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Improved Extraction Chromatographic Materials for the Separation and Preconcentration of Metal Ions

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IMPROVED EXTRACTION CHROMATOGRAPHIC MATERIALS FOR THE SEPARATION AND PRECONCENTRATION OF METAL IONS

By

Abdul Momen

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ABSTRACT

IMPROVED EXTRACTION CHROMATOGRAPHIC MATERIALS FOR THE SEPARATION AND PRECONCENTRATION OF METAL IONS

by

Abdul Momen

The University of Wisconsin-Milwaukee, 2015
Under the Supervision of Professor Mark L. Dietz, Ph.D.

Growing public health and safety concerns over the use of nuclear materials have increased the demand for improved methods for the separation and preconcentration of various metal ions from environmental and biological samples for subsequent determination. Historically, solvent extraction and ion-exchange have often been the methods of choice for these separations. Solvent extraction, however, is cumbersome and can generate substantial volumes of organic wastes. Ion-exchange, while less cumbersome, lacks adequate selectivity and requires careful control of pH for satisfactory separation. Moreover it is generally not compatible with acidic samples, such as are commonly encountered in the analysis of biological and environmental samples.

Extraction chromatography (EXC) combines the selectivity of solvent extraction with the ease of operation of an ion-exchange column. Since its origins in the late 1950's, a wide variety of EXC materials have been described, and a number of these materials are now commercially available. The performance of EXC materials is deficient in several important respects, however, including modest retention, physical stability, column efficiency, and metal ion sorption capacity. The objective of this work, therefore, is to address these deficiencies and thus, to produce improved extraction chromatographic materials. With this in mind, a systematic study of the effect of the properties of the solid support, the extractant, and the diluent on these characteristics of EXC materials has been undertaken. Four different approaches have been followed: incorporation of ionic-liquids into EXC materials to improve metal ion retention, extractant encapsulation in silica sol-gels to improve the physical stability, stagnant pore plugging to improve the chromatographic efficiency, and the use of polysulfone capsules to improve the capacity. Unexpectedly, the use of an ionic liquid as a diluent for a crown ether (CE) was not found to provide an EXC material capable of strontium ion retention greater than that achievable with a conventional octanol-based material employing the same extractant. Encapsulation of the crown ether in a sol-gel glass or a polysulfone capsule, however, was found to yield strontium sorbents with improved physical stability, strontium ion uptake, or column efficiency. Lastly, it was found that the chromatographic efficiency of commercially available EXC resins can be significantly improved simply by blocking the relatively inaccessible pores with an inert filler. All of these results represent important steps towards the development of commercially viable alternatives to existing extraction chromatographic materials.

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CHAPTER 1:

INTRODUCTION

1.1 Overview and Scope

Liquid-liquid extraction (LLX), also known as solvent extraction (SX), and ion-exchange (IX) are among the most well-established techniques for the separation and preconcentration of metal ions in solution. During World War II, the potential of nuclear energy and weapons was recognized, and to provide the needed quantities of purified fissile radionuclides, in particular isotopes of uranium and plutonium, SX was scaled up from the analytical to the process-scale (1.1, 1.2). Since 1951, when the first large-scale Plutonium-Uranium Recovery and Extraction (PUREX) facility was established in United States (1.3), solvent extraction has evolved into a technique with important hydrometallurgical (1.4-1.6), nuclear, and waste treatment applications (1.2, 1.7-1.9). Interestingly, however, its utility as an approach to analytical separation has declined, a consequence of the availability of less cumbersome alternatives (*e.g.*, solid-phase extraction), its frequent reliance on toxic and/or volatile solvents, and its tendency to generate substantial volumes of organic waste (1.10) when large numbers of samples are processed.

More than a century ago, Tswett's work on chromatographic methods using calcium carbonate as a stationary phase (1.11) paved the way for the eventual introduction (in 1935) of ion-exchange resins. Since this time, IX has developed significantly and is now widely employed for the separation of ionic and ionizable compounds, a result in part of the convenience and ease of handling of ion-exchange materials (1.12). Ion-exchange procedures typically require careful pH control for satisfactory separations, however (1.13). In addition, ion exchange is generally not suitable for samples containing high concentrations of acid, such as those frequently encountered in analyses of biological, geological, and environmental samples.

Extraction chromatography (EXC) combines the best features of these two techniques, coupling the selectivity of liquid-liquid extraction with the ease of operation of an ion-exchange column (1.14). First proposed by Siekierski in 1959 (1.15), this method has since come to be employed in the separation of a variety of metal ions from a wide range of sample types (1.16-1.20). There are three major components of an EXC system: the inert (typically) support, the stationary phase (*i.e.,* an extractant, either alone or dissolved in an appropriate diluent) and the mobile phase. The great advantage of EXC in separations lies in the wide variety of possible stationary phases. That is, each extractant has specific characteristics (*i.e.,* extraction efficiency and selectivity) that allow the EXC system to resolve a particular separation problem. While widely applied and generally recognized as offering significant advantages over other methods for metal ion separation and preconcentration, extraction chromatography is not without its limitations (1.21). First, because the extractant is not chemically bonded to the support, the physical stability of typical EXC materials is inadequate for many purposes. Along these same lines, the inability of the supports employed to retain significant quantities of extractant means that the metal ion uptake capacity of typical EXC materials is not high. Lastly, the large particle size of most EXC resins leads to elution band that are quite broad, rendering the separation of species having similar extraction behavior difficult or impossible. Overall, the performance of an extraction chromatographic system is defined in terms of many parameters, including not just efficiency, capacity, and physical stability, but also retention, selectivity, resolution, chemical stability, ease of preparation and regeneration (*i.e*, analyte recovery), and reproducibility. Considering all of these parameters, their interrelationship, and their relative importance in the context of the way EXC is usually practiced, it becomes clear that improvements in EXC materials require extractants of improved selectivity and/or complexing power and supports or support/extractant/diluent combinations that provide higher efficiency, capacity, and physical stability.

The objective of the present studies is to address these deficiencies and thus, to produce vastly improved extraction chromatographic materials. With this in mind, a systematic study of the behavior of solid supports and the role of extractant and diluents, all important components of EXC materials, has been undertaken. Four different approaches to improving the performance of EXC materials have been pursued: ionic liquid-based sorbents for improved retention, extractant encapsulation in silica sol-gel glasses for improved stability, stagnant pore plugging to improve efficiency, and polysulfone capsule-based materials for improved capacity.

1.2 Liquid-liquid extraction

Liquid-liquid extraction is often the method of choice for the large-scale separation and preconcentration of metal ions. In an extraction process, the metal ion-containing solution (usually aqueous) is contacted with a solution of a metal-ion-specific extractant in a water-immiscible organic solvent. Solutes distributing between two immiscible phases reach an equilibrium concentration according to the Nernst partition isotherm, where the distribution of a solute X between phases is a constant expressed mathematically as follows:

$$K = \frac{[X]_{org}}{[X]_{aq}} \qquad (1-1)$$

A thermodynamic partition coefficient, of course, should be expressed using the activities of the species. Unfortunately the necessary activity coefficients are often unavailable. For many practical applications, therefore, the ratio of the total concentration of a metal ion solute, M, present in the organic and aqueous phases, expressed as the distribution ratio (D), is used:

$$D = \frac{[M]_{org}}{[M]_{aq}} \qquad (1-2)$$

The extractant and the metal ion form an organic-soluble (and thus, extractable) metal complex that is transferred to the organic phase. Contact of the separated organic phase containing the extracted metal ion complex with an appropriate aqueous phase reverses the process, leading to stripping of the metal from the extractant and its return to the aqueous phase. By appropriate choice of extractant, organic solvent, and aqueous phases, a highly selective metal ion separation can be achieved. Although this would appear straightforward, the design of a practical extraction process for many types of samples (*e.g.,* nuclear waste) is complicated by the properties of the extractants and solvents and the need to satisfy various engineering, environmental, cost, and safety requirements. For example, in developing processes suitable for treatment of nuclear materials, any solvents used must have a high flash point and low toxicity and should not generate any toxic or corrosive by-products upon prolonged heating or irradiation.

Additionally, they should be readily available and inexpensive. Also, the extractants employed must allow for simple stripping chemistry. Although these considerations are probably most relevant to process-scale applications of solvent extraction, many are also pertinent to analytical-scale use of the method. It is important to note, however, that despite its many virtues, SX has come to be regarded as too time-consuming for routine use when large numbers of samples are involved. In addition, as ordinarily practiced solvent extraction can generate substantial volumes of toxic organic wastes, thus running counter to recent efforts to devise “green” (*i.e.*, more environmentally friendly) approaches to separations.

1.3 Extraction chromatography

1.3.1 Background

One way to circumvent these problems while still retaining the positive characteristics of solvent extraction is to immobilize the extractant, either neat or in an appropriate solvent, in the pores of a solid support. This approach, commonly known as extraction chromatography (EXC), can be thought as a special type of liquid-liquid partition chromatography, in which the stationary phase is an organic extractant and the mobile phase is an aqueous solution. In conventional partition chromatography, solute molecules undergo little, if any, chemical change (apart from association or proton exchange) in the process of partition. In contrast, in EXC the transport of the ionic solute from the aqueous phase into the organic phase is generally accompanied by complex chemical changes involving many interactions and equilibria, ultimately leading to the extraction of a metal complex. The sorption of an ion by an EXC sorbent, similar to the process of extraction itself, is actually a combination of several processes: partitioning of the extractant molecule or its adsorption at the organic-aqueous interface, formation of the metal complex, and partitioning of the metal-complex (Figure 1.1).

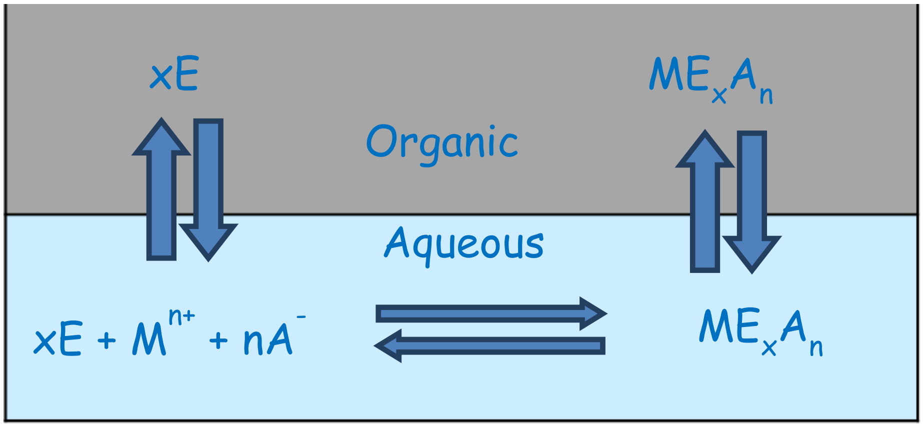

Figure 1.1: Extraction process equilibria, where E is the extractant, M is a metal ion of charge n, and A$^-$ is the counteranion required with neutral extractant molecules such as crown ethers (1.22).

If the assumption made is that the predominant form of the metal ion (M) in the organic phase is the complex (MA_nL_m) and that in the aqueous phase the uncomplexed metal ion predominates, then the distribution ratio of the metal ion can be expressed as follows:

$$D = \frac{K_p\,\beta_i}{K'^m_p}\,[A^-]^n[L]^m_{org} \qquad (1-3)$$

where K_p is the distribution constant of the extracted complex, β_i is its formation constant, K'_p is the distribution constant of the extractant itself, m and n are the number of extractant molecules and anions present in the extracted complex respectively, $[A^-]$ is the aqueous phase anion concentration, and $[L]_{org}$ is the organic-phase extractant concentration. This equation clearly indicates the important parameters in determining the distribution of a given metal ion between the organic and aqueous phases in a liquid-liquid system and thus, the extent of sorption in the corresponding EXC system. The metal ion distribution ratio (D) in a liquid-liquid system is related to the retention of the ion in the corresponding extraction chromatographic system (*i.e.*, the weight distribution ratio (D_w)) through equation 1-4.

$$D = D_w \cdot \frac{d_{extr}}{\%wt\ extr} \qquad (1-4)$$

Where d_{extr} is the density of the extractant and %wt extr is the extractant loading in grams of extractant per gram of resin. In turn, the weight distribution ratio (D_w) can be converted to a resin capacity factor, k’ (*i.e.*, the number of free column volumes of the eluent required to reach the peak maximum), by taking into account the density of the extractant or its solution and the value of v_s/v_m (the ratio of the volumes of the stationary and mobile phase).

$$k' = D_w \cdot \frac{(d_{extr} \, . \, v_s)}{(\%wt\ extr \, . \, v_m)} \qquad (1-5)$$

In actual practice, weight distribution ratios are usually not calculated from LLX data, but rather are measured by determining the extent to which the metal ion concentration of a solution is reduced by contact with a known mass of the EXC resin.

$$D_w = \left(\frac{A_0 - A_s}{W}\right) \bigg/ \frac{A_s}{V} \qquad 1-6$$

Here A_0 and A_s represent the aqueous concentration of the metal ion before and after equilibration, respectively. W is the weight of the sorbent (in grams), and V is the volume of aqueous phase used (in milliliters).

Although LLX data often represent a valuable guide to the design of EXC systems, certain aspects of the performance of an EXC materials are not predictable from LLX data, as many more factors are involved in a dynamic chromatographic process than in a batch (*i.e.*, static) process like LLX (1.23). As already noted, the behavior of the EXC materials is normally described in terms of seven parameters: retention, selectivity, efficiency, capacity, stability (both chemical and physical), ease of preparation and reuse, and reproducibility. The retention and selectivity of an EXC material are governed primarily by the properties of the extractant and the mobile phase composition. Column efficiency, typically expressed in terms of HEPT or N, is a complex function of a number of system characteristics, including mobile phase velocity, diffusion coefficients of the metal ion in the mobile and stationary phases, particle diameter, temperature, kinetics of extraction and stationary phase thickness. The ideal EXC resin, from the perspective of efficiency, is one consisting of uniform, small-particle size supports bearing a thin, homogeneous layer of a non-viscous extractant capable of rapid reaction with the metal ion(s) of interest. Few, if any, EXC materials approach this ideal. The capacity of an EXC material is obviously dependent on the amount of extractant that can be loaded into the support. For analytical-scale applications, capacity is usually regarded as secondary consideration. Maintaining a constant capacity *i.e.*, stability, however, is very important. To be useful, an EXC material must exhibit satisfactory chemical and physical stability. Although the chemical stability is not normally an issue, the physical stability of the EXC materials is another matter. As mentioned earlier, because of weak interactions between extractant and support, loss of extractant into the mobile phase is quite common. In fact, poor stability arising from the dissolution or the shearing off of the stationary phase from the support is regarded as the single biggest obstacle to the widespread use of EXC (1.24, 1.25). After all, it is the physical and chemical stability of an EXC column that determines the ease with which it can be re-used and the reproducibility of results obtained with it. Considering all of these parameters, it is evident that much can be done to improve the performance of existing EXC materials for application in metal ion separation and preconcentration.

Despite the need for improvement, extraction chromatographic methods often compete favorably with ion-exchange liquid chromatography (IELC), particularly in the trace metal ion separations such as are often encountered in radiochemical separations. In IELC, the properties of the ion-exchanger and the composition of the aqueous phase determine the selectivity of the ion-exchange process. Unfortunately, in the case of two ions having same charge and similar ionic radii, the properties of the ion-exchanger (*e.g.*, acidity or basicity, degree of cross-linking) are generally not such as to provide effective separation. To effect a separation, an appropriate complexing agent must be added, and the selectivity observed is thus due to differences in either metal-ligand stability constants or in the charge or structure of the complex formed. In contrast, the stationary phase of an EXC material exhibits complex-forming properties that potentially render it adequately selective.

Conventional EXC materials are prepared by the physical impregnation of a porous substrate with an extractant employing any of several techniques (1.26-1.28). Typically, the support material is contacted with a solution of extractant (or extractant-diluent mixture) in a volatile solvent, which after a period of equilibration is slowly removed by evaporation under vacuum. In the alternative, the extractant can be incorporated into the support during its preparation. For instance, EXC materials have been prepared from macroporous styrene-divinylbenzene copolymers containing an extractant added to the mixture of monomers during polymerization (1.29, 1.30). Regardless of the method in which an EXC is made, the retention of the extractant by the support is solely the result of physical interactions, not covalent bond formation between the extractant and the support.

1.3.2 Extractants and diluents

Since the introduction of EXC, many of these materials have been employed for metal ion separation and preconcentration (1.31). For the separation of actinide elements, for instance, tri-*n*-butyl phosphate (TBP) (1.32, 1.33), tri-*n*-octyl amine (1.34, 1.35), Aliquat 336 (tri-caprylylmethylammonium chloride) (1.36, 1.37), *bis*(2-ethylhexyl) phosphoric acid (HDEHP) (1.38, 1.39) and many other extractants have been used. These extractants have been coated onto any of a variety of substrates, including diatomaceous earth, silica, powdered cellulose, and various polymers (1.40). Table 1.1 lists some of these materials and other "classical" resins, along with their active components and selectivities for a number of elements or groups of elements. Because of various limitations, including inadequate selectivity, poor stability, and limited capacity, very few of these EXC materials have actually found widespread application.

