Few extractants satisfy these requirements.

Prior work in this laboratory has established that efficient and selective strontium extraction from acidic nitrate media can be effected by a solution of di-*tert*-butylcyclohexano-18-crown-6 (shown below, and hereafter abbreviated DtBuCH18C6)



in any of a variety of oxygenated aliphatic diluents, most commonly 1-octanol (1-OAlc) (3, 4). The success of this extraction system derives not only from the choice of extractant but also from careful selection of the diluent. All other things being equal, within a given family of oxygenated aliphatic solvents, there is a linear relationship (on a log-log scale) between the efficiency of strontium extraction (as reflected in $K'_{ex,Sr}$, the conditional equilibrium constant for extraction of the strontium nitrato crown ether complex) and the water content of the organic solvent at saturation, $[H_2O]_{org}$ (5). The choice of 1-OAlc thus represents a compromise between the need for high-solvent water content and the requirement for physical properties (e.g., high flash point) suited to the demands of process scale solvent extraction (4).

Many of the same considerations that govern the choice of solvent and extractant for process-scale strontium separation also apply to analytical-scale separation and preconcentration of radiostrontium from various environmental or biological samples for subsequent determination (6). For example, like nuclear wastes, environmental and biological samples are variable and frequently complex. In addition, the solutions that arise from the leaching or digestion of these samples, like wastes, are often highly acidic. As is the case for waste treatment, a method for radiostrontium recovery for determination requires a very selective separation medium that is effective even for highly acidic samples. Although in principle, solvent extraction using an octanol solution of DtBuCH18C6 could provide the basis for such a method, in actual practice, SX is too cumbersome and generates too much waste for routine use on large numbers of samples. These problems can be easily overcome, however, by employing the 1-OAlc/DtBuCH18C6 system in the extraction chromatographic mode, specifically, as a 1 M solution of the crown ether in 1-OAlc supported on beads of a porous polyester, Amberlite XAD-7. This material (referred to hereafter as "Sr resin") has been shown to offer significant advantages over competing approaches for the separation and preconcentration of strontium (7, 8). For example, the material is easily prepared (particularly when compared with metal ion sorbents involving chemically bound macrocycles), making it comparatively inexpensive. In addition, it exhibits excellent selectivity for strontium over the major inert constituents of many environmental or biological samples (e.g., $Fe^{3+}$, $Al^{3+}$) and over many potential interferents (e.g., $Ca^{2+}$). Finally, the material is simple to use. These advantages have led to the widespread adoption of this resin for environmental, biological, and geological analyses (9–15).

Since its introduction, several shortcomings of the Sr resin have become evident. For example, the capacity of the material is limited, only ~10 mg Sr/mL resin. In addition, the water solubility of 1-OAlc is such that the passage of a sufficient volume of sample/mobile phase through a column of the resin can lead to an appreciable loss of the alcohol from the support (16). This represents a problem not just because of the possible adverse impact of the presence of traces of organic solvent in the column effluent but also because of changes in metal ion retention behavior that accompany the loss of 1-OAlc. Such changes obviously complicate column reuse. Although this problem might be addressed by employing a higher molecular weight (and, therefore, less water soluble) alcohol as the stationary phase diluent for DtBuCH18C6, the decrease in $[H_2O]_{org}$ that accompanies this change (5) would lead to reduced strontium retention. A final limitation concerns the application of the resin to the separation of cations more weakly retained than strontium, particularly barium and radium. Although barium is sorbed a factor of ~7 more strongly than radium (8), its retention is nonetheless insufficient to permit an efficient Ba/Ra separation to be carried out without preliminary preconcentration steps. Because of the modest column efficiency (and therefore, the wide elution bands) typically observed on the Sr resin (8), the breakthrough volume for $Ba^{2+}$ is significantly less than the elution volume corresponding to its peak maximum. Because $Ba^{2+}$ elution peaks after passage of less than 20 free column volumes (FCV) of mobile phase (8), its breakthrough will occur well before elution of radium is complete. To deal with this problem, the retention of barium obviously must be increased, preferably without decreasing Ba/Ra selectivity. Although this might be accomplished by employing a lower molecular weight alcohol as the stationary phase diluent, it would almost certainly yield a material even less stable than conventional Sr resin.