Table 1.1: "Classical" extraction chromatographic resins

Support	Stationary Phase	Selectivity	Ref.
Kel-F	HDEHP/TTA in isobutyl ketone	U	1.41, 1.42
Alumina	HDEHP	Rare earth	1.43
Cellulose	HDEHP	Rare earth	1.44
Celite-545	Aliquat-336	Cf, Am	1.45
Hyflo Super Cel	TBP	Np	1.46
Teflon-6	MIBK	Sn	1.47
Activated charcoal	Di-octylpyrophosphoric acid	U	1.48
Teflex	Dipicrylamine in nitrobenzene	Rb, Cs	1.49
Copolymer of polystyrene with DVD	TBP	U	1.50

Table 1.2: Commercially available extraction chromatographic resins

EXC materials	Stationary Phase	Selectivity	Ref.
TRU resin	0.75 M CMPO in TBP	Actinides (III, IV, VI), Ln(III)	1.51
UTEVA resin	Undiluted diamyl amylphosphonte	U(VI)	1.52
TEVA	Undiluted Aliquat 336	Th(IV), Np(IV), Pu(IV), Tc(VII)	1.53
Sr-resin/Pb-resin	1 M DtBuCH18C6 in 1-octanol	Sr, Pb	1.17
Ln-resin	Undiluted HDEHP	Ln(III)	1.54
Actinide resin	Bis(2-ethylhexyl)methanediphosphonic acid (H_2DEH[MDP])	Actinides	1.55
Cs resins	AMP, KNiFC	Cs	1.56
Nickel resin	Dimethylglyoxime (DMA)	Ni	1.57
RE resin	1 M CMPO in TBP	Th, U, Np, Am, Cm, rare earth elements	1.58

More recently, a variety of new EXC materials have been introduced for the separation and preconcentration of metal ions from various sample types. Many of these materials are now commercially available (Table 1.2). Advances in molecular design and synthetic methodology have led to a variety of new extractants, including crown ethers (1.59, 1.60), cryptands (1.60), and calixarenes (1.61). These compounds are capable of stronger and more selective binding of certain metal ions than has been achieved with previously available reagents. Applying such extractants has led to significant improvements in EXC methods for the separation and preconcentration of radiostrontium ion, isotopes of which ($^{89/90}$Sr) are of great interest in environmental radiochemistry. Since WWII, the use of nuclear materials has increased dramatically, and the potential for environmental contamination has also increased (*e.g.,* Chernobyl and Fukushima). Because of the ability of strontium-90 (half life ≥ 29 yrs) to replace calcium in bone, it represents a potential human health hazard. As a result, there is an urgent need to determine the radiostrontium in environmental and biological samples.

Previously, Akaza (1.41) and Lieser *et al.* (1.42) described the separation of strontium from other alkaline earth metals using thenoyltrifluoroacetone (TTA) in isobutyl ketone and *bis*(2-ethylhexyl)phosphoric acid (HDEHP) respectively, supported on polytrifluorochloroethylene (Kel-F). The problem with both of these reagents and other such "classical" extractants is that their strontium selectivity is not sufficient to analyze environmental and biological samples. In addition, these reagents are not effective for highly acidic sample solutions, a significant limitation given that a number of procedures for the determination of radionuclides in urine (1.62), feces (1.63), soils (1.64, 1.65), and natural waters (1.65) involve either sample acidification or leaching and/or digestion of the sample with acid.

In the early 1990's, workers at Argonne National Laboratory developed an LLX process for the removal of radiostrontium from acidic nuclear waste streams (1.66-1.68). This process, known as the SREX (StRontium EXtraction) process, incorporates a macrocyclic polyether, di-(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6, Figure 1.2), in 1-octanol to extract strontium as a strontium-nitrato-crown ether complex. It was subsequently demonstrated that impregnation of a polymeric support (*e.g.,* Amberlite XAD-7) with a 1 M solution of this crown ether in 1-octanol yields an EXC resin (Sr-resin) that exhibits both good retention and selectivity of strontium from acidic nitrate media (1.16-1.18).

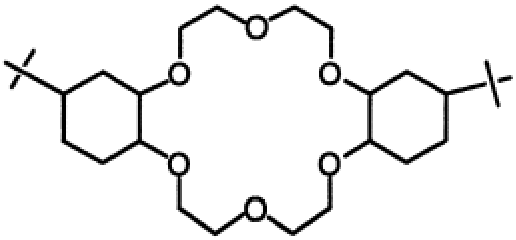

Figure 1.2 Di-(tert-butylcyclohexano)-18-crown-6 (DtBuCH18C6).

The application of this crown ether-based EXC material in the separation and preconcentration of strontium is now well established, and a number of studies detailing its use in various analyses have appeared in the literature (1.20, 1.64-1.67). It has been reported, however, that despite its many advantages, the material does suffer from certain limitations, among which is inadequate physical stability. Figure 1.3 illustrates the effect of column washing on the behavior of strontium-85 on Sr-resin. It shows that passage of even a modest volume (250 free column volumes, FCV) of eluent (*i.e.*, here, 1 M HNO_3) through the column leads to a significant shift in the position of the elution band. As a consequence, attempts to reuse the material are complicated by changing column behavior induced by sample loading, column rinsing, and strontium recovery. The elution band is shifted to higher volumes upon column washing, consistent with loss of diluent (here, 1-octanol) from the support. This observation suggests that the stability of the resin might be improved by changing or even eliminating the diluent.

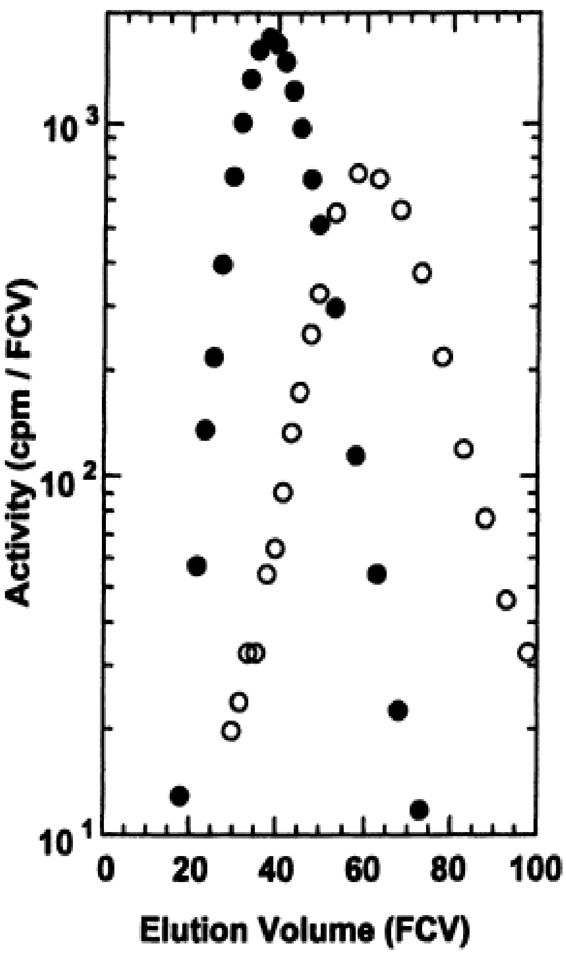

Figure 1.3 Effect of column washing on the elution behavior of Sr-85 on a conventional, strontium-selective extraction chromatographic material ("Sr Resin"). (Eluent: 1 M HNO_3; Flow rate: 1-2 mL/cm^2/min; Temperature: ca. 23°C; Particle size: 100-150 μm; Filled circles: unwashed resin; Open circles: washed (259 FCV) resin) (1.21).

Previously, it had been shown that a change to a higher molecular weight (and thus, less water-soluble) alcohol would be expected to lead to a decrease in strontium retention by the resin (1.66, 1.20). Complete elimination of the diluent would also seem to be out of question, as prior studies have clearly established the important role played by the alcohol in strontium extraction from acidic nitrate media (1.66). However, the elution behavior of Sr-85 on an EXC resin comprising only DtBuCH18C6 dispersed on an appropriate polymeric support is barely distinguishable from that observed on the conventional resin in which the stationary phase consists of a 1-octanol solution of the crown ether, as shown in Figure 1.4. This unexpected result has been partially explained by the ability of DtBuCH18C6 itself to extract significant amounts water, much like aliphatic alcohols (1.21). Additionally, a volume of mobile phase that had induced a significant change in the elution behavior of conventional resin has no discernible effect on Sr-85 elution on octanol-free materials (1.21). This study opens the possibility of utilizing undiluted DtBuCH18C6 not only on polymer-based supports but also other supports (*e.g.*, silica) to address the poor stability of the Sr-resin.

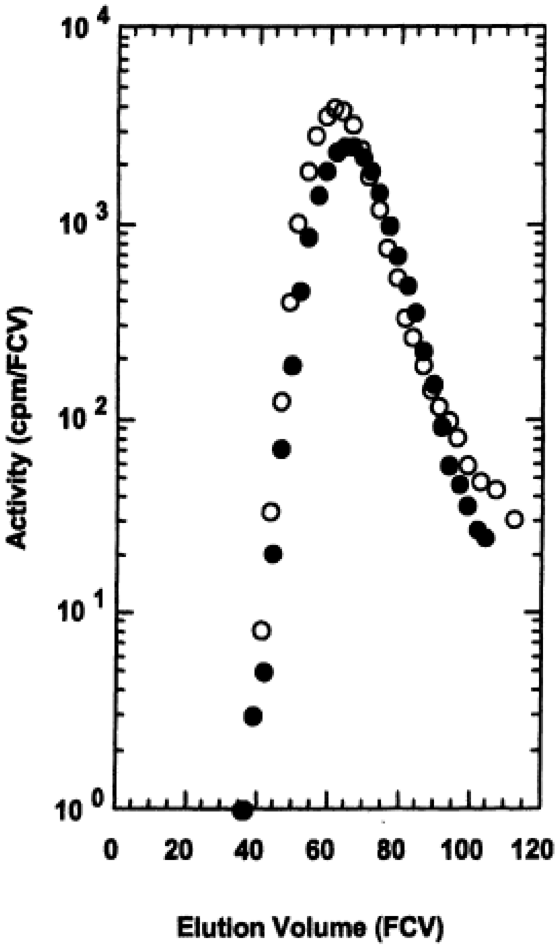

Figure 1.4: Comparison of the elution of Sr-85 on a conventional (filled circles) and an octanol-free (open circle) strontium-selective extraction chromatographic materials. (Conditions are as noted in figure 1.3) (1.21).

1.3.3 Solid supports

In the last few years, there has been growing awareness of the possibility of employing support properties to enhance the performance of EXC materials. It is known that the physical properties of a support influence certain aspects of chromatographic separations. For instance, improved column efficiency resulting from the use of smaller particle size supports is well-established (1.74). Recently, the effect of chemistry of the support on the behavior of EXC materials, either using different support surfaces to manipulate the adsorptive forces for a typical extraction chromatography or actually participate in metal ion uptake, has been explored. EXC materials designed on the basis of adsorptive forces between extractant and the support are known as ‘inert substrate”, while those for which the support itself or surface-bound functional groups participate in metal ion uptake are termed as “active substrate”.

In conventional extraction chromatography, supports are specifically chosen to be inert to the extractant, diluent (if any), and the constituents of the sample. The inert support is made up of a porous organic polymer or inorganic materials typically ranging in size from 50 to 150 μm in diameter (for special applications other smaller or larger particles have been studied). Conventional EXC materials have shown significant degradation (*i.e.*, physical instability) during use (1.21), and this may be related to the pore width of the beads, as previous work suggests that larger pores provide faster kinetics and smaller pores provide slower kinetics (1.75). If EXC materials could be designed with intermediate pore widths appropriate for both good kinetics and extractant retention, then the long-standing issue of the stability of EXC materials might be corrected.

In an effort to exploit support chemistry, active substrate EXC materials have been prepared by the impregnation of a material capable of acid-base interactions or ion exchange with an extractant bearing an appropriate functional group (*e.g.*, an anionic functionality capable of interaction with an anion-exchanger). A variety of studies have been performed with such systems, extending from early investigations by Akaiwa (1.76), Tanaka (1.77-1.80) and Lee (1.81) to more recent work by Sarzanini (1.82), Warshawsky (1.83, 1.84) and Khalifa (1.85). Most often, a sulfonated extractant has been sorbed on a strong anion-exchanger and the metal ion sorption properties of the resultant materials determined. These studies have shown that the retention of the extractant is likely due to a combination of adsorption and ion-exchange, with the latter being predominant. This retention is sometimes sufficiently strong for the resin to withstand contact with acids and bases. However, two limitations in these materials have become evident. First, the capacity of certain of the resins is less than that expected on the basis of extractant loading, suggesting that not all of the extractant is available for complexation (1.81). Secondly, it appears that the binding ability of certain immobilized extractants is less than that of the free extractant (1.82).

Along these same lines (*i.e.*, utilization of the surface chemistry to improve an EXC material), another approach has been described in which macroporous beads of a copolymer of chloromethylstyrene and methylmethacrylate are prepared using divinylbenzene as a cross-linker, then surface-functionalized to leave unreacted carbon-carbon double bonds (1.86, 1.87). Following impregnation of the support with an extractant, a pair of water-soluble monomers (N,N’methylenebis(acrylamide/glycidyl methacrylate)) are polymerized in the presence of the beads, resulting in the formation of a polymer film anchored to the bead by what had been the surface carbon-carbon double bonds. This approach to stabilizing an EXC material initially showed some promising results, but it was subsequently found that the polymer film decomposes upon contact with acids to release formaldehyde. Up until now, the performance of EXC materials based on functionalized supports has not been shown to be sufficiently better than that of analogous “inert substrate” resins to represent a compelling advantage over conventional ones.

Another limitation of EXC materials, capacity, can in principle, also be improved by utilizing the property of the solid supports. Because of the ability of available solid supports to hold and retain an extractant is limited and because extractants are frequently diluted with an organic solvent to improve the kinetics of metal ion uptake (by reducing the stationary phase viscosity), the capacity (*i.e.*, the maximum loading of metal ion available) of conventional EXC materials is typically low, often only a few mg per mL of bed volume. As a result, in many applications, inconveniently large columns may be required to avoid extractant saturation (*i.e*., column overload). To overcome this problem, higher capacity of EXC materials are clearly required. Previous work indicates that polymer microencapsulation techniques may yield materials containing much more extractant per unit mass than is found in any conventional material (1.88-1.89). In one study, for example, applying a modified dry impregnation technique (described below) yielded microcapsules containing up to 11.8 mL solvent per gram of (polysulfone) capsules (1.88). This enormous capacity for solvents clearly opens up the possibility of producing very high capacity (*i.e*., high extractant content) EXC materials.

The separation of ions of similar charge and comparable size (e.g., actinides vs. lanthanides, americium vs. curium) remains a challenge and very few works describing the application of EXC materials to these separations have been reported in the literature (1.90-1.92). The major limitation of the existing chromatographic materials is the significant band broadening of the elution curves (1.93, 1.94), indicative of the poor efficiency typical of the extraction chromatographic materials. Column efficiency, typically expressed in terms of height equivalent of theoretical plate (HETP) or number of theoretical plates (N), is a complex function of a number of system characteristics, including mobile phase velocity, diffusion coefficients of the metal ion in the mobile and stationary phases, particle diameter, temperature, kinetics of extraction and stationary phase thickness (1.21). Of these factors, diffusion is the critical one, and obviously the diffusion of a metal ion into and out of the deep pores of a chromatographic resin takes more time than the same process for shallow pores. Thus by designing support materials that contain predominantly shallow pores, the problem of poor efficiency can be at least partly addressed.

If the limitations of current EXC materials can be addressed, either through the use of "active substrate" supports or manipulation of the physical properties of a more conventional support, then the utility of extraction chromatography as a method for the separation and preconcentration of metal ions is certain to increase.

1.4 Overview of the Chapters

Chapter 2 describes an evaluation of solid-supported ionic liquids containing crown ethers as media for metal ion separation and preconcentration. In this study an effort has been made to extend the extraordinary performance of ILs in the liquid-liquid extraction of strontium using crown ethers to extraction chromatographic configuration. The results demonstrate that the translation of the solvent extraction properties of an IL to extraction chromatography is not always straightforward.

Chapter 3 explores the effect of solid support properties on the performance of extraction chromatographic materials. Specifically, extractant chromatographic materials based on silica sol-gel encapsulated extractants have been synthesized and characterized. A silica network is shown to be capable of encapsulating up to ~50% DtBuCH18C6 (w/w). Optimized silica-based extraction chromatographic materials show better radiostrontium uptake than a conventional Sr-resin, along with other characteristics suggesting that this sol-gel-based EXC material may represent a viable alternative to conventional Sr-resin.

Chapter 4 describes efforts to develop high-efficiency extraction chromatographic materials using stagnant pore plugging. In this work, beads of a commercial porous polymer were filled with polypropylene glycol. Following removal of the peripheral filler, the support was impregnated with extractant, yielding an EXC material exhibiting high column efficiency vs. conventional EXC resins.

Chapter 5 demonstrates the development of high capacity extraction chromatographic materials based on polysulfone capsules for metal ion separation and preconcentration. Polysulfone capsules in the 50-100 μm size range (desirable for EXC) have been synthesized. Extractant loading studies of these capsules have shown that they can retain up to ~65% (w/w) extractant, is a significant improvement over conventional EXC materials.

Finally, Chapter 6 offers a summary of the accomplishments of this study and recommendations for future research in this field.

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CHAPTER 2:

EVALUATION OF SOLID-SUPPORTED ROOM-TEMPERATURE IONIC LIQUIDS CONTAINING CROWN ETHERS AS MEDIA FOR METAL ION SEPARATION AND PRECONCENTRATION

2.1 Introduction

The retention of metal ions on many EXC materials is at times insufficient, even in the absence of competing ions that might be expected to consume a significant fraction of the sorption sites on the material. For example, although an EXC resin selective for radiostrontium (2.1-2.3) has long been commercially available, its modest strontium retention makes it poorly suited for large-volume samples and complicates efforts to miniaturize chromatographic separations employing it.

Prior work has shown that metal ion extraction by crown ethers such as that on which the commercial strontium resin is based (di-*tert*-butylcyclohexano-18-crown-6, hereafter abbreviated as DtBuCH18C6) is strongly influenced by the organic solvent in which the extractant is dissolved (2.4, 2.5). For example, strontium extraction into a solution of dicyclohexano-18-crown-6 (DCH18C6) (and by analogy, its retention on a crown ether-based EXC resin (2.1, 2.6)) has been found to increase as the molecular weight of the solvent is decreased within a given diluent family (*e.g.*, *n*-alcohols), the apparent result of the greater solubility of water in lower molecular weight solvents and the accompanying increase in the ease of solvating the co-extracted anion (2.4). As a compromise between the need to maximize strontium retention and to minimize the loss of the stationary phase (*i.e*, the crown ether/diluent) due to its solubilization in the mobile phase during a separation, 1-octanol is employed as the stationary phase solvent in the commercial resin (2.1, 2.2). Recent work suggests that better results, in particular far stronger retention of strontium, might be achieved by employing ionic liquids (ILs), a novel class of solvents typically comprising a bulky, asymmetric organic cation in combination with any of a wide variety of organic or inorganic anions (2.7), as the basis of the stationary phase. Specifically, various studies have shown that under certain conditions, metal ion partitioning far exceeding that seen with conventional (*i.e.*, molecular) solvents can be obtained in liquid-liquid systems employing solutions of an appropriate extractant in any of a variety of ILs (2.8-2.10). For example, using solutions of DCH18C6 in *N,N'*-dialkylimidazolium-based ILs, Dai *et al.* (2.8) have demonstrated that strontium distribution ratios 10^4 times larger than those observed in 1-octanol can be obtained. This suggests that an EXC resin employing an appropriate IL as a component of the stationary phase may provide strontium ion retention significantly greater than that obtained with conventional EXC resins.

In the past decade, a number of metal ion sorbents have been described which comprise an ionic liquid dispersed in/on a solid support (2.11-2.21). Much less common are sorbents in which an ionic liquid is employed as the diluent for a supported metal ion extractant (2.22-2.26). In this chapter, we describe the preparation and preliminary characterization of a series of strontium sorbents incorporating a mixture of a crown ether and various *N,N'*-dialkylimidazolium-based ILs, supported in either a porous polymer matrix (as is often done in extraction chromatography) or a sol-gel glass. Unexpectedly the results obtained indicate that the performance (*e.g.*, strontium retention) of these new sorbents is not necessarily superior to that of the conventional (*i.e.*, commercial) EXC resin.

2.2 Experimental

2.2.1 Materials and Methods

Reagents. Dicyclohexano-18-crown-6 (DCH18C6) was obtained as a mixture of the *cis*-*syn*-*cis* (A) and *cis*-*anti*-*cis* (B) isomers from Parish Chemical Company (Orem, UT). The 4,4'(5')-di-(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6) was obtained from EichroM Technologies, Inc. (Darian, IL) and used without further purification. Amberchrom^{TM} CG-71m was purchased from Rohm and Haas (Philadelphia, PA) and pretreated as previously described (2.27). The tetramethyl orthosilicate (TMOS) and 1-octanol were obtained from Alfa Aesar (Heysham, UK), while the formic acid (98%) was obtained from Sigma-Aldrich (St. Louis, MO). All were used as received. Optima™ grade nitric acid and HPLC grade methanol were obtained from Fisher Scientific Company (Waltham, MA). All water was obtained from a Milli-Q2 system and had a specific resistance of at least 18 MΩ-cm. The ionic liquids employed in this work, 1-decyl-3-methylimidazolium *bis*[(trifluoromethyl)sulfonyl]imide ($C_{10}C_1imTf_2N$) and 1-(12-hydroxydodecyl)-3-butylimidazolium *bis*[(trifluoromethyl)sulfonyl]imide ($C_{12}OHbimTf_2N$), were prepared by reaction of the corresponding bromides with $LiTf_2N$ and purified using methods described previously (2.7, 2.28, 2.29). Sample purity was verified by ^{1}H- and ^{13}C-NMR (DMSO), as detailed in previous reports (2.7, 2.28, 2.29). The NMR spectra were acquired on a Bruker DPX300 NMR spectrometer operating at 300.13 MHz for proton and 75.47 MHz for carbon-13, and equipped with a z-gradient broadband (BBO) probe. Spectra were obtained using solutions in dimethylsulfoxide-d_6 (Aldrich, 99.96 atom% D), and all chemical shifts were reported relative to tetramethylsilane.

2.2.2 Procedures

2.2.2.1 Liquid-liquid extraction studies

The distribution of a Sr-85 radiotracer (PerkinElmer, Shelton, CT) between the aqueous and organic phases of interest was determined by equilibrating equal volumes of a tracer-spiked nitric acid solution and either 1-octanol or an ionic liquid. Prior to the distribution measurement, the organic phase was pre-equilibrated *via* two contacts with twice its volume of an appropriate acid solution. From the measured activity of the aqueous and organic phases after equilibration (determined by gamma spectroscopy according to standard procedures on a Perkin-Elmer 2480 Automatic Gamma Counter), the distribution ratio of strontium was calculated from the equation:

$$D_{Sr} = [Sr]_{org,\ eq} / [Sr]_{aq,\ eq}$$

2.2.2.2 Polymer-supported IL-crown ether mixtures

The EXC resins comprising polymer-supported IL-crown ether mixtures were prepared in a manner analogous to that described previously for mixtures of crown ethers and conventional organic solvents (2.1, 2.2).

2.2.2.3 Sol-gel-encapsulated IL-crown ether mixtures

To synthesize the silica-based EXC materials, an acid-catalyzed sol-gel procedure was employed (2.30). In a typical preparation, DtBuCH18C6 (50 mg) was dispersed into a mixture of TMOS (1 mL) and formic acid (2 mL). This route yielded a “solvent-less” (*i.e.*, no diluent added) sorbent. To determine the impact of the presence of a solvent, the same route for preparation was followed, but neat DtBuCH18C6 was replaced with a 1M solution of the crown ether in either the IL or 1-octanol. For all preparations, the quantity of DtBuCH18C6 used was maintained at 50 mg. After a week of standing, during which time gelation and the volatilization of hydrolysis products (CH_3OH and $HCOOCH_3$) occurred, a monolithic glass composite consisting of DtBuCH18C6 or its solution in the IL or 1-octanol entrapped in the silica network (2.31) was obtained. The composite glass material was crushed and sieved to collect material of the desired size range (~50-100 μm diameter) for subsequent metal ion uptake experiments. Following sieving, the ground material was examined by scanning electron microscopy using a Hitachi Model S-4800 field emission SEM.

2.2.2.4 Equilibrium metal ion uptake

Solid-liquid (weight) distribution ratios (D_w) for strontium were determined radiometrically using a commercial ^{85}Sr radiotracer. Specifically, the sorption of the tracer from nitric acid solutions by the resins was measured by contacting a known volume (typically 1.0 mL) of ^{85}Sr-spiked acid solution of appropriate concentration with a known mass of resin. The ratio of the aqueous phase volume (mL) to the weight of the chromatographic material (g) typically ranged from 40-50. (This ratio is determined primarily by the need to produce an easily measured decrease in the aqueous activity by contact with the resin). Contact times of two and four hours (with occasional swirling) were employed for the polymeric and silica-based EXC materials, respectively. After equilibration, an aliquot of the aqueous phase was withdrawn from each culture tube and filtered through a 0.22 μm poly(vinylidene fluoride) (PVDF) filter to ensure that no dispersed resin was present. On the basis of the initial and final activity of a measured aliquot of this aqueous phase, the weight distribution ratio (D_w) of strontium was calculated from the following equation:

$$D_w = [(A_0 - A_f)/A_f]\ (V/w)$$

where A_0 and A_f represent the aqueous phase activity (cpm) before and after equilibration respectively, w is the mass of the resin taken (g), and V is the volume of the aqueous phase (mL).

2.2.2.5 Metal ion uptake kinetics

Into a series of screw-cap test tubes, each containing the same (± 10%) amount (20 mg) of EXC resin, was introduced a known volume (typically 1 mL) of an appropriate nitric acid solution containing a Sr-85 radiotracer. At various time intervals following the introduction of the tracer solution (during which the samples were periodically mixed to ensure equilibration), the aqueous phase was withdrawn from one of the test tubes and filtered through a 0.22 μm poly(vinylidene fluoride) (PVDF) filter. From the initial and final (residual) activity of the aqueous phases, D_w values were determined as described above and a plot of the time dependence of D_w was prepared.

2.3 Results and Discussion

2.3.1 Liquid-liquid extraction studies.

In an earlier report, Horwitz and Dietz (2.32) examined the relationship between the efficiency with which a given metal ion is extracted in a liquid-liquid (l-l) system (as reflected in the metal ion distribution ratio, D_M) and its retention on an extraction chromatographic sorbent based on this l-l system (as reflected in the weight distribution ratio, D_w for the ion). For lanthanide (Ln) extraction by several organophosphorus acids, it was found that despite some differences between the observed and expected (on the basis of D_M) values of k' (*i.e.*, the capacity factor) for the Ln ions, the overall trends (*e.g.*, decreasing metal ion affinity for the organic phase with rising acidity) were generally the same in both the l-l and EXC systems. On the basis of this and similar observations by a number of other investigators on a variety of extraction systems (2.33-2.40), it is now well-established that the extraction behavior of a metal ion is often a useful predictor of its retention behavior on the corresponding EXC resin. For this reason, efforts to develop an ionic liquid-based EXC material for strontium began with a consideration of the extraction behavior of strontium into a series of ILs incorporating DCH18C6 or its di-*tert*-butyl- analog, compounds known to exhibit substantial affinity for Sr^{2+} in conventional solvent systems (2.41-2.43).

Figure 2.1 shows the nitric acid dependency of the extraction of strontium ion by DCH18C6 into two ionic liquids, one alkyl-substituted ($C_{10}C_1imTf_2N$) and the other hydroxyl-functionalized ($C_{12}OHC_4imTf_2N$). Also shown for purposes of comparison are the results obtained under the same conditions using a conventional molecular diluent, 1-octanol, as the organic solvent. In addition, the corresponding results for Na^+ extraction into both 1-octanol and $C_{10}C_1imTf_2N$ are provided. As can be seen, extraction into the molecular diluent follows the expected trend (2.45), namely (generally) increasing extraction efficiency (D_M) with rising aqueous acid (*i.e.*, nitrate) concentration. Note that at sufficiently high acidities, competition for the extractant between the acid present and the metal ion (2.45) eventually leads to a rollover of the acid dependency for sodium ion. The net result is an increase in the strontium/sodium separation factor, $\alpha_{Sr/Na}$, with acidity.

For the ionic liquids also, strontium extraction generally rises with increasing aqueous acidity, indicating (as noted in prior studies (2.10)) that ion-pair extraction/extraction of a neutral strontium-crown ether-nitrato complex is the predominant mode of extraction under the experimental conditions. In contrast, the extraction of sodium ion into $C_{10}C_1imTf_2N$ declines over the entire range of acidities examined, behavior consistent with the predominance of ion-exchange in the overall extraction process (2.10, 2.46). In this extraction system too then, $\alpha_{Sr/Na}$ varies with acidity, in this case peaking at *ca*. 3 M HNO_3 (the acidity most commonly employed for sample loading in procedures incorporating commercial resins for strontium sorption) at a value *ca*. 64, approximately three times that obtained in 1-octanol (2.47). These results, together with the higher values of D_{Sr} observed in the 1-3 M HNO_3 range, suggest that it should be possible to significantly improve the performance of established commercial strontium sorbents simply by replacing the diluent employed (1-octanol) with an appropriate ionic liquid.

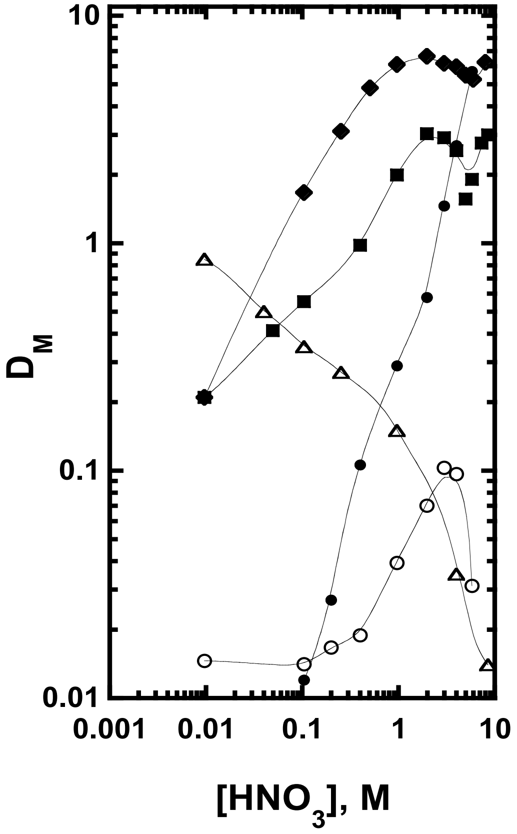

Figure 2.1: Effect of nitric acid concentration on the extraction of Sr^{2+} into 1-octanol (●),$C_{10}C_1imTf_2N$ (■), or $C_{12}OHbimTf_2N$ (♦) and Na^+ into 1-octanol (○) or $C_{10}C_1imTf_2N$ (△) by DCH18C6 (0.1 M). (The smooth curves are intended only as a guide to the eye.) (2.69)

Because the not insignificant water solubility of DCH18C6 (2.48) would be expected to make an EXC material prepared from it unstable, its more hydrophobic di-*tert*-butyl-substituted analog, DtBuCH18C6, was next evaluated. Figure 2.2 depicts the nitric acid dependency of D_{Sr} for this compound, again in 1-octanol, $C_{10}C_1imTf_2N$, and $C_{12}OHC_4imTf_2N$, along with analogous results for sodium ion in 1-octanol and $C_{10}C_1imTf_2N$. In the conventional molecular diluent (*i.e.*, 1-octanol), the dependency for both Sr and Na extraction generally exhibits the increase with rising acidity expected for neutral complex extraction, and the Sr/Na separation factor ($\alpha_{Sr/Na}$) approaches 100 at the highest acidities (*ca*. 6 M). For the ionic liquids, D_{Sr} again generally increases with aqueous acidity, although some flattening or rollover of the dependency is observed above *ca*. 2 M HNO_3. At acidities greater than *ca*. 0.25 M, the value of D_{Sr} is typically a factor of 5-10 greater than that obtained with DCH18C6, as would be expected from the greater hydrophobicity of the di-*t*-butyl-substituted compound. Equally important is that strontium-sodium separation factors of 50-100 are observed in $C_{10}C_1imTf_2N$ for 1-6 M HNO_3. Overall then, the use of the more hydrophobic crown ether yields strontium extraction efficiencies significantly higher than those seen with DCH18C6, while preserving its excellent strontium extraction selectivity. In addition, when combined with an IL, DtBuCH18C6 provides D_{Sr} values much greater than those seen with 1-octanol. Taken together, these results further reinforce the notion that a substantial improvement in the performance of an EXC material for strontium might be effected by use of an ionic liquid diluent.

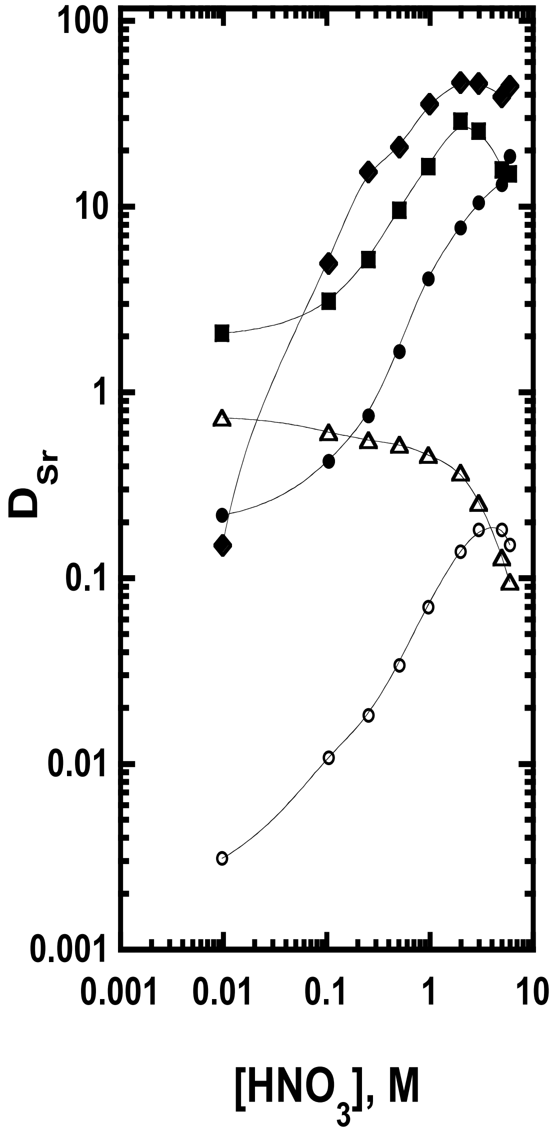

Figure 2.2: Effect of nitric acid concentration on the extraction of Sr^{2+} into 1-octanol (●), $C_{10}C_1imTf_2N$ (■), or $C_{12}OHbimTf_2N$ (♦) and Na^+ into 1-octanol (○) or $C_{10}C_1imTf_2N$ (△) by 4z, 5'z-csc-DtBuCH18C6 (0.1 M). (The smooth curves are intended only as a guide to the eye.) (2.69)

2.3.2 Metal ion uptake studies on polymer-supported crown ether-ionic liquid mixtures

To investigate this possibility, extraction chromatographic resins incorporating 40% (w/w) of a 1.0 M solution of DtBuCH18C6 in 1-octanol, $C_{10}C_1imTf_2N$ or $C_{12}OHC_4imTf_2N$ were prepared and evaluated for strontium uptake. Figure 2.3 shows the nitric acid dependence of strontium uptake (as reflected in the weight distribution ratio, D_w) by the three resins. It is immediately apparent that contrary to expectations, the IL-based resins actually provide *poorer* retention of Sr^{2+} than does the conventional (*i.e.*, commercial) octanol-based material in the acidity range of interest (*ca*. 1-6 M). In addition, and again contrary to results observed in the l-l extraction studies, there is little difference between strontium retention by materials based on the dialkyl- and hydroxyalkyl-ILs. Thus in contrast to the conventional solvent system (*i.e.*, 1-octanol), for which it has been shown that solvent extraction and extraction chromatographic behavior are reasonably well correlated (2.1, 2.2, 2.44), l-l extraction data for the ionic liquids considered here are of little apparent value in predicting the behavior of the EXC resins prepared from them.