In this report, we describe a simple approach to the problems of inadequate physical stability, insufficient retention, and limited capacity that characterize the Sr resin. Specifically, we show that an improved extraction chromatographic material for strontium can be prepared simply by dispersing a crown ether alone on an appropriate support. This "solvent-free" resin retains many of the best characteristics of the original Sr resin, while exhibiting good physical stability and offering the possibility of higher capacity and stronger cation retention.

## EXPERIMENTAL

### Materials

The 4,4′(5′)-bis-*tert*-butylcyclohexano-18-crown-6 (DtBuCH18C6) was obtained from EIChroM Technologies, Inc. (Darien, IL) and used as received. Its 4(z), 4′(z) *cis-syn-cis* isomer was isolated from the commercial reagent according to published procedures (17). The 1-OAlc (99 + %, A.C.S. reagent grade) was obtained from Aldrich Chemical Company (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 reagent grade and were used as received. Details of the preparation of the extraction chromatographic resin have been described previously (7, 8). For the preparation of "solvent-free" Sr resin, published procedures were modified only by omission of 1-OAlc from the formulation.

### Procedures

#### Radiometric measurements and chromatographic characterization of extraction chromatographic materials

Methods for radiometric measurements and for column preparation/characterization, as well as for the determination of weight distribution ratios, the effect of matrix constituents on strontium retention, and the elution profile of strontium have been reported previously (8).

#### EXAFS measurements and analysis

A complete description of the preparation of strontium-loaded, octanol-free Sr resin for EXAFS measurements and the methodology employed in the acquisition and analysis of the EXAFS data has been provided previously (18).

## RESULTS AND DISCUSSION

### The Role of Water in Strontium Ion Uptake by Conventional and "Solvent-Free" Sr Resin

As already noted, in a solvent extraction system comprising DtBuCH18C6 in an aliphatic alcohol, such as 1-OAlc, the extent to which strontium is extracted is dependent on the water content of the alcohol (5). Implicit in this observation is that the presence of a high water content diluent is required for satisfactory metal ion sorption in the same system employed in extraction chromatographic mode. As is clear from Fig. 1, however, which compares the elution behavior of strontium-85 on conventional Sr resin with another chromatographic material from which 1-OAlc has been omitted, this is not the case. (Note that in both materials, the support is loaded to ~24% w/w with the crown ether.) In fact, the elution behavior of strontium on the two materials is nearly indistinguishable. Thus, contrary to expectations, the presence of 1-OAlc is not required.

If, as seems likely, stationary-phase water plays an important role in determining the behavior of the material even in the absence of

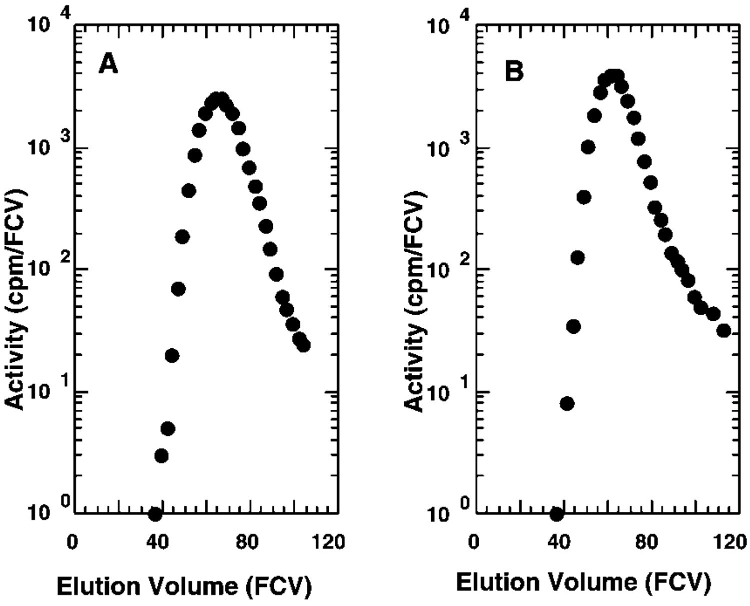


*Figure 1.* Comparison of the elution behavior of Sr-85 on the conventional (panel A) and an octanol-free (panel B) strontium-selective extraction chromatographic material (eluent: 2.96 M $HNO_3$; flow rate: 1–2 mL/cm$^2$/min; temperature: ~23°C; particle size: 50–100 μm).