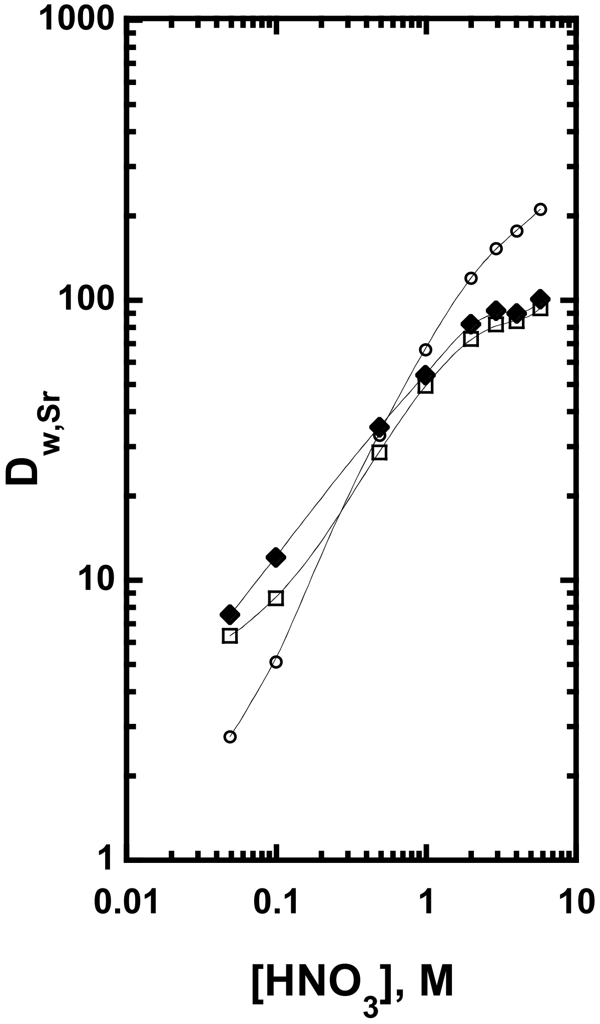

Figure 2.3: Effect of nitric acid concentration on the uptake of strontium ion by extraction chromatographic resins comprising a solution of DtBuCH18C6 (1 M) in 1-octanol (○), $C_{10}C_1imTf_2N$ (☐), or $C_{12}OHbimTf_2N$ (♦) on Amberlite XAD-7. (The smooth curves are intended only as a guide to the eye.)

2.3.3 Effects of stationary phase viscosity

In principle, if the partitioning mechanism for a metal ion in a liquid-liquid extraction system and the corresponding extraction chromatographic resin are the same, then the adaptation of the solvent extraction system to a solid support should be straightforward (2.49). There are, however, several additional issues that must be considered when attempting to understand the relationship between the behavior of the two systems for the ILs, among them the effect of solvent viscosity. According to the Stokes-Einstein Equation, the diffusion coefficient of a solute in a medium is inversely proportional to the viscosity of the medium:

$$D = k_B T / 6\pi \eta r$$

where D is the diffusion coefficient of a spherical particle, k_B is Boltzmann's constant, T is the absolute temperature, η is the viscosity, and r is the radius of the particle (2.50). As applied to extraction chromatography, this equation indicates that the rate of diffusion of a solute (*e.g.*, strontium ion) into the pores of the EXC resin beads will be reduced as the viscosity of the solution with which the resin has been impregnated increases. In addition, it suggests that the accessibility of extractant molecules within the pores of a support may be limited when the viscosity of the stationary phase is high. That is, for a solute to interact with an extractant, a path for solute/extractant transport must be provided. If providing such a path requires that relatively large IL molecules rotate or translate, however, the high viscosity of the medium could render this difficult, thus restricting the availability of the extractant to the solute. For 1-octanol, a viscosity of 7.2 cP has been reported at standard temperature and pressure (2.51), while for typical ionic liquids, viscosities of 300-1000 cP are observed under the same conditions (2.52). Clearly then the differences in viscosity of the two solvents are substantial, and thus may at least partially account for the observations.

2.3.4 Extractant concentration effects

The effect of extractant concentration must also be considered. That is, while the solvent extraction experiments described here were carried out using a 0.1 M solution of DtBuCH18C6, the stationary phase of the EXC resin comprises a 1 M solution of the same extractant, a factor of ten more concentrated. Table 2.1 summarizes the results of l-l extraction experiments in which the dependence of the distribution ratio of strontium on the concentration of DtBuCH18C6 in either $C_{10}C_1imTf_2N$ or 1-octanol was determined.

Table 2.1: Effect of DtBuCH18C6 concentration in 1-octanol or $C_{10}C_1imTf_2N$ on the extraction of strontium ion from 1.0 M nitric acid solution. (2.69)

1-octanol

[DtBuCH18C6], M	mole ratio (1-OAlc:crown)	D_{Sr}
0.25	22	8.7
0.50	9.4	15.1
0.75	5.4	19.4
1.00	3.1	26.5

$C_{10}C_1imTf_2N$

[DtBuCH18C6], M	mole ratio (IL:crown)	D_{Sr}
0.25	8.0	25.1
0.40		34.5
0.50	3.5	43.2
0.60		47.9
0.75		33.1
1.00	1.2	- [a]

---

[a] Precipitation of the crown ether is observed.

As can be seen, in the conventional solvent, an increase in extractant concentration is accompanied by a (roughly) proportional increase in the value of D_{Sr}. (A log-log plot of D_{Sr} *vs*. [DtBuCH18C6], in fact, yields a line of near-unit slope (0.78).) As also shown in the table, this increase in extractant concentration is (obviously) also accompanied by a decrease in the mole ratio of solvent to extractant. Even at the highest DtBuCH18C6 concentration, however, a significant excess of the solvent remains. For the ionic liquid, however, neither of these observations applies. That is, as the extractant concentration is increased, D_{Sr} initially increases, but then declines. Moreover, in the most concentrated DtBuCH18C6 solutions, the very high molar mass of the ionic liquid means that the solvent-to-extractant mole ratio is quite low (falling to only 1.2 at 1 M extractant). Thus, in these solutions, the system is rapidly approaching one in which the ionic liquid is no longer the majority component. This dearth of solvent apparently has a destabilizing effect, as upon standing in contact with an acidic aqueous phase, the crown ether precipitates from the most concentrated solutions, thus limiting the solubility of DtBuCH18C6 to *ca.* 0.6 M. This strongly suggests that precipitation of the extractant in the pores of the support may be at least partly responsible for the unexpectedly poor performance of the IL-based EXC resins.

It is interesting (and also somewhat unexpected) to note that precipitation of the extractant from the hydroxyl-functionalized IL $C_{12}OHC_4imTf_2N$ (which by design, bears resemblance to an aliphatic alcohol) occurs to essentially the same extent observed for $C_{10}C_1imTf_2N$ (albeit more slowly) when the solution is allowed to stand in contact with an acidic aqueous phase (*e.g.*, 1 M HNO_3). That acid contact induces precipitation in this system as well indicates that formation of an insoluble crown ether-hydronium ion adduct is likely responsible. Such precipitation is not without precedent; in fact, the precipitation of a DtBuCH18C6-H_3O^+ adduct from *n*-hexane (induced by perchloric acid contact) has been employed as a means of purifying DtBuCH18C6 (2.53). Moreover, although seemingly vastly different than hexane, ionic liquids bearing long alkyl chains (as is the case for both ILs considered here) have been found to form nanostructured domains in which the polar head groups and hydrophobic side chains are arranged in such a way as to provide regions differing greatly in polarity (2.54-2.56). Here the hydrophobic domains would likely resemble a long-chain alkane, not unlike hexane.

It is also worth noting here that over a short time frame (*i.e.*, minutes to hours), solutions of DtBuCH18C6 in $C_{10}C_1imTf_2N$ more concentrated than its apparent equilibrium solubility can be prepared and studied. As shown in Table 2.1, for example, strontium distribution ratios can be measured for even a 0.75 M solution of DtBuCH18C6 with no sign of precipitation over the time span of the measurement. Curiously, however, D_{Sr} values at these higher concentrations are *lower* than those observed at lesser crown ether concentrations. In fact, the extraction of strontium by a 0.75 M solution of the crown ether is essentially identical to that seen at 0.40 M extractant. In an effort to understand the source of this anomaly, the extraction of strontium by DCH18C6 (which is not plagued by such solubility limitations) into the same IL was revisited. Figure 2.4 (a) shows the dependence of D_{Sr} and D_{Na} on the concentration of DCH18C6 in $C_{10}C_1imTf_2N$ at a fixed aqueous acidity (3.00 M HNO_3).

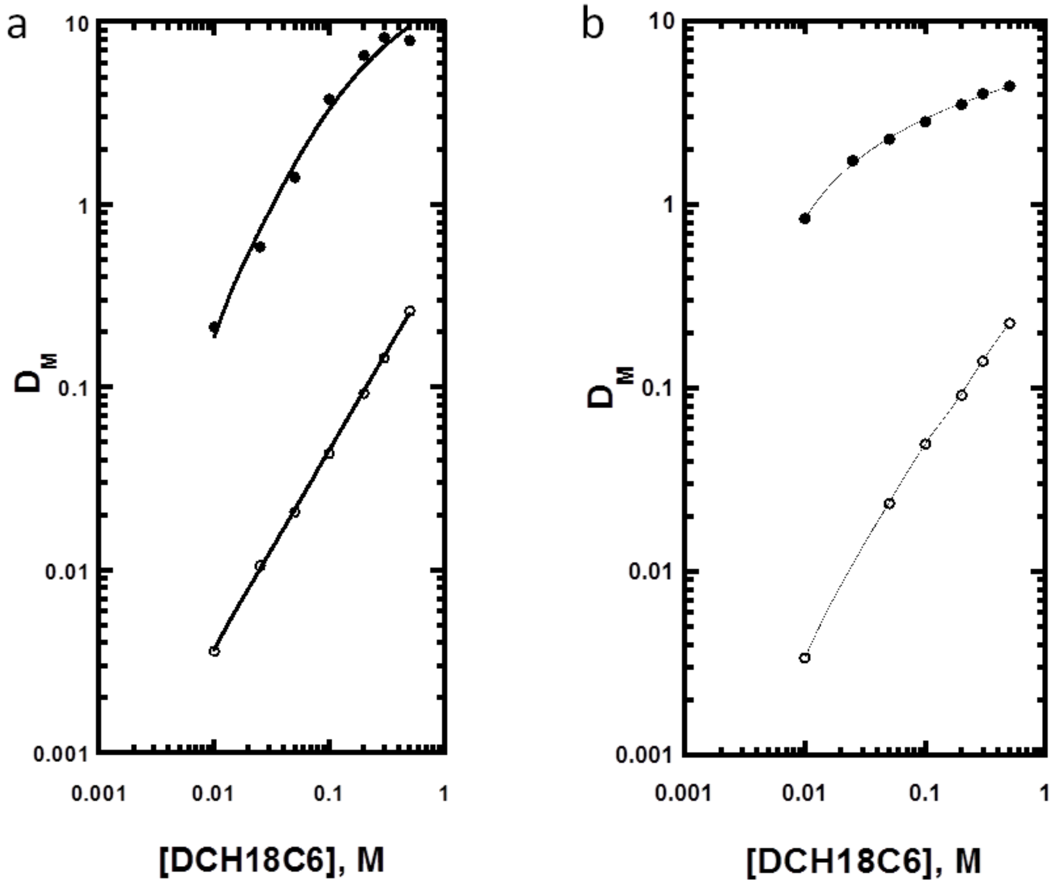

Figure 2.4. Effect of DCH18C6 concentration on the extraction of strontium (●) and sodium (○) ions from 3.0 M nitric acid into $C_{10}C_1imTf_2N$ (panel A) or 1-octanol (panel B). (Lines represent least-squares fits to the data.) (2.69)

For purposes of comparison, the corresponding results for 1-octanol are provided in Figure 2.4 (b). As can be seen, in the conventional solvent, D_M for the monovalent cation (*i.e.*, Na^+) increases linearly with rising extractant concentration, an observation consistent with extraction of a neutral sodium nitrato-crown ether complex, a process depicted in Equation 2.1 (with n=1):

$$M^{n+}_{aq} + DCH18C6_{org} + n\ NO_3^-{}_{aq} \leftrightarrow M(NO_3)_n{\cdot}DCH18C6_{org} \qquad (2.1)$$

For the divalent cation (*i.e.*, Sr^{2+}), in contrast, significant flattening of the dependency is observed (although D_{Sr} values do continue to increase with [DCH18C6]), a consequence (as has been described in detail previously (2.45)) of appreciable aqueous phase complex formation in the strontium-DCH18C6 system.

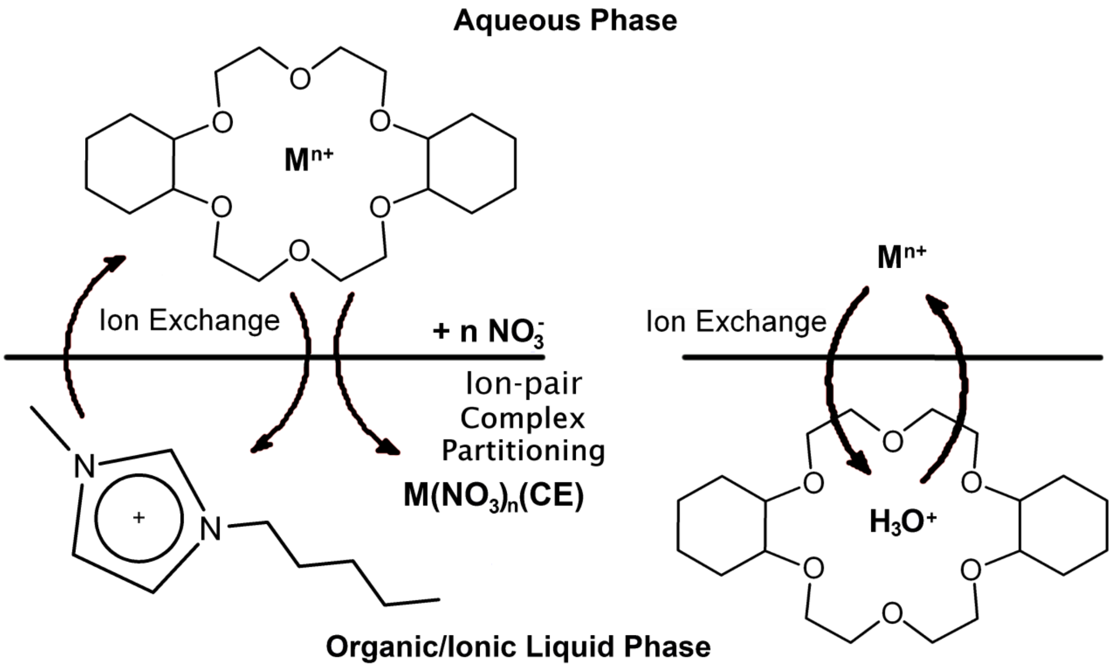

Figure 2.5: The three-path model for alkali and alkaline earth cation partitioning between nitric acid solutions and $C_nC_1imTf_2N$ ionic liquids in the presence of DCH18C6.

For the extraction of sodium into the IL, increasing DCH18C6 concentration again yields a proportional increase in D_M. In this instance, however, extraction proceeds predominantly *via* two types of ion-exchange processes (Figure 2.5), one in which the sodium-crown ether complex initially formed is exchanged for the cationic component of the IL, and the other a two-step process involving the initial formation of a 1:1 hydronium ion-DCH18C6 complex and the subsequent exchange of the complexed H_3O^+ for Na^+ (2.46), as depicted in Equations 2.2 and 2.3:

$$H_3O^+_{aq} + DCH18C6_{IL} \leftrightarrow DCH18C6 \cdot H_3O^+_{IL} \quad (2.2)$$

$$Na^+_{aq} + DCH18C6 \cdot H_3O^+_{IL} \leftrightarrow DCH18C6 \cdot Na^+_{IL} + H_3O^+_{aq} \quad (2.3)$$

Here, increasing the DCH18C6 concentration promotes formation of additional hydronium ion-crown ether complex, which can then undergo ion exchange (IX) with the sodium ion present.