1-OAlc, the question arises as to what factors contribute to its presence. There are numerous possibilities: that water is brought into the stationary phase by residual methanol remaining in the crown ether from the impregnation process, by impurities in the crown ether, by the crown ether itself, by the support, or by a combination of these factors. As shown in Fig. 2, which depicts the effect of impregnation solvent on the nitric acid dependency of $D_{w,sr}$ [defined as in Reference (8)] on the octanol-free Sr resin (again loaded to ~24% w/w with DtBuCH18C6), resin preparation using hexane yields a material indistinguishable from that prepared using methanol to deposit the crown ether on the support. The absence of any difference between the two dependencies, one for a resin prepared with a water-miscible impregnation solvent, the other with a water-immiscible solvent, indicates that traces of residual methanol in the stationary phase are

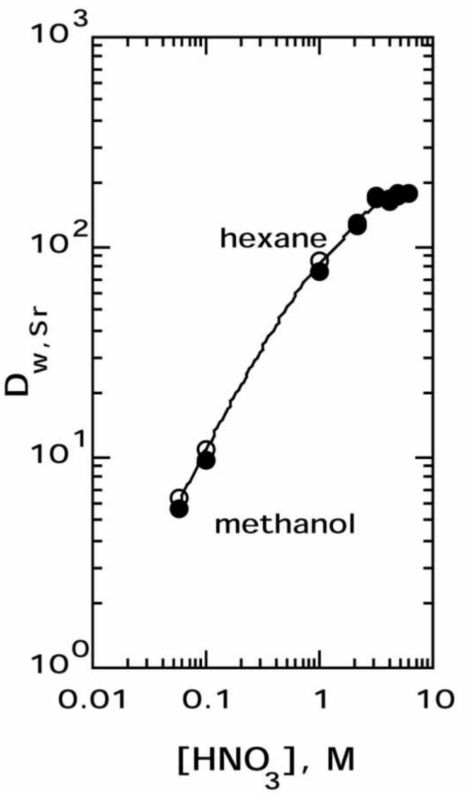


***Figure 2.*** Comparison of the $D_{w,Sr}$ nitric-acid dependencies for octanol-free Sr resin prepared using methanol (closed circles) or hexane (open circles) as the impregnation solvent.

not responsible for the behavior of the resin. That impurities in the crown ether are also unlikely to be responsible for the behavior of the resin is demonstrated by the fact that a $D_{w,Sr}$ value of 235 (vs. 3 M $HNO_3$) is obtained for a material prepared by loading XAD-7 with a purified single isomer [the 4(z), 4′(z) *cis-syn-cis* form (17)] of DtBuCH18C6. A partial explanation is found instead in the results presented in Fig. 3, in which the water content of 1-OAlc is shown as a function of crown ether concentration, here for a mixture of the *cis-syn-cis* (A) and *cis-anti-cis* (B) isomers of dicyclohexano-18-crown-6 (DCH18C6), chosen because of its availability in high purity in gram quantities. The results, which have been corrected for the water content of 1-OAlc itself under the same conditions (2.1 M), show that DCH18C6 (and by analogy, DtBuCH18C6) is itself an excellent extractant for water. At the highest crown ether concentrations, in fact, water extraction by the crown approaches that of 1-OAlc.

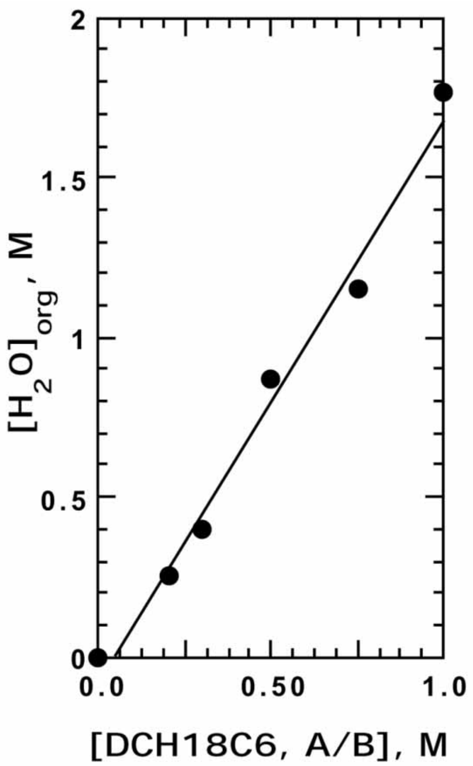


***Figure 3.*** Crown ether concentration dependence of the extraction of water from 1 M nitric acid into 1-octanol by DCH18C6 (mixture of A and B isomers), corrected for extraction of water by 1-octanol alone.

Water extraction by the crown ether is not, by itself, sufficient to explain the sorption behavior of the resin, however. Comparison of the equilibrium uptake of Sr by XAD-7-supported DtBuCH18C6 to that observed with an identical loading of the crown ether on either silica or Amberlite XAD-2 indicates that strontium uptake is also strongly influenced by the support material. In fact, strontium retention is a factor of 7 ($D_{w,Sr} = 142$ versus 20) greater for XAD-7- than for XAD-2-supported DtBuCH18C6. Although these two resins are dissimilar in several respects, it is likely that differences in water regain [an empirical measure of the ability of a support to sorb water (19)] are responsible for their differing suitability as supports here. Previous workers have noted the importance of water regain in determining cation uptake by various extraction chromatographic resins (20). Moreover, Amberlite XAD-2 has a lower regain value (0.67) than XAD-7 (2.01), consistent with the higher equilibrium uptake of strontium on the latter resin. Strontium retention on the octanol-free resin thus depends on both water extraction by the crown ether and the wettability of the support. It is tempting to speculate that just as solvent water content determines the efficiency of strontium extraction in a crown-ether-based SX system, so too will the water regain of the support determine the efficiency of strontium sorption in the corresponding extraction chromatographic system. Additional data are required to demonstrate this, however.

## Chromatographic Characterization of “Solvent-Free” Sr Resin

In conventional Sr resin, the support is loaded to ~40% w/w with a 1 M solution of DtBuCH18C6 in 1-OAlc. Both the extractant concentration used and the loading of the support were chosen to maximize strontium retention from 1–3 M $HNO_3$. Neither value can be increased, the crown ether concentration because 1 M represents the limit of its solubility in 1-OAlc, the loading because a 40% w/w material corresponds to complete filling of the pores of the support. Because the conventional resin contains ~16% w/w 1-OAlc, its elimination frees up a significant fraction of the pore volume. This raises a question as to the extent to which this newly available volume should be filled with crown ether in the “solvent-free” resin. The answer to this question will depend upon the application envisioned. If, for example, the objective is to increase the retention of some ion beyond that possible with the conventional resin, then maximum loading of the support with DtBuCH18C6 is obviously preferable. As shown in Fig. 4, the retention of strontium from highly acidic (3–6 M $HNO_3$) solutions, for example, can be increased by approximately 50% vs. the conventional Sr resin by employing a support fully loaded with the crown ether. Although this greater retention is of only limited utility in the application of the resin-to-strontium determination, the ability to “tune” metal ion uptake by the resin via

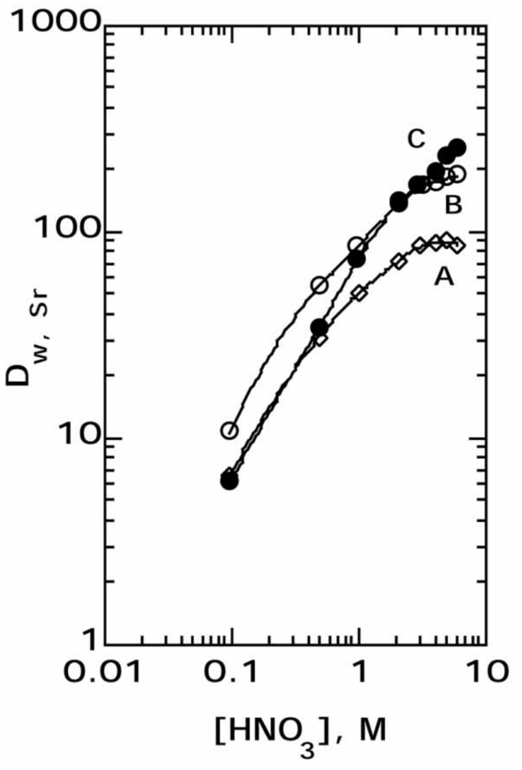


*Figure 4.* Effect of support loading on the nitric-acid dependency of strontium retention on the octanol-free Sr resin (temperature: ~23°C; particle size: 50–100 μm; DtBuCH18C6 loading: A: 10%; B: 20%; C: 40% w/w).

changes in extractant loading may prove useful in other applications of the resin, most notably in the separation of barium and radium. (This separation, as noted above, cannot be conveniently effected on the conventional resin.) Increased loading also boosts the resin capacity from ~10–14 mg Sr/mL resin, although this increase is somewhat smaller than would be expected on the basis of the nearly 70% increase in crown ether content, suggesting that not all of the crown is readily accessible.