For strontium extraction into the IL, the values of D_M eventually begin to decline (albeit slightly) as the extractant concentration rises. This decline becomes even more evident as the aqueous acidity is decreased (Figure 2.6). These observations can be explained by recognizing that under the experimental conditions, a not insignificant contribution to the overall extraction of strontium is made by so-called "crown ether-mediated ion exchange" (2.46, 2.47), analogous to the process shown for sodium ion extraction above. In this instance, however, the initial formation of the 1:1 hydronium ion-crown ether complex is followed by a process in which *two* molecules of this adduct react with the metal ion, as necessitated by the electroneutrality requirement:

$$Sr^{2+}_{aq} + 2\ DCH18C6{\cdot}H_3O^+_{IL} \leftrightarrow DCH18C6{\cdot}Sr^{2+}_{IL} + 2\ H_3O^+_{aq} + DCH18C6_{IL} \quad (2.4)$$

Clearly a process such as this, which results in the production of free DCH18C6 molecules, would not be expected to be favored by increasing concentrations of extractant in the IL phase. Thus, as the initial concentration of the free crown ether in the IL phase is increased, the propensity to extract a divalent cation by crown ether-mediated IX is likely to diminish. The result, apparently, can be a decline in D_M with increasing extractant concentration.

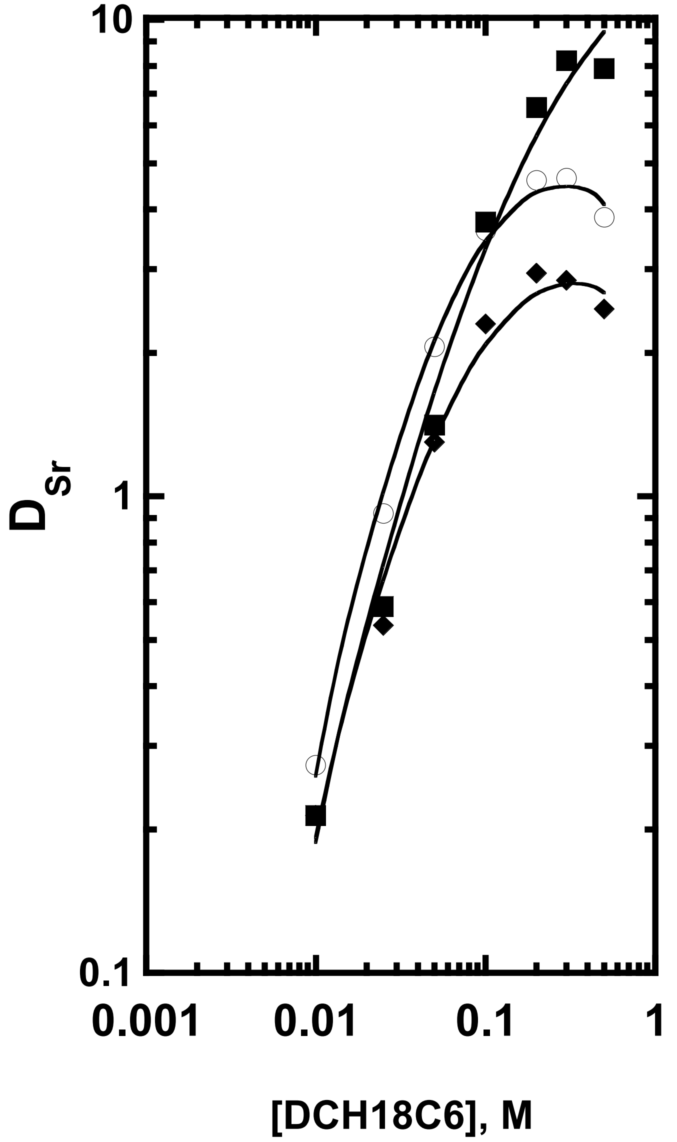

Figure 2.6. Effect of DCH18C6 concentration on the extraction of Sr^{2+} from 0.050 M HNO_3 (♦) 1.0 M HNO_3 (○) and 3.0 M HNO_3 (■) into $C_{10}C_1imTf_2N$. (The smooth curves are intended only as a guide to the eye.) (2.69)

2.3.5 Sorption capacity studies

An obvious solution to the problem of extractant precipitation is to reduce its concentration in the IL. Such a reduction, however, would also lower the strontium sorption capacity relative to that of the commercial resin. If, for example, the concentration of DtBuCH18C6 in the IL were reduced to its solubility limit (*ca*. 0.6 M), a 21% decline in the capacity *vs*. that of a 1-octanol-based sorbent (from 4.74 to 3.74 mg/mL of bed) would be expected. Capacity determinations on the $C_{10}C_1imTf_2N$-based and conventional sorbents, however, yield an even greater difference between the actual capacities of the two materials. That is, while the measured capacity of the commercial resin is (in agreement with a prior report (2.2)) 74% of the theoretical value (3.51 mg/mL), that of the IL-based resin is only 1.78 mg/mL, 57% of its theoretical value. Given that precipitation of the crown ether is not expected at this concentration, lower accessibility of the pore volume of the sorbent due to the high stationary phase viscosity is a likely contributor to the lower than anticipated capacity.

2.3.6 Sol-gel encapsulated crown ether-ionic liquid mixtures

That the properties of the support can exert an influence on the behavior of an extraction chromatographic material is by now well-established (2.57). In 1977, for example, Parrish (2.57) showed that the rate of copper (II) uptake by the extractant Kelex 100 supported on any of a variety of macroporous polymers (*e.g.*, XAD-series resins) was affected by the water regain (*i.e.*, hydrophobicity) of the support, with more hydrophilic materials yielding faster copper ion uptake under a given set of conditions. Subsequent work by other investigators (2.38, 2.58-2.62) has confirmed the often significant influence of support characteristics on the chromatographic performance of EXC resins. Such results suggest that it may be possible to at least partly overcome the apparent limitations of the polymer-supported crown ether-IL system by appropriate choice of support. Recent work by Makote and Dai (2.30) concerning the properties of ionic liquid-crown ether mixtures encapsulated in sol-gel glasses lends additional credence to this notion. In particular, these investigators demonstrated that while a DCH18C6-impregnated sol-gel glass exhibited only limited uptake of strontium ($D_w = 0.5$) from a pH 4 aqueous phase when the crown ether employed was neat (*i.e.*, undiluted), addition of the ionic liquid 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)-sulfonyl]imide ($C_2C_1imTf_2N$) resulted in a dramatic (*i.e.*, thousand-fold) increase in strontium retention under the same conditions. This suggests that a sol-gel glass matrix may be especially well-suited as the basis for metal ion sorbents employing crown ether-ionic liquid mixtures.

With this in mind, sol-gel glasses (Figure 2.7) incorporating either undiluted DtBuCH18C6 or its solution (1 M) in $C_{10}C_1imTf_2N$ were prepared and characterized. For purposes of comparison, a third material incorporating a solution of the crown ether (1 M) in 1-octanol was also examined. Figure 2.8 depicts the nitric acid dependence of strontium uptake (as reflected in the weight distribution ratio, D_w) by these sorbents. As shown, in contrast to the results obtained by Makote (2.30) for DCH18C6, the sorbent incorporating only DtBuCH18C6 displays significant retention of radiostrontium, yielding a D_w of nearly 80 at the highest acidities examined. Similar strontium ion retention behavior is seen for the sorbent incorporating a solution of DtBuCH18C6 in 1-octanol (although a rollover in the acid dependency is seen at sufficiently high aqueous acidities). This observation is consistent with previous results for polymer-based EXC resins, for which little effect on strontium ion retention by a crown ether-loaded support was noted upon introduction of 1-octanol (2.63). Again in contrast to the results of Makote (2.30), however, much the same strontium ion uptake is observed for the sorbent incorporating a solution of the crown ether in the ionic liquid.

Figure 2.9 shows the results of strontium ion uptake kinetics measurements for a sol-gel glass incorporating either neat (*i.e.,* undiluted) DtBuCH18C6 or its solution (1 M) in 1-octanol or $C_{10}C_1imTf_2N$. For the sol-gel-based materials, equilibration times exceeding two hours are observed, consistent with prior reports for sol-gel glasses incorporating a tetracarboxylic acid-functionalized aza-crown ether (2.64) or a thiacrown ether (2.65), for which equilibration times of up to 24 hours have been found. This observation may also be explained by the relatively smaller pore size of the silica materials (2.66), as suggested by the SEM images of the surface of the material (Figure 2.7). For the XAD-based sorbents, however, published reports indicate that strontium uptake for both the "solvent-less" (2.63) and conventional (2.1, 2.2) resin is typically complete in 40 minutes or less, with the former exhibiting slightly slower uptake, a result consistent with the higher viscosity of the undiluted extractant.

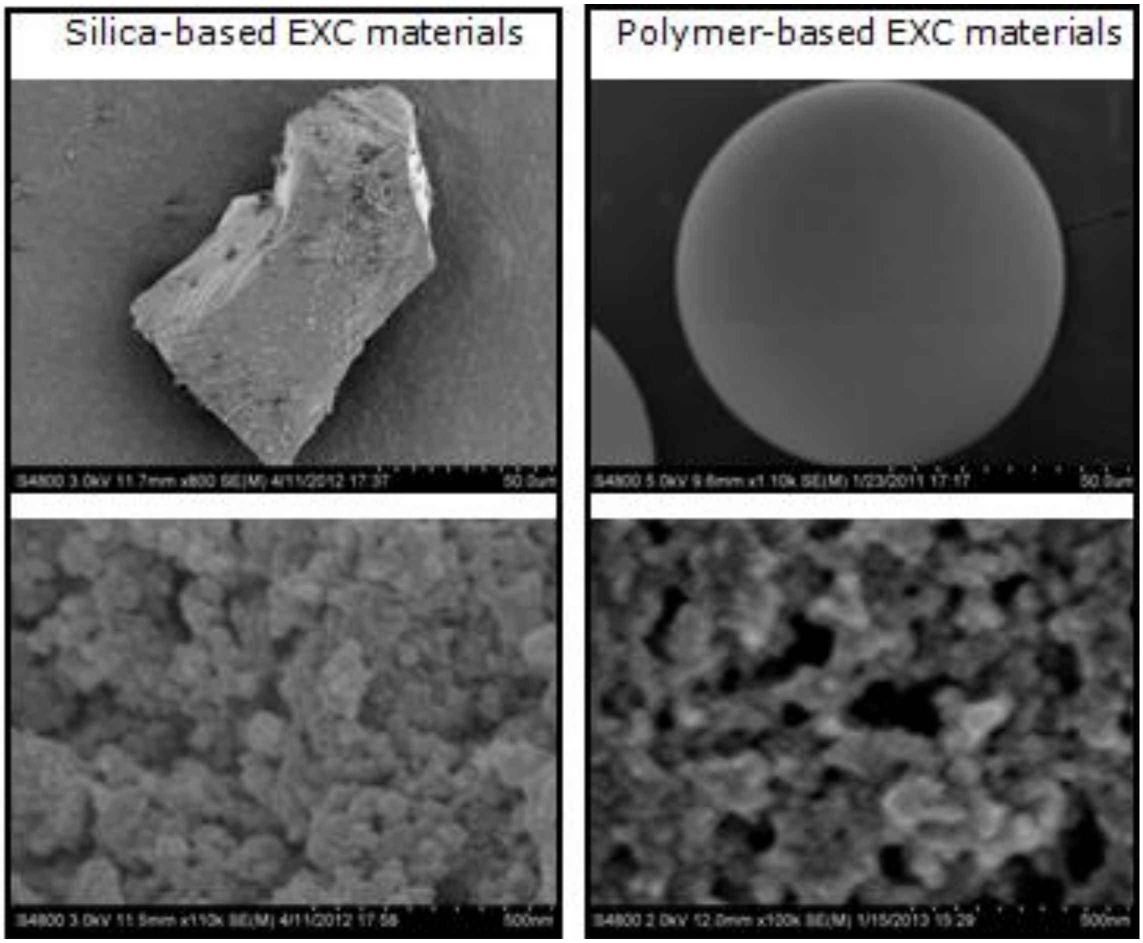

Figure 2.7: Physical appearance of silica sol-gel-based and polymer-based extraction chromatographic materials.

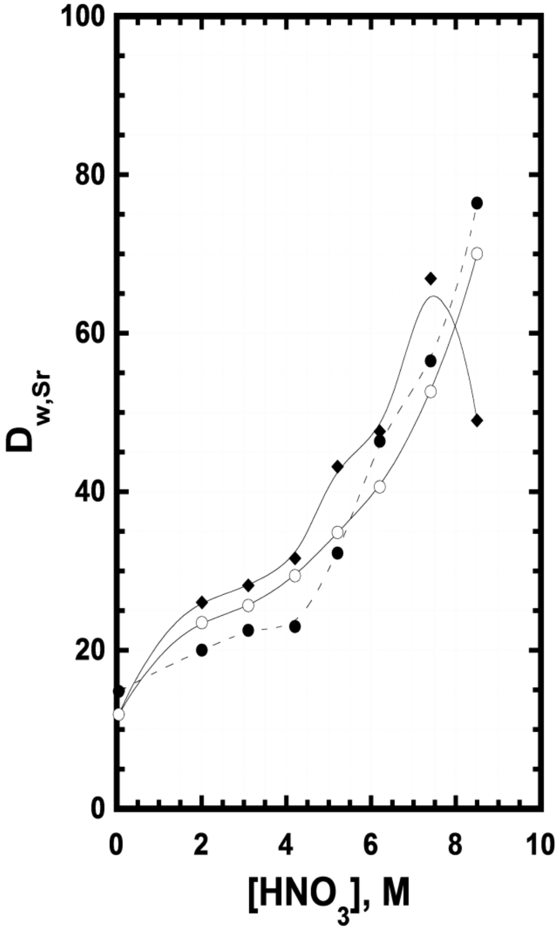

Figure 2.8. Effect of nitric acid concentration on the uptake of strontium ion by silica sol-gel glass-encapsulated DtBuCH18C6, incorporated as either the neat extractant (●) or a 1 M solution in $C_{10}mimTf_2N$ (○) or 1-octanol (♦). (The smooth curves are intended only as a guide to the eye.)

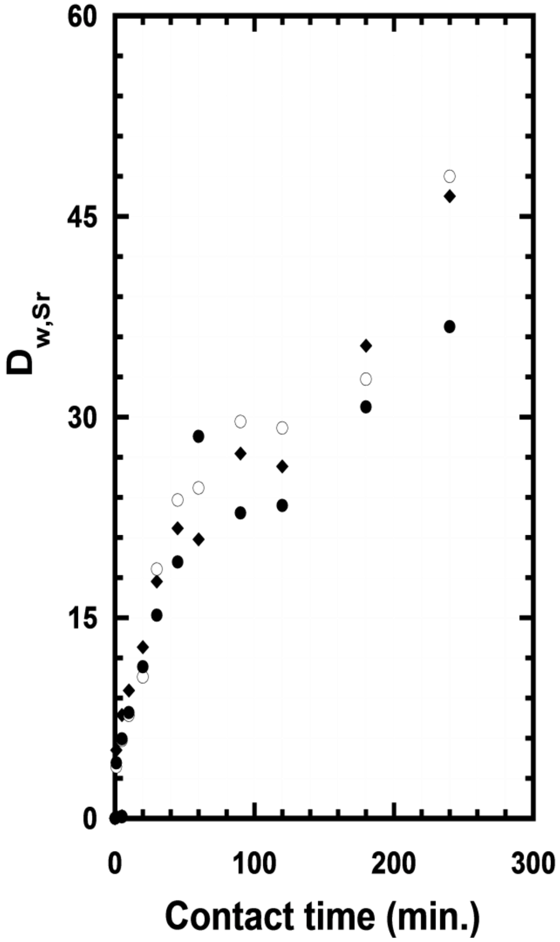

Figure 2.9: Kinetics of the uptake of strontium ion by silica sol-gel-based EXC materials from 6.2 M HNO_3 using neat DtBuCH18C6 (♦) or its solution (1 M) in 1-octanol (○) or $C_{10}C_1imTf_2N$ (●) as the stationary phase.

2.4 Conclusions

The results presented here, while preliminary, do indicate that the transfer to a solid-supported (*i.e.,* extraction chromatographic) configuration of metal ion separations methodology developed using ionic liquid-based liquid-liquid extraction systems may not be straightforward. Most notably, the significant stationary phase viscosities arising from the high extractant concentrations required to maximize the uptake of the ions of interest and the inherently high viscosity of typical ILs reduce the sorption of strontium by IL-based EXC materials. Along these same lines, given the microheterogeneous nature of ILs incorporating long alkyl chains (2.55-2.57) (in particular, the existence therein of alkane-like regions) and the need for such hydrophobic ILs to suppress undesirable extraction pathways (*i.e.,* ion-exchange processes (2.10)), along with the modest solubility of various extractants (and/or extracted complexes) in unmodified alkanes (2.67, 2.68), inadequate extractant solubility in the IL phase represents another significant potential problem area.

This is not to say that ILs cannot provide the basis of EXC materials. Indeed, as already noted, a number of sorbents have already been described in which an IL alone is employed as both the diluent and the extractant. Much work remains to be done, however, before sorbents incorporating extractant-IL combinations can achieve their full potential. Among the variety of unresolved issues, the optimum level of extractant-diluent loading on the support, the preferred support hydrophobicity and porosity, and the characteristics of the extractant and the IL yielding the most satisfactory stationary phase behavior are especially important.