In many instances, such as in a typical strontium separation for subsequent determination, the advantages of increased capacity and retention afforded by the fully loaded resin are probably not sufficient to offset its significantly higher cost. Of particular interest then is the behavior of a material employing the same loading of crown ether (~24% w/w) used in the conventional resin. Figure 5 illustrates the physical stability of this octanol-free Sr resin. Insufficient physical stability has long been recognized

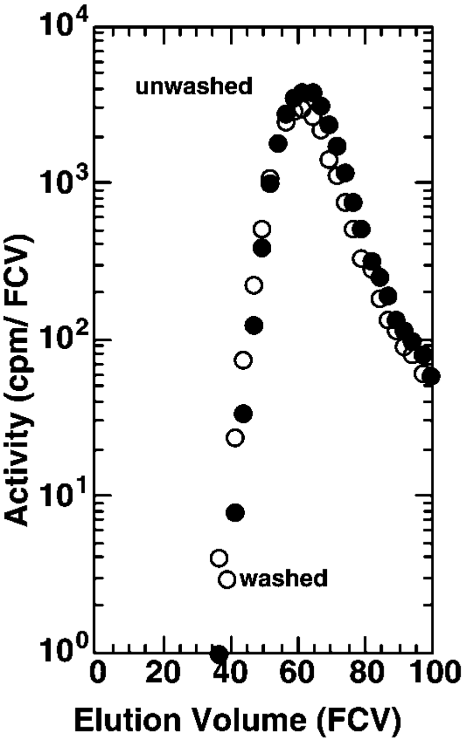


***Figure 5.*** Effect of column washing on the elution behavior of Sr-85 on the octanol-free strontium-selective extraction chromatographic material (eluent: 2.96 M $HNO_3$; flow rate: 1–2 mL/cm$^2$/minute; temperature: ~23°C; Particle size: 50–100 μm; filled circles: unwashed resin; open circles: washed resin [261 FCV].

as the factor limiting the more widespread adoption of metal ion sorbents based on extraction chromatography. Accordingly, there has been considerable interest in the development of means by which to reduce the loss of stationary phase (i.e., extractant and/or diluent). As can be seen, unlike the conventional material, for which washing with as little as 250 FCV of water results in a significant shift in the location of the peak maximum for elution of strontium (21), such a wash volume has no discernible impact on the elution behavior of Sr-85 on the octanol-free resin under the experimental conditions. In fact, even a 1000-FCV wash (not shown) yields only a 10% change in the position of the peak maximum.

Figure 6 compares the rate of strontium uptake by the octanol-free resin to that observed for conventional Sr resin from 2 M $HNO_3$. As can be seen, the time required to reach equilibrium (i.e., 90% of $Dw_{Sr,\ final}$) is somewhat longer for the octanol-free resin than for the conventional resin (10–15 min

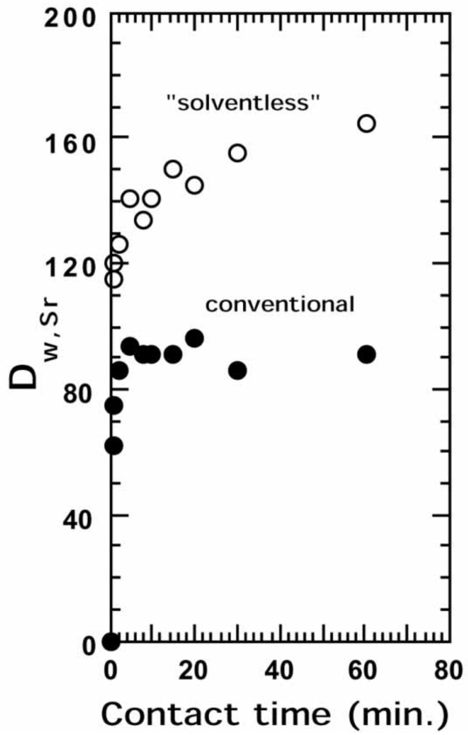


***Figure 6.*** Uptake kinetics for Sr-85 on conventional and octanol-free Sr resin from 2 M $HNO_3$ (temperature: ~23°C; particle size: 50–100 μm).