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CHAPTER 3:

SOL-GEL GLASS-ENCAPSULATED CROWN ETHERS FOR THE SEPARATION AND PRECONCENTRATION OF STRONTIUM FROM ACIDIC MEDIA

3.1 Introduction

Although extraction chromatography is widely applied and generally recognized as offering significant advantages over other methods for radionuclide separation (3.1-3.9) and preconcentration, it is not without limitations (3.1). Many of these limitations have their origins in the fact that extraction chromatographic (EXC) materials are prepared simply by impregnating an appropriate support (most frequently, porous polymers) with a metal ion extractant or a solution of the extractant in an appropriate solvent. Because the extractant is not chemically bonded to the support, the physical stability of EXC resins is inadequate for many applications. The extractant is sorbed onto support solely by weak van der Waals forces, and because of these weak interactions, loss of extractant in mobile phase is quite common. In fact, dissolution or shearing off of the stationary phase from the support is the reason for the poor stability of EXC materials. This instability complicates the regeneration of the sorbent and leads to unsatisfactory reproducibility of its performance (3.10, 3.11).

For some time now, there has been interest in the possibility of employing the properties of the support to enhance the performance of EXC materials (3.12). For example, in an effort to prepare more stable EXC resins, various studies have been performed in which a support capable of acid-base interactions or ion-exchange is impregnated with an extractant bearing an appropriate (*e.g.*, charged) functional group (3.13-3.22). The capacity of these materials is generally less than that expected on the basis of the extractant loading, however, suggesting that immobilization reduces the amount of extractant available for complexation (3.18). Along these same lines, EXC materials have been prepared in which the extractant is incorporated into a mixture of monomers during their polymerization to yield the support (3.23). Because the polymerization process can be adversely affected by the presence of the extractant, however, only certain types of extractants have physical and chemical properties appropriate for this type of incorporation (3.24, 3.25).

A less-commonly investigated approach to the improvement of EXC materials involves the use of inorganic supports, such as silica. While EXC resins employing silica as the support material are by no means uncommon (3.26-3.29), there has been little systematic effort to employ silica to enhance the stability, capacity, or metal ion uptake efficiency exhibited by sorbents prepared with a given extractant. The use of inorganic supports offers several potential advantages over porous polymers, among them improved mechanical stability and chemical inertness, and negligible swelling (3.30). The use of silica offers an additional advantage, namely facile preparation through the application of well-established sol-gel methodology (3.31-3.33). Sol-gel glasses doped with various organics or biomolecules have already proven to be of significant utility in a number of areas of chemical analysis, among them the fabrication of optical and electrochemical sensors (3.34) and the preparation of molecularly-imprinted sorbents (3.35-3.37). Such studies have demonstrated that in most cases, dopant molecules retain their chemical properties upon incorporation into the glass matrix (3.38-3.46). Sol-gel-derived ion-sensing materials and electrode membranes encapsulating crown ether ligands, for example, have been shown to retain the ion-selectivity of the crown ether while exhibiting good sensitivity and response time, despite the high rigidity of the matrix (3.47, 3.48). More recently, sol-gel glass-encapsulated crown ethers have been investigated for metal ion separations. Yost *et al*. (3.31), for example, found that a sorbent incorporating 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-*bis*(malonate) (Na_4oddm) will selectively remove more than 90% of the strontium present in an aqueous solution containing a substantial excess of competing ions (*e.g.*, Ca^{2+}). Subsequent work by Makote *et al.* (3.32) showed, however, that dicyclohexano-18-crown-6 (DCH18C6) encapsulated in a sol-gel glass exhibits only limited uptake of Sr^{2+} ($D_{w,Sr} = 0.5$) from a pH 4 aqueous phase if the crown ether is employed neat (*i.e*., undiluted). Such results leave open the question of whether extraction chromatographic materials for metal ions superior to those presently available can be prepared by incorporation of a crown ether into a sol-gel glass matrix.

In this study, our preliminary efforts to employ sol-gel glasses as a support for ionic liquid-based EXC materials (Chapter 2) have been extended to an evaluation of silica sol-gel encapsulation of extractants as an approach to improving the stability of the EXC materials. To this end, a series of EXC materials were synthesized by encapsulating the macrocylic polyether di-*tert*-butylcyclohexano-18-crown-6 (DtBuCH18C6) in a sol-gel glass matrix. These silica-based materials have been characterized and their properties compared to those of a well-established (16-18) commercial EXC resin incorporating the same extractant into a porous polymer (Sr-resin).

3.2 Experimental

3.2.1 Materials

The 4,4',(5')-di-(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6) was obtained from EichroM Technologies, Inc. (Darian, IL), and used as received. Tetramethyl orthosilicate (TMOS) and 1-octanol were obtained from Alfa Aesar (Heysham, UK). Tetraethyl orthosilicate (TEOS), formic acid (98%) and cetyltrimethylammonium bromide (*i.e.*, hexadecyltrimethyl-ammonium bromide; CTAB) were purchased from Sigma Aldrich (St. Louis, MO), and used as received. Trace metal grade nitric acid (Fisher Scientific, Waltham, MA) was used for metal ion uptake kinetics experiments with the silica sol-gel glasses, while the Optima™ reagent was used for all other studies. All water was obtained from a Milli-Q2 system and exhibited a specific resistance of at least 18 MΩ-cm. All methanol used was HPLC grade (Fisher Scientific). Radiostrontium isotope (Sr-85) was received from PerkinElmer (Shelton, CT).

3.2.2 Instrumentation

Radiotracers were assayed using a Perkin-Elmer 2480 Automatic Gamma counter. All thermograms were obtained using a TA Instruments Model Q50 thermogravimetric analyzer. Scanning electron microscopy (SEM) was carried out on a Hitachi Model S 4800 field-emission scanning electron microscope (SEM). The porosity of the materials was evaluated *via* BET measurements, specifically, the determination of N_2 adsorption-desorption isotherms at 77 K using a Micromeritics ASAP 2020 instrument.

3.2.3 Methods

3.2.3.1 Preparation of crown ether-doped sol-gel glasses.

Acid-catalyzed sol-gel processes (3.32) were employed to synthesize the silica sol-gel EXC materials incorporating the crown ether. Typically the solution gelled after one day and glass formation was complete after one week. To evaluate the effect of the level of crown ether incorporation on the properties of the sorbents, materials were prepared containing from ~10% to ~60% (w/w) extractant, dispersed in the mixture of TMOS or TEOS (1 mL) and formic acid (2 mL) (3.32). The effect of a porogen, CTAB, was evaluated by adding it to this composition immediately after mixing. In all cases, evaporation of the hydrolysis products of the reaction (CH_3OH and $HCOOCH_3$) left behind a monolithic crystalline glass composite consisting of DtBuCH18C6 entrapped in the silica network. For the most highly loaded material, ~60% (w/w), a stable silica monolith could not be obtained. In all other cases, however, the formation of a stable glass was observed. These glasses were crushed and sieved to obtain materials in the desired particle size range (~50-100 μm) for use in subsequent metal ion uptake studies. Control (blank) sol-gel glass samples not containing DtBuCH18C6 were prepared from TMOS or TEOS following the same procedures. For glasses containing the crown ether, thermogravimetric analysis (TGA) was employed to determine the level of DtBuCH18C6 incorporation achieved. Figure 3.1 summarizes the synthesis of silica-based EXC materials.

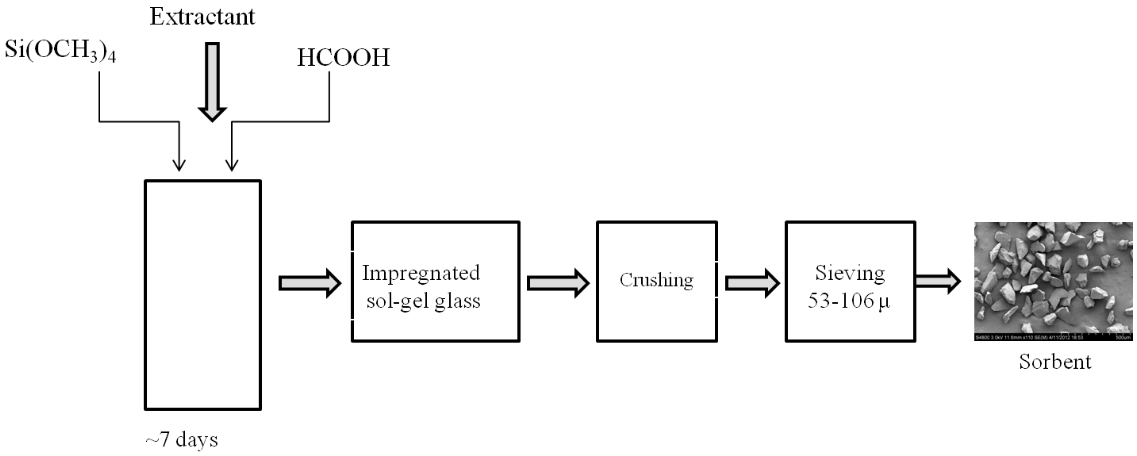

Figure 3.1 Preparation of silica sol-gel-based EXC materials

For sol-gel glasses prepared in the presence of CTAB, crushing and sieving was followed by porogen removal *via* Soxhlet extraction (solvent : water; T : 40-60 °C; time : 10-15 hrs), yielding silica powders of various porosities. Following overnight calcination at 275 °C, the porosity of the materials was evaluated *via* BET measurements, specifically, the determination of N_2 adsorption-desorption isotherms at 77 K.

3.2.3.2 Determination of weight distribution ratios

Solid-liquid (weight) distribution ratios (D_w) for strontium were measured radiometrically using a commercial ^{85}Sr radiotracer. Specifically, the uptake of the tracer from a series of nitric acid solutions by the sorbents was measured by contacting a known volume (typically 1.0 mL) of ^{85}Sr-spiked acid solution of appropriate concentration with a known quantity of resin. The ratio of the aqueous phase volume (mL) to the weight of the sorbent/EXC material (g) typically ranged from 40-50. (This ratio is determined by the need to produce a readily measureable decrease in the aqueous activity by contact with the sorbent). A contact time of four hours (with occasional swirling) was employed for all silica-based EXC materials. Following equilibration, an aliquot of the aqueous phase was withdrawn from each culture tube and filtered through a 0.22-µm poly(vinylidene fluoride) (PVDF) filter to ensure that no sorbent fragments were present. On the basis of the initial and final activity of a measured aliquot of this aqueous phase, (determined *via* gamma spectroscopy according to standard procedures on a Perkin-Elmer 2480 Automatic Gamma Counter), the weight distribution ratio (D_w) of strontium was calculated from the following equation:

$$D_w = [(A_0 - A_f)/A_f]\ (V/w) \qquad (3.1)$$

Here A_0 and A_f represent the aqueous phase activity (cpm) before and after equilibration, respectively, w is the mass of the resin taken (g), and V is the volume of the aqueous phase (mL).

3.2.3.3 Metal ion uptake kinetics

Into a series of screw-cap test tubes, each containing the same (± 10%) amount (20 mg) of EXC material, was introduced a known volume (typically 1 mL) of an appropriate nitric acid solution containing a Sr-85 radiotracer. At various time intervals following the introduction of the tracer solution, during which the samples were periodically swirled to facilitate equilibration, the aqueous phase was withdrawn from one of the test tubes. After filtration through a 0.22 μm poly(vinylidene fluoride) (PVDF) filter, its activity was determined. When the amount of sorbent available was limited, the series of test tubes was replaced with a single screw-cap tube containing *ca*. 25 mg of sorbent in contact with a known volume (typically 1 mL) of an appropriate nitric acid solution containing a Sr-85 radiotracer. At various times following the addition of the tracer solution, a small aliquot (20 μL) of the aqueous phase was withdrawn and counted. From the initial and final (residual) activity of the aqueous phase, D_w values were determined as described above and a plot of the contact time dependence of D_w was prepared.

3.2.3.4 Column preparation and characterization

To pack a column, a small quantity of the silica-based EXC material was slurried in 18.2 MΩ water, and aliquots of this slurry were transferred onto a Bio-Rad Econocolumn (5.0 mm i.d. by 5 cm in length). Packing was carried out under gravity flow. When the column bed reached the desired height or volume, a small plug of glass wool was placed atop it so that it would not be disturbed by the introduction of a sample. The packed sorbent was then rinsed with several bed volumes of deionized water. Immediately prior to the introduction of a sample, the column was preconditioned with 5-10 bed volumes of an appropriate nitric acid solution. Flow rates of ~2-3 ml/ cm^2.min were typically employed.

3.3 Characterization of Crown Ether Encapsulated Silica Sol-Gel EXC Materials

3.3.1 Extractant loading in the silica matrix

The preparation of a conventional EXC resin employing a pre-formed support, whose capacity is obviously related directly to the available pore volume of the material, generally involves mixing of a calculated amount of extractant with a known quantity of support in the presence of a volatile solvent and its subsequent evaporation. Therefore, the percent composition of extractant is simply obtained from the quantity of the extractant and the solid support. For systems in which the support is fabricated in the presence of the extractant, as is the case for the formation of a sol-gel glass encapsulating a crown ether, the situation is less straightforward, however. That is, it is not possible to know *a priori* the precise level of extractant incorporation achievable, particularly given that at sufficiently high concentrations, the extractant may interfere with the synthesis of the support (3.23). For this reason, it is important to determination of the effect of crown ether encapsulation on the properties of the resultant glass and the maximum incorporation of DtBuCH18C6 consistent with a stable support. To this end, a series of mixtures were prepared combining a fixed amount of the sol-gel glass precursors with increasing quantities of the crown ether. Following a period of gelation and glass formation (as described above), the product glasses were examined.

As a first step, a pair of “control” glasses to which no extractant had been added were prepared. Figure 3.2 shows the results of TGA analyses of these samples, one derived from TMOS and the other from TEOS according to the following reactions:

$$Si(OCH_3)_4 + 2HCOOH \rightarrow SiO_2 + 2CH_3OH + 2HCOOCH_3 \qquad (3.2)$$

$$Si(OCH_2CH_3)_4 + 2HCOOH \rightarrow SiO_2 + 2CH_3CH_2OH + 2HCOOCH_2CH_3 \quad (3.3)$$

Both thermograms show two distinct mass loss steps. The first, which occurs below 200 °C, has been attributed to desorption of water and evaporation of the alcohol. The second, less-distinct peak occurring above 200 °C has been described as arising from the decomposition of residual organics and the evaporation of water molecules trapped within the silica (3.49). Both materials, in fact, apparently contain similar levels (*ca*. 15%) of residual starting materials (*i.e*., TMOS or TEOS and formic acid) and reaction by-products (*i.e*., methanol or ethanol; methyl formate or ethyl formate) from their synthesis. Not unexpectedly, TEOS yields somewhat less silica backbone than TMOS under the same conditions.

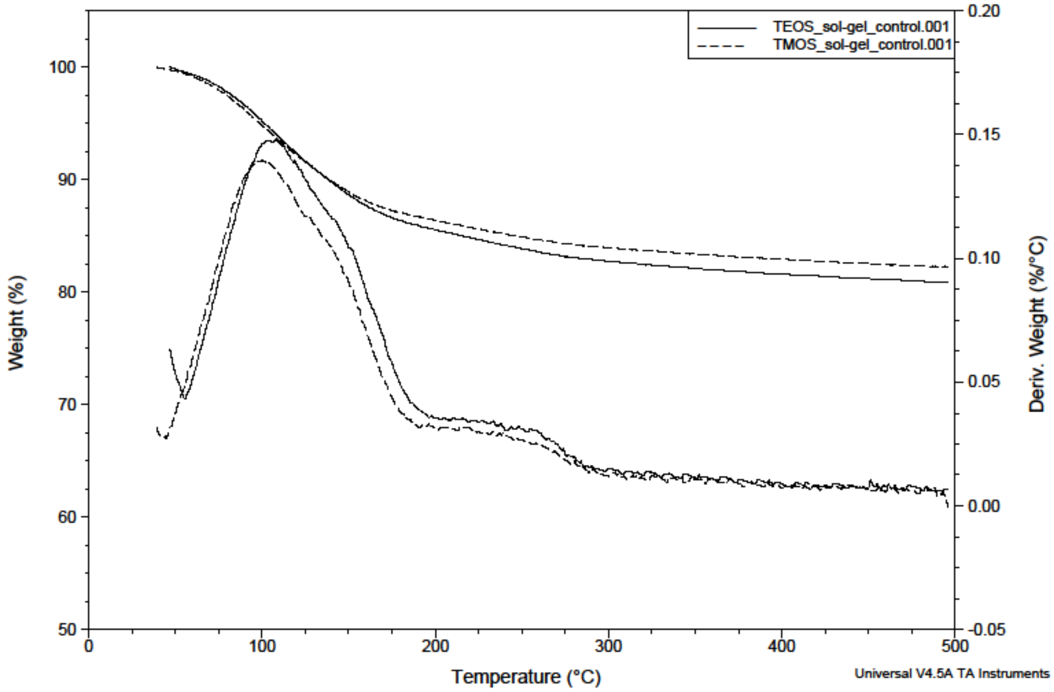

Figure 3.2: Thermograms for silica sol-gel glasses prepared from TMOS and TEOS in the absence of added extractant (i.e., "control" samples). Peaks in the derivative plots correspond to the maximum mass loss.

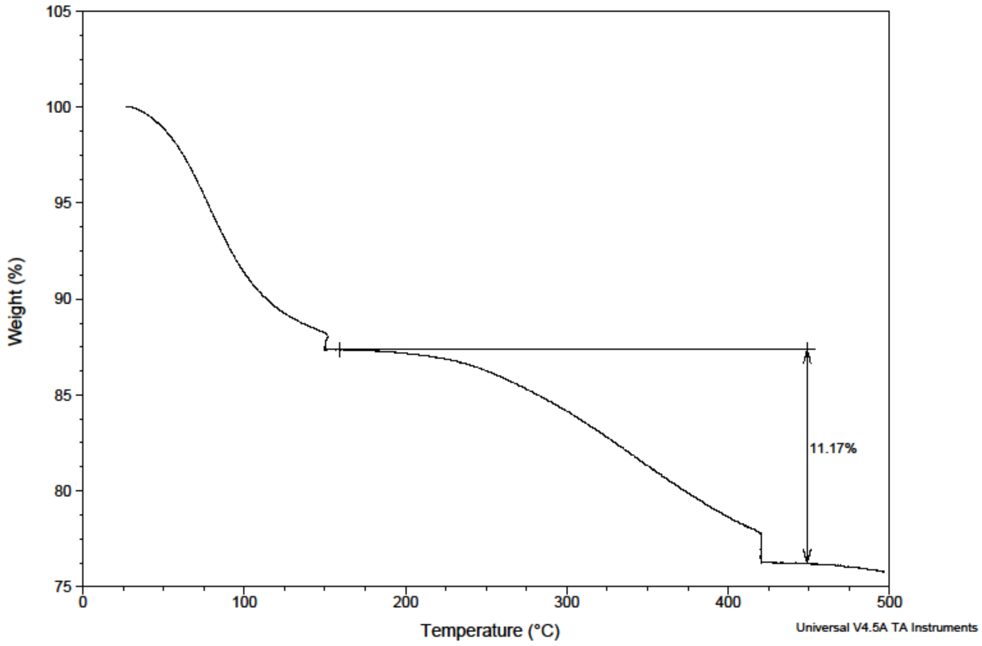

Figure 3.3: Thermogram for silica-encapsulated DtBuCH18C6 (10% (w/w)).

Figure 3.3 shows the results of TGA analysis of a representative sol-gel glass incorporating DtBuCH18C6, in this case, one prepared to contain *ca*. 10% (w/w) of the crown ether. (Given the similarity of the properties of the TMOS- and TEOS-derived glasses, this and all subsequent crown ether encapsulation studies were performed only with the TEOS-based glass.) In a typical run, the temperature is first raised to 150 °C, where it is held for 20 minutes to remove water, residual starting materials, and reaction by-products (as mentioned above) from the glass. A further increase in temperature, initially to 420 °C and finally, to 500 °C, results in removal of the crown ether. On the basis of studies of the thermal stability of a variety of crown ethers (3.54), in particular, the known onset temperature for mass loss upon heating for DCH18C6 and the effect of the addition of a *tert*-butyl group to a molecule on T_{onset} values, it would be anticipated that loss of DtBuCH18C6 would occur at *ca*. 300 °C, substantially lower than the temperature actually required for its removal. The apparent greater stability of the encapsulated crown ether is consistent with the results of Saad *et al.* (3.49) for sol-gel immobilized thiacrown ethers, whose thermal stability was found to be significantly enhanced (by *ca*. 200-300 °C) upon incorporation into the glass. For this sample, the observed mass loss at the higher temperatures corresponds to incorporation of 11.2% (w/w) DtBuCH18C6, in good agreement with the expected ("as prepared") composition. Greater deviations from the expected values were observed for several other samples, however, a likely result of sample-to-sample variations in the efficiency of extractant encapsulation. Thus, TGA represents the most reliable means for determining the precise composition of the crown ether-loaded sol-gel sorbents. In the course of these experiments, it is important to note, it was found that the presence of more than ~50% (w/w) of the crown ether or more than ~ 65%(w/w) crown ether and CTAB (*i.e.*, porogen) prevents the formation of a stable glass. As a result, all subsequent experiments were confined to systems incorporating no more than these amounts of crown ether or the crown ether and porogen combination. The composition of porogen treated materials (*i.e.*, percent of extractant and porogen) were also determined by thermogravimetric analysis.

3.3.2 Physical properties of the silica sol-gel materials

Table 3.1 summarizes the surface area, pore volume, and average pore width data (obtained by BET measurements) for the same materials. For purposes of comparison, the corresponding values for Amberchrom CG-71m, the support employed for the preparation of the commercially available Sr-selective EXC resin (3.8, 3.9), are also shown. For the Amberchrom resin, the surface area determined here, 577 m^2/g, is in good agreement with that reported by the manufacturer (500 m^2/g) (3.50). For both sol-gel glass samples, slightly (*ca*. 20%) larger surface areas were observed, along with substantially lower pore widths and volumes. The BET isotherms for these materials exhibit a very small hysteresis loop, indicating that micropores (<2 nm), not mesopores (2-50 nm), represent the primary contributor to the observed porosity. These results are consistent with those typically observed for glasses prepared *via* acid-catalyzed sol-gel synthesis (3.33). It has been reported that for sorbents exhibiting simple pore geometry, diffusion coefficients (and thus, diffusion rates) will decrease with decreasing pore size (3.51). From the perspective of the development of EXC materials then, the small pore sizes observed for these glasses are a matter for concern, as they suggest that access to the encapsulated extractant may be hindered, and thus, the kinetics of metal ion uptake/stripping poor.

Table 3.1: BET characterization of the silica sol-gel-based EXC materials

Silica sol-gel EXC materials	BET surface Area (m^2/g)	Pore volume (cm^3/g)	Avg pore width (Å)
TMOS control	678	0.42	25
TEOS control	678	0.41	24
TEOS ~40% CTAB (w/w)	583	0.81	55
TEOS ~50% CE (w/w)	915	0.96	42
TEOS ~60% (CE + CTAB) (w/w)	726	1.12	62
Amberchrom CG-71 m	577	1.27	88

3.3.3 Metal ion uptake and uptake kinetics studies

Figure 3.4 shows the acid dependency of strontium ion uptake on a series of sol-gel glasses containing amounts of DtBuCH18C6 in the 10-50% (w/w) range. As would be expected (and is observed for commercially available Sr sorbents (3.8-3.10)), at all extractant levels, strontium retention is generally found to increase with rising nitric acid concentration, consistent with the sorption of a strontium-nitrato-crown ether complex:

$$Sr^{2+} + 2\ NO_3^- + CE_{org} \rightarrow Sr(NO_3)_2 \bullet CE_{org} \quad (3.4)$$

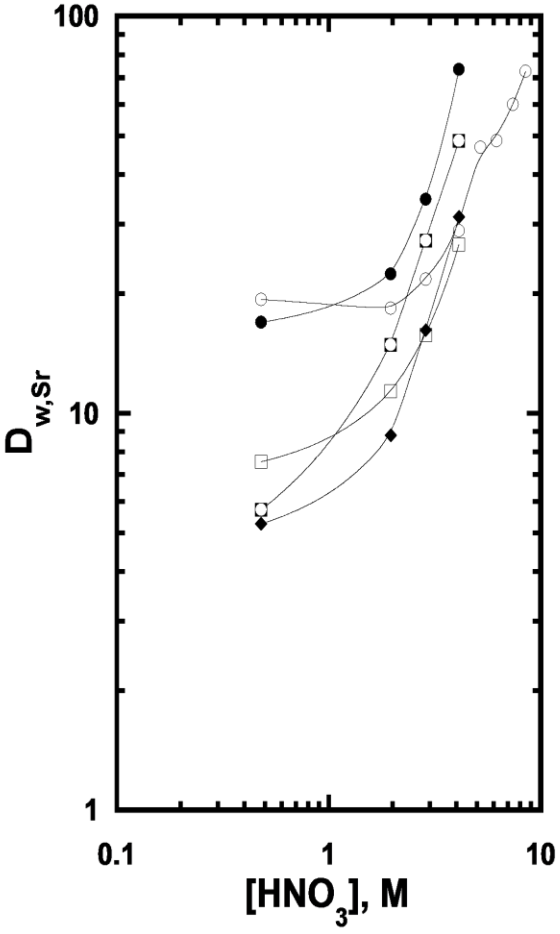

Figure 3.4: Effect of nitric acid concentration on the extraction of strontium ion by silica-encapsulated DtBuCH18C6 (~10% (o), ~20% (♦), ~30% (□), ~40% (◘), ~50% (●) (w/w)). (The smooth curves are intended only as a guide to the eye.)

Unexpectedly, however, there appears to be no simple relationship between the extent of strontium uptake at a given acidity and the amount of DtBuCH18C6 incorporated. For example, over a nearly ten-fold range of acidity, $D_{w,Sr}$ is actually *lower* for a sorbent incorporating 20% (w/w) crown ether than for one containing 10% extractant. This indicates that not all encapsulated extractant is available for interaction with the metal ion, and that the available fraction varies with the extent of crown ether incorporation. From the perspective of the characteristics required of an EXC material for radiostrontium, the uptake behavior of the sorbent incorporating 50% (w/w) DtBuCH18C6 is clearly superior to that of the others. That is, this material provides a comparatively high value of $D_{w,Sr}$ at high (1-3 M HNO_3) acidities (albeit slightly lower than that obtained with the 40% (w/w) material) and exhibits greater sensitivity to decreasing aqueous acidity than do sorbents prepared using other levels of extractant loading, thus facilitating strontium recovery. Unfortunately "bleeding" of the extractant from the support is generally observed for silica-based materials containing more than ~10% (w/w) of the crown ether, particularly at high acidities (≥4 M HNO3). The extractant loss is especially severe when the sorbent containing 50% (w/w) crown ether is allowed to stand in contact with aqueous nitric acid. As a result, this material was not considered a viable candidate for further evaluation. Instead material containing ~40% (w/w) extractant was selected for a more detailed examination of its uptake behavior.

Figure 3.5 depicts the kinetics of strontium ion uptake from nitric acid solution by this sorbent. As can be seen, the uptake is not especially rapid. In fact, equilibrium is approached only after 4 hours. Like the results shown in Figure 3.3 then, these suggest that not all of the encapsulated extractant is readily accessible to metal ions. Indeed as noted by Lin and Liu (3.52), rapid complex formation between a metal ion in solution and the encapsulated extractant can initially occur at the surface of the sorbent, but as the availability of these surface sites decreases, the metal ion must diffuse into the pores of the silica network before reacting with the extractant, a slower process. Similarly slow uptake, it should be noted, was reported by Dai *et al*. (3.31) for the sorption of Sr^{2+} by Na_4oddm and by Khan *et al.* (3.55) for the uptake of Hg(II) by 1,5-diphenylcarbazide, both incorporated into a sol-gel-derived glass. Thus this observation is not simply a feature of the present system, but rather may be a general characteristic of encapsulated extractants.

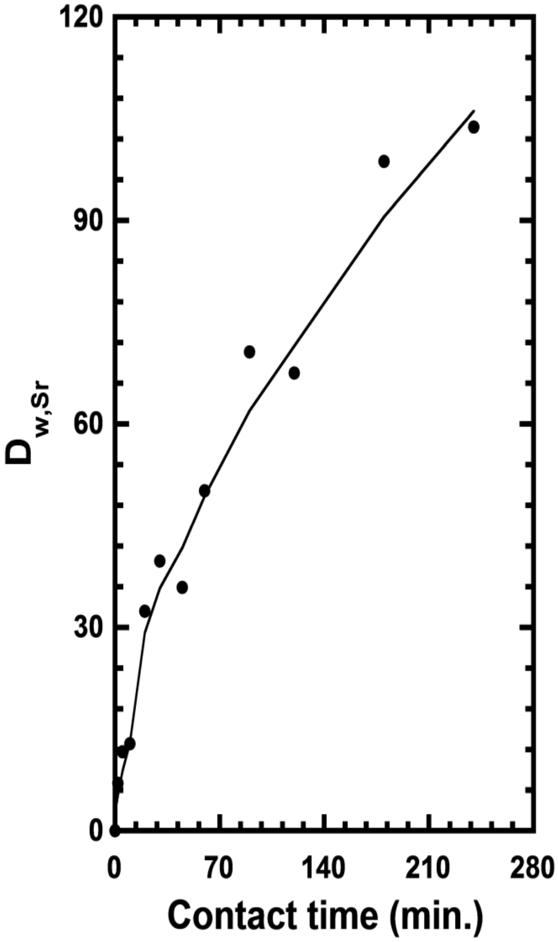

Figure 3.5: Kinetics of the uptake of strontium ion from 4.7 M HNO3 by silica-encapsulated DtBuCH18C6 (~40% w/w). (The smooth curve is intended only as a guide to the eye.)

As already noted, the average pore size of the unloaded (*i.e.*, control) sol-gel glass is substantially less than that of the commercial polymeric support, providing a partial explanation for the sluggish kinetics. As part of our initial investigation of glass formation in these systems, it was observed that the presence of a crown ether does lead to glasses exhibiting a higher porosity and larger average pore size than are observed in its absence (Table 3. 1). Nonetheless the pore size remains well below that measured for Amberchrom CG-71. In an effort to further increase the support porosity, the effect of the addition of a porogen (*i.e.*, the surfactant, CTAB) during the glass formation process was examined. It has long been known that the pore size of silica can be "tuned" by intercalation of layered silicates with surfactant molecules (3.53). It has also been reported that, for simple pore geometry, diffusion coefficients rise with increasing pore size (3.51). With the objective of "opening up" the silica network, a series of sol-gel glasses were prepared in the presence of CTAB and its effect on the glass porosity determined. As shown in Table 3.I, CTAB addition yields a substantial (two-fold) increase in pore volume and width *vs.* the control materials. When combined with the crown ether (which itself, improves the porosity), the effect of CTAB on the support porosity is even greater, with the resultant glass exhibiting a total pore volume approaching that of Amberchrom CG-71 and an average pore width only one-fourth less.

3.4 Optimization and Characterization of the Silica-based EXC Materials

In an effort to optimize the composition of the silica sorbents, a series of materials were prepared by adding varying amounts of extractant and porogen to a fixed (1:2 v/v) mixture of the silica precursor (TEOS) and formic acid. As noted earlier, the 40% and 57% (w/w) extractant-loaded materials showed comparatively good metal ion uptake (Figure 3.3). Therefore, in this study, the loading of the extractant and porogen was maintained in the range from ~40-65% (w/w). Table 3.2 summarizes the compositions of the materials. As can be seen, when the amount of porogen exceeds 200 mg, the loss of the dopents (*i.e.*, CE and CTAB) upon Soxhlet extraction is substantial, reaching >90% when 468 mg of CTAB are used. As porogen content is reduced, the loss generally declines. As can also be seen, however, the loss upon washing is also influenced by the amount of crown ether present. It appears, in fact, that for a fixed amount of porogen, increasing amounts of crown ether have a stabilizing effect until high levels of loading are reached. The best results were obtained by using 150 mg CE with 200 mg CTAB, and this material was chosen for further investigation. To place the results obtained in context, additional experiments were also performed on materials containing other amounts (10, 26, and 46%) of the crown ether/porogen after washing.

Table 3.2: Composition of the porogen treated silica sol-gel based sorbents

TEOS (mL)	Formic Acid (mL)	Crown ether (mg)	Surfactant (mg)	% (CE+CTAB) encapsulation as prepared	% (CE+CTAB) encapsulation after wash	% (CE + CTAB) lost to washing
1	2	118	468	64	6	91
1	2	118	200	49	10	80
1	2	250	350	64	17	73
1	2	95	200	46	26	43
1	2	150	200	51	43	16
1	2	250	200	60	46	23
1	2	400	200	64	32	50

Figure 3.6 summarizes the results of strontium uptake kinetics experiments on these materials. It was anticipated that the greater porosity arising from CTAB addition would be accompanied by an increase in the rate of strontium uptake by the sorbent. Indeed as shown, strontium sorption by the porogen-treated material containing 43% and 46% (w/w) DtBuCH18C6 and CTAB is significantly faster than for in the untreated material (Figure 3.5). Interestingly, the rate of uptake is even faster when the amount of encapsulated extractant/porogen is reduced. In fact, uptake rates comparable to those observed for the commercial Sr resin (3.8-3.10) are observed for loading levels at or below 26% (w/w), an observation which may have its origins in the decreased stationary

phase thickness expected to accompany reduced levels of extractant encapsulation. (This reason may also explain the relatively slow kinetics of the 46% (w/w)-loaded materials.) While the kinetics of uptake are an important consideration in optimizing the performance of a metal ion sorbent, they are clearly not the only consideration. In fact, the extent to which the metal ion is sorbed (*i.e.*, $D_{w,M}$) is equally, if not more, important. When this is considered in conjunction with the kinetics results and available information concerning stability, it becomes clear that the composition involving 43% (CE + CTAB) loading (hereafter referred as SSG-Sr resin) represents the best choice for additional study.

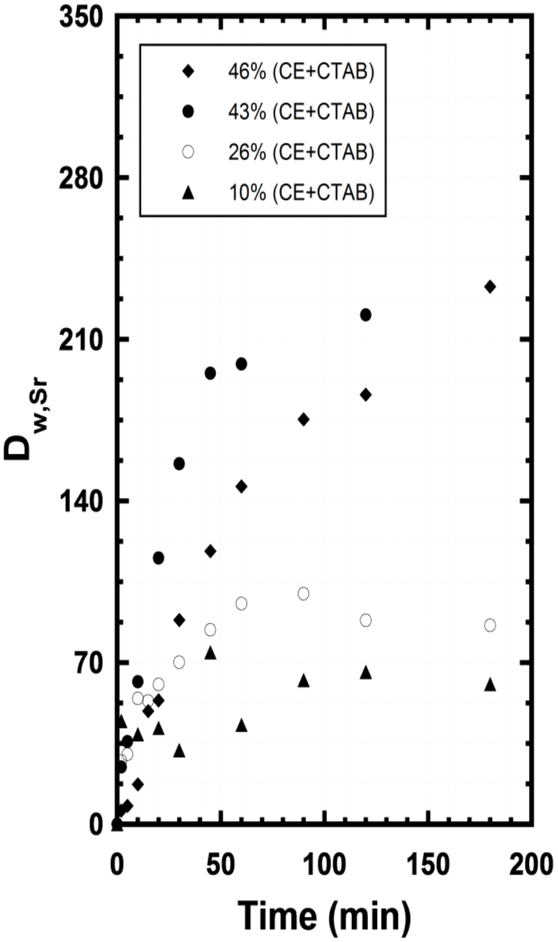

Figure 3.6: Kinetics of the uptake of strontium ion from 6.2 M HNO_3 using porogen-treated silica-encapsulated DtBuCH18C6 (~10% (▲), ~26% (○), ~43% (●), ~46% (♦) (w/w)).