vs. 5 min). This is not entirely unexpected given that the viscosity of DtBuCH18C6 is greater than that of its solution in 1-OAlc. The increased stationary phase viscosity also impacts the observed column efficiency (i.e., chromatographic bandwidths for strontium elution). Figure 7 depicts the elution of Sr-85 on the octanol-free Sr resin using 3 M $HNO_3$ as the eluent. From the retention volume and the width of the elution band at half height, the number of theoretical plates present can be determined (22) to be 79, indicating that the conventional resin is slightly more efficient (93 plates) under the same conditions than the "solvent-free" resin, a likely result of slower ion transfer in and out of the more viscous DtBuCH18C6 stationary phase. It is important to note here that neither the slower metal ion uptake kinetics nor the slightly lower column efficiency have any practical significance as regards the utility of the new resin.

Figure 8 summarizes the behavior of selected alkali and alkaline–earth cations on the octanol-free Sr resin. Just as the absence of 1-OAlc makes little difference in the elution behavior of $Sr^{2+}$ (Fig. 1), so too does its

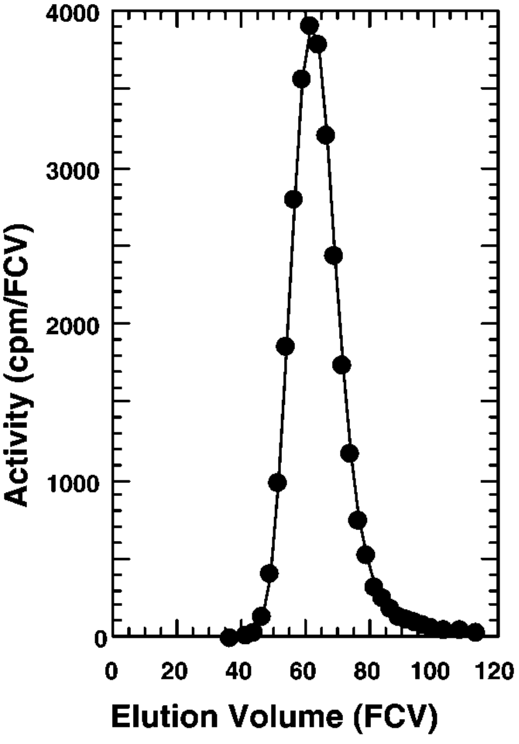


***Figure 7.*** Elution curve for Sr-85 on octanol-free Sr resin (particle size: 100–150 μm; bed volume: 0.59 mL; bed length: 10.1 cm; temperature: ~ 23°C; flow rate: 1–2 mL/cm$^2$/minute; eluent: 2.96 M $HNO_3$).

absence have little appreciable effect on the behavior of the other cations tested. Although for several cations, subtle differences in the shapes of the acid dependencies vs. those observed on the conventional material are seen (e.g., barium retention by the "solvent-free" resin peaks at ~ 0.5 M rather than 1 M $HNO_3$), none of these differences are sufficient to impact application of the resin. Most notably, the remarkable strontium selectivity characteristic of the Sr resin (7, 8) is preserved in the octanol-free material.

Figure 9 shows the effect of various matrix constituents, chosen because of their presence in soils, minerals, or groundwaters ($Na^+$, $Ca^{2+}$) or bioassay samples ($K^+$, $NH_4^+$), on the retention of strontium by the new resin. As can be seen, $Na^+$ and $Ca^{2+}$ have no effect on strontium retention until their concentration exceeds 0.1 M. As expected from the known affinity of $K^+$ for 18-crown-6 compounds, its effect on strontium sorption is more significant, with an appreciable decrease in $D_{w,\ Sr}$ evident by only 0.05 M $K^+$. The effect of ammonium ion on strontium sorption falls between that

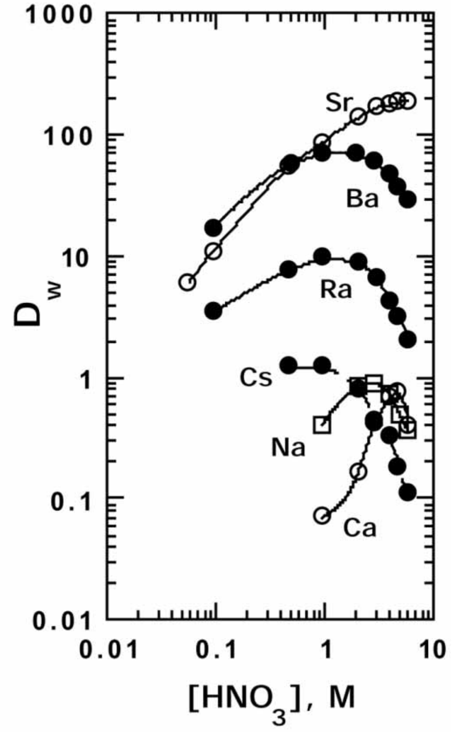


*Figure 8.* Acid dependency of the retention (expressed as a weight distribution ratio, $D_w$) of alkali and alkaline–earth cations on the "solvent-free" Sr resin (temperature: ~23°C; particle size: 50–100 μm).

of $Na^+/Ca^{2+}$ and $K^+$, consistent with the known formation constant values for these ions with 18C6 (23) and with the behavior of conventional Sr resin (8).

In summary, although characterization of the octanol-free Sr resin is incomplete at present, it appears thus far that the metal ion retention properties of the new resin closely parallel those of its conventional analog. Unlike the conventional resin, however, the "solventless" Sr resin exhibits physical stability sufficient to allow reuse.

## EXAFS Characterization of the "Solvent-Free" Sr Resin

Despite a now-extensive literature concerning the properties and performance of crown ether-based (and other) extraction chromatographic resins (6, 24–26), certain of the fundamental aspects of these materials remain incompletely understood. Among the more important of these is the nature

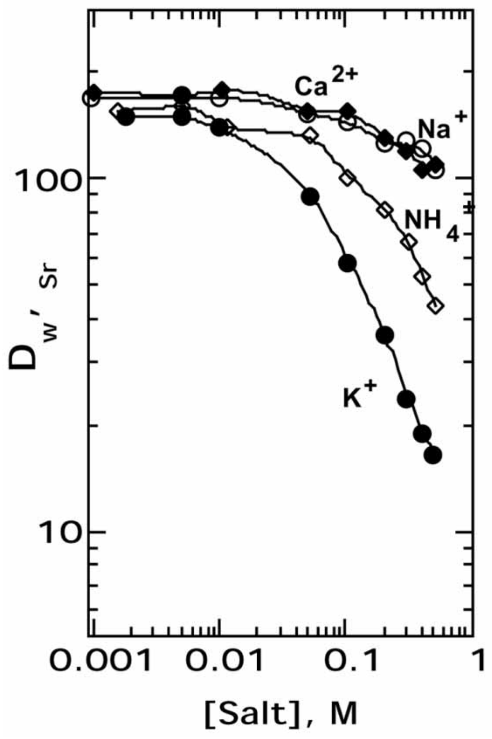


*Figure 9.* Effect of matrix constituents on the retention of strontium by the octanol-free Sr resin (temperature: ~23°C; particle size: 50–100 μm).

of the coordination environment of sorbed metal ions. Although chromatographic characterization (such as that described previously) provides data useful in applying a resin to various separations, it yields little insight into the basic chemical phenomena underlying these separations. To obtain such insight, various equilibrium models that describe the distribution of a metal ion between an aqueous phase and extractant solutions can be applied, but such an approach provides only indirect evidence of the nature of the system. Recently, extended X-ray absorption fine structure (EXAFS) measurements have been shown to be applicable to the elucidation of the coordination environment of metal ions sorbed on a variety of organic and inorganic substrates (27–32), thus suggesting that the technique could provide a direct means of obtaining information on the coordination environment of strontium in the octanol-free Sr resin. For example, although electroneutrality considerations dictate that the sorbed strontium crown ether complex incorporate two nitrate anions, it is unclear if they are present in the inner [i.e., $Sr(NO_3)_2(CE)$] or outer [i.e., $Sr(H_2O)_n(CE) \cdot 2NO_3$] coordination sphere. Along these same lines, the importance of stationary phase water to the uptake of strontium by the resin, noted previously, raises questions as to the details of its participation in complex formation. EXAFS studies, by providing answers to such questions, may shed light on the fundamental complexation chemistry underlying the behavior of the new Sr resin.