Figure 3.7 compares the strontium ion uptake of this optimized sol-gel glass-based material to that of the conventional Sr-resin. The silica-based material clearly shows higher metal ion uptake at acidities >1 M, with the difference being most apparent at high acidities (>3 M). In addition, the acid dependency of strontium ion uptake is steeper for the SSG-Sr resin, which indicates that stripping of the sorbed strontium should be more facile.

To determine the stability of the optimized silica-based material, a column packed with the sorbent was subjected to 500 FCV of water wash. The themograms before and after the water wash (Figure 3.8) showed that the loss of the stationary phase (here, extractant and porogen) was minor (<5%), consistent with good sorbent stability. To further investigate the stability of the materials, the water washed sorbent was subjected to further washing, this time with 100 FCV of 3 M HNO_3. The thermogram after this acid wash again shows (Figure 3.8) only minor stationary phase loss (again, *ca.* 10%).

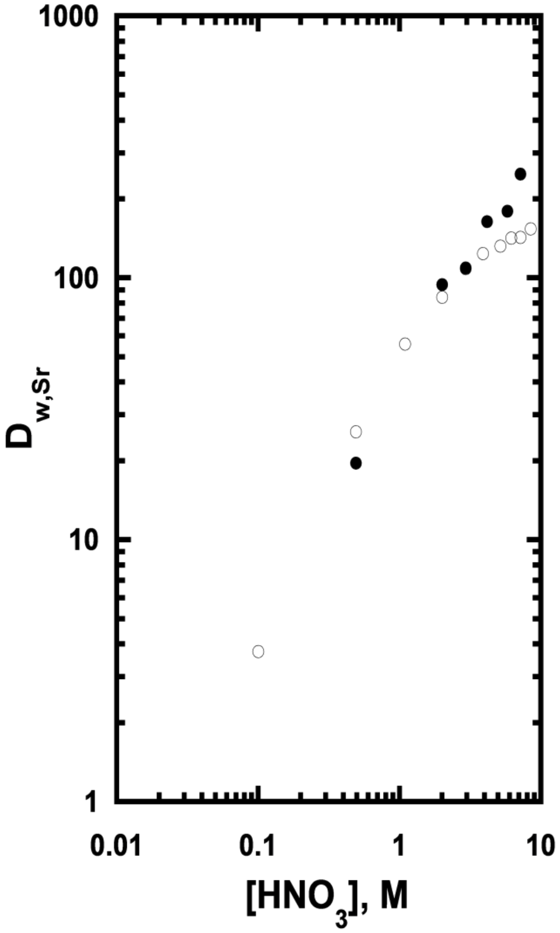

Figure 3.7: Effect of HNO₃ concentration on the extraction of strontium ion by optimized silica sol-gel based EXC materials (●) and conventional Sr-resin (○).

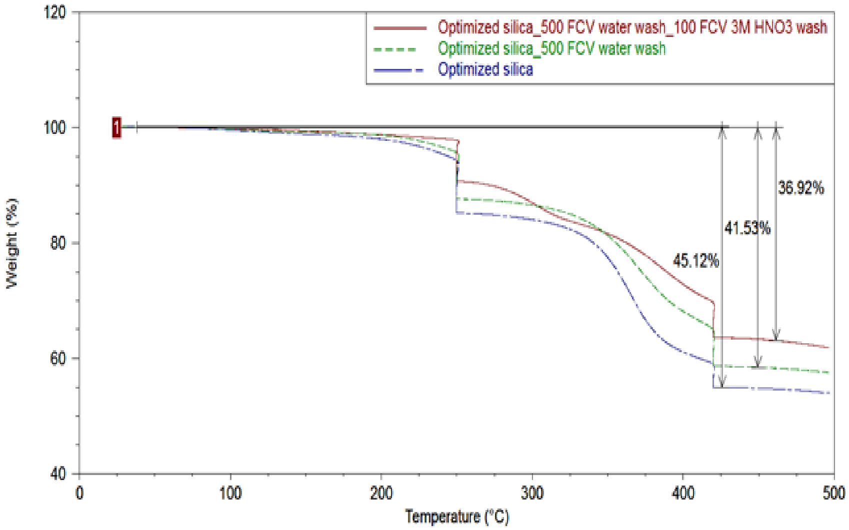

Figure 3.8: Thermograms for optimized silica sol-gel sorbents. Before washing (— -), after 500 FCV water wash (- - - -) and after 500 FCV water wash and 100 FCV 3 M HNO_3 wash (—–).

Chromatographic characterization of the water and acid-washed silica-based material was carried out to determine its performance (Figure 3.9). The characteristics of the SSG-Sr resin and the packed column are summarizes in Table 3.3. Interestingly, this highly washed material yields a satisfactory elution profile of strontium ion, with a workable breakthrough volume (~15 FCV) and a peak maximum at a k'of 75. The number of theoretical plates (N) calculated from the elution curves (3.56), which indicates the column efficiency, is 2, whereas that of for Sr-resin packed column is 8. As mentioned before, the irregular shape of the silica particle and the slow kinetics may be responsible for this lower efficiency.

Table 3.3 Characteristics of SSG-Sr resin and packed column

Bulk materials	**SSG-Sr resin**
Stationary phase	DtBuCH18C6 + CTAB
Support	Silica
Particle diameter	53- 106 µm
Extractant loading	~43%
Density of extractant-loaded beads	1.42 g/mL
Packed column	
V_s, mL/mL of bed	0.17
Bed density (g/mL)	0.47
V_m, mL/mL of bed (also FCV)	0.67
V_s/V_m	0.25

Figure 3.10 shows that this same material yielded good loading and stripping behavior. Up to 16 FCV (*i.e.*, the load and rinse used for this experiment), no breakthrough of strontium was observed. In addition, the recovery of sorbed strontium using 0.01 M HNO_3 was essentially complete (after ~ 50 FCV). Notwithstanding the acid dependency results (see above), stripping of the column proved to be less facile than the conventional Sr-resin. Using ~9 FCV of strip solution (0.01 M HNO_3), it is possible to recover ~95% of the loaded strontium ion from a Sr-resin column, whereas only ~65% of the strontium ion is recovered from SSG-Sr resin loaded resin in the same volume. Slower desorption kinetics for the SSG-Sr resin may be the cause of this difference.

Following these experiments (washing and chromatographic characterization), the effect of nitric acid concentration on the uptake of strontium ion by the sorbent was evaluated. By this point, it should be noted, the SSG-Sr resin had experienced ~500 FCV water wash, ~225 FCV 3M HNO_3 wash, and ~65 FCV 0.01 M HNO_3 wash. Nevertheless, the resin showed (Figure 3.11) almost identical strontium ion uptake compared to unwashed SSG-Sr resin, suggesting that the physical stability of the silica sol-gel glass encapsulated extractant-based materials is excellent.

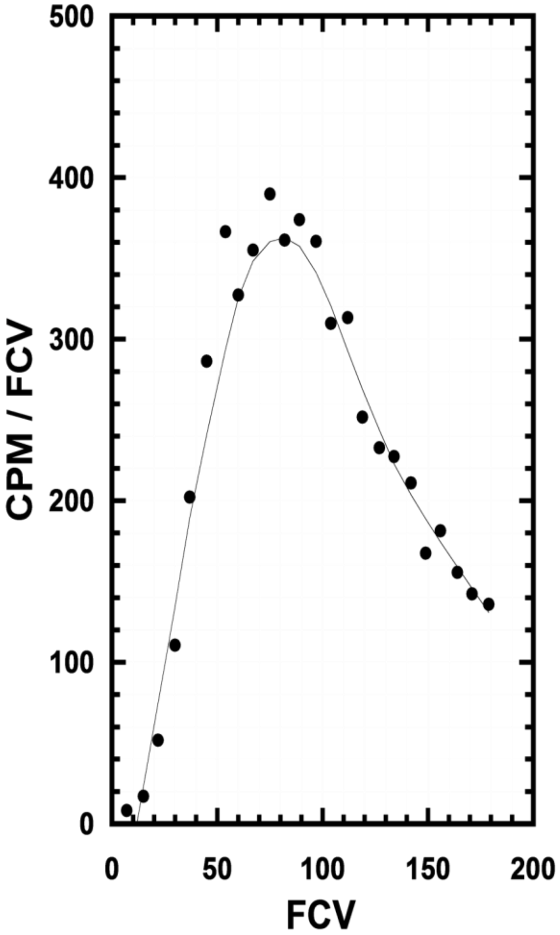

Figure 3.9: Elution behavior of strontium ion on a water- (500 FCV) and acid (100 FCV) washed SSG-Sr resin. (eluent : 3 M HNO_3)

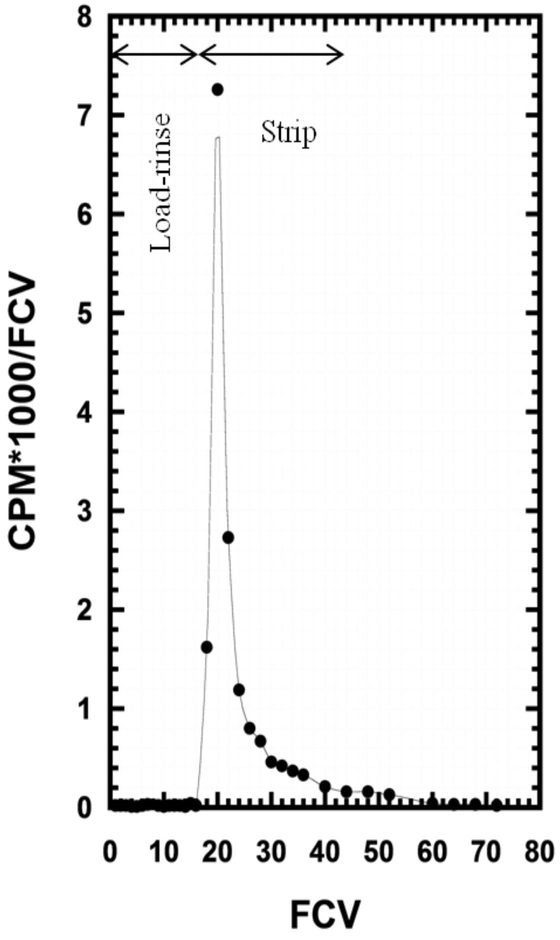

Figure 3.10: load-rinse-strip experiment on SSG-Sr resin; loading and rinsing of strontium ion using 3 M HNO_3 and striping using 0.01 M HNO_3. (The smooth curve is intended only as a guide to eye)

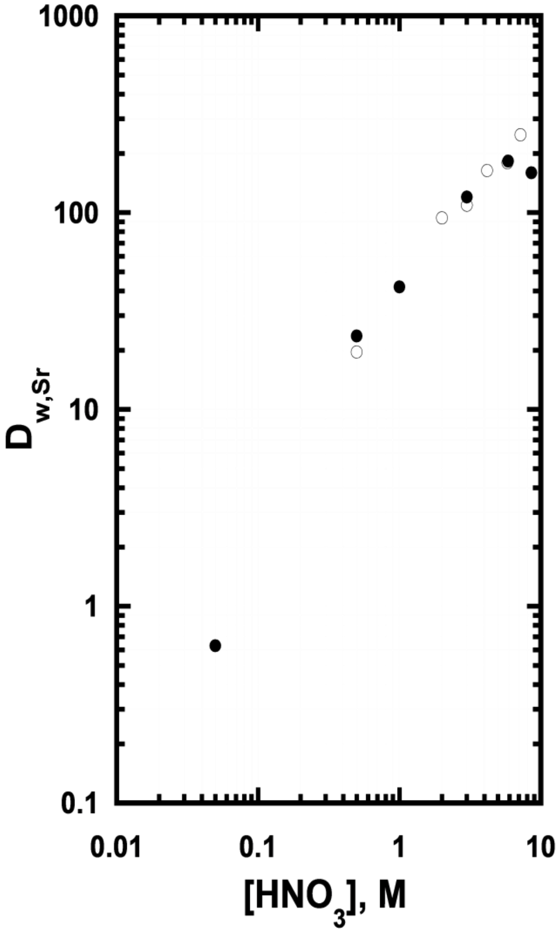

Figure 3.11: Effect of nitric acid concentration on strontium ion uptake by the washed SSG-Sr resin (●) and unwashed SSG-Sr resin (○).

3.5 Conclusions

The results presented here suggest that silica encapsulation may provide a route to the preparation of new and useful metal ion sorbents for radiostrontium. As has been shown, using well-established sol-gel chemistry, it is possible to produce materials incorporating up to 50% (w/w) of a crown ether. Although the rate of metal uptake by these materials is not rapid and leaching of extractant at high acidities is observed, modification of the properties of sorbent by porogen treatment can be easily accomplished, thereby yielding sorbents with improved strontium uptake kinetics, greater retention, and improved stability. The optimization of the sorbent composition (*i.e.*, extractant and porogen percentages) yielded a material that showed better strontium ion uptake than the conventional Sr-resin. The kinetics of the optimized material is still somewhat slower than conventional material, but not unacceptably so. Moreover, porogen treatment does provide a significant improvement in kinetics over the non-porogen-treated material. The optimized SSG-Sr resin showed good stability, with only few percent of the extractant being lost upon extensive water and acid washing. The elution profile of strontium on the washed material demonstrates that satisfactory breakthrough volume and k’ can be obtained. In addition, the stripping of sorbed strontium ion is feasible.

Although significant progress has been made, much remains to be accomplished before materials comprising a silica-encapsulated extractant could be regarded as a viable alternative to existing extraction chromatographic resins. For example, the current route to preparation yields an assortment of irregular particles (resembling shards of glass) whose chromatographic properties are unlikely to be entirely satisfactory. Clearly then, a facile means to prepare uniform, porous, spherical glass particles containing an extractant is required.

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CHAPTER 4:

STAGNANT PORE PLUGGING AS A MEANS OF IMPROVING THE CHROMATOGRAPHIC EFFICIENCY OF EXC RESINS

4.1 Introduction

A variety of extraction chromatographic materials have been developed over the years and evaluated in a wide range of applications, particularly in the environmental radiochemistry. One of the most important challenges in the use of these materials is the separation of very similar metal ions (*i.e.,* ions of comparable charge and size), which are frequently encountered in nuclear waste treatment, spent fuel reprocessing, and radiochemical analysis. For example, actinide-lanthanide separations remain a challenge despite significant developments in the fields of solvent extraction and ion exchange (4.1). To minimize the long-term radiotoxicity of the by-products of uranium-based nuclear fission, it is important to remove and recover the transuranic elements plutonium, neptunium and americium. Several separation systems are available to effect the separation of plutonium and neptunium (see Chapter 1, Table 1.2). The isolation of americium ($^{241/243}$Am), however, remains difficult due to its chemical similarity to curium and certain lanthanides.

Existing methods for this separation rely on group separations (*e.g.,* Am/Cm from lanthanides) that exploit the presence of ligand donor atoms (extractants) softer than oxygen (*e.g.,* nitrogen, sulfur) for preferential bonding with actinides (4.1). A wide array of ligands have been immobilized onto polymer supports for the separation of actinide elements, including tri-*n*-butyl phosphate (TBP) (4.2, 4.3), tri-*n*-octylamine (4.4, 4.5), Aliquat 336 (tri-caprylylmethylammonium chloride) (4.6, 4.7), *bis*(2-

ethylhexyl)phosphoric acid (HDEHP) (4.8, 4.9), and many others. These extractants have been dispersed onto substrates such as diatomaceous earth, silica, powdered cellulose, and various polymers (4.10). Because of various limitations, however, including inadequate stability and limited capacity, very few of these EXC materials have found widespread application. Especially problematic is their poor selectivity, which makes them unsuitable for the separation of metal ions having the same charge and comparable ionic radii (4.11). Recently, for example, a study on trivalent actinide extraction using commercially available actinides resins (TEVA, TRU, DGA(N), actinide, Ln, Ln2, and Ln3 as manufactured by Eichrom Technologies) found that the elution curves of americium and curium overlap significantly (4.12).

Despite its obvious importance, relatively little attention has been devoted to the separation of such similar cations by EXC, and few systematic studies have been reported in the literature (4.13-4.16). This is likely the result of what has been a major limitation of existing extraction chromatographic materials, namely the significant band broadening of the elution curves (an indication of the poor chromatographic/column efficiency of the materials) normally observed (8.19). Column efficiency, typically expressed in terms of the height equivalent of a theoretical plate (HETP) or number of theoretical plates (N), is a complex function of a number of system characteristics, including mobile phase velocity, the diffusion coefficients of the metal ion in the mobile and stationary phases, particle diameter, temperature, the kinetics of extraction, and the stationary phase thickness (4.17). The ideal EXC resin, from the efficiency perspective, is one consisting of uniform, small-particle size supports bearing a thin, homogeneous layer of a non-viscous extractant capable of rapid reaction with the metal ion(s) of interest. Few, if any, extraction chromatographic materials approach this ideal, however.

Conventional support materials for extraction chromatography contain openings comprising both deep and shallow pores. It is obviously assumed that more time is required for a metal ion to diffuse in and out of a deep pore than a shallow