Figure 10 compares the Sr K-edge EXAFS results for three systems: solid $Sr(NO_3)_2$(18-crown-6) [for which a solid-state X-ray crystal structure has been reported previously (33)], a solution of $Sr(NO_3)_2$(DCH18C6) in 1-OAlc [for which more detailed EXAFS results have been recently published (34)], and XAD-7-supported DtBuCH18C6, upon which Sr has been sorbed from $Sr(NO_3)_2$ solution. As can be seen, the measured EXAFS are remarkably similar for the three systems. The most prominent features of the results are 10 coordinated oxygen atoms at an average distance of 2.65 Å from the strontium atom and the 12 carbon atoms comprising the crown-ether backbone at an average distance of 3.53 Å. Also observed is a strong scattering signal from two distal (i.e., uncoordinated) nitrate oxygen atoms at an average distance of 4.33 Å. Taken together, these coordination numbers and bond distances demonstrate that in all three systems, the strontium ion resides in the center of the crown ether ring and that a pair of coordinated nitrate

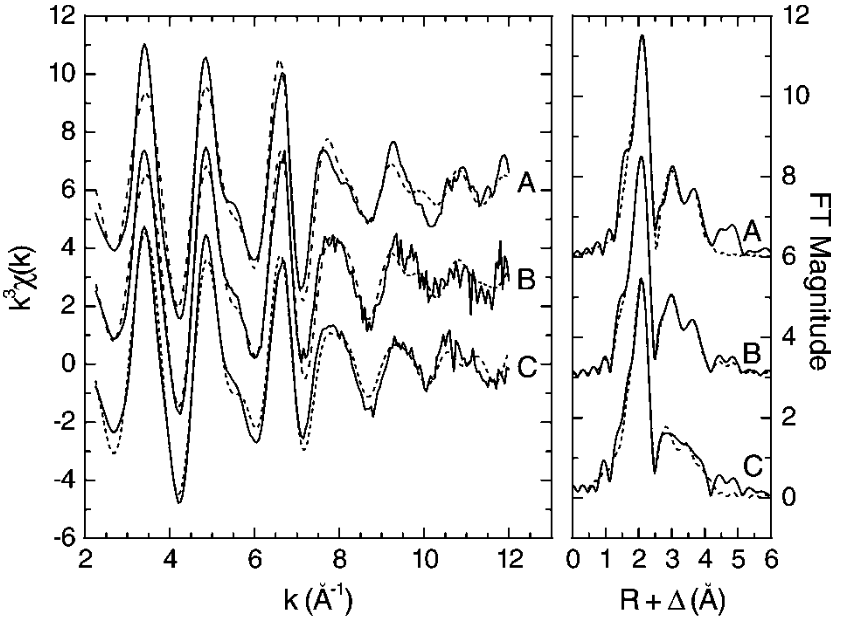


*Figure 10.* Sr K-edge EXAFS (—) and FEFF8.00 best fit (---) of the Sr-crown ether complexes present as (**A**) $Sr(NO_3)_2$(18C6) solid, (**B**) $Sr(NO_3)_2$(DCH18C6) in 1-octanol, and (**C**) $Sr(NO_3)_2$ (DtBuCH18C6) on solid support. Fourier transformations are not phase-shift corrected.

ions occupy the axial positions. Thus, the coordination environment for the 18-crown-6 complex of strontium ion in the solid state and for the complex formed in the liquid–liquid extraction of strontium from nitric acid solution into 1-OAlc by DCH18C6 is identical to that observed in the octanol-free extraction chromatographic resin system.

## CONCLUSIONS

Despite its many favorable properties, conventional Sr resin has several limitations, most notably insufficient retention of certain ions (e.g., barium), limited capacity, and inadequate physical stability. Unexpectedly, these deficiencies can be partly addressed by omitting the diluent, 1-OAlc, from the resin and, in some instances, replacing it with additional crown ether. The resultant materials retain the properties that have made conventional Sr resin so useful; in particular, its excellent selectivity for strontium over most other cations. EXAFS examination of the strontium-loaded resin provides a partial explanation for this observation, demonstrating that the coordination environment of strontium sorbed on the solvent-free resin is identical to that observed in analogous SX systems using an octanol solution of an 18-crown-6.

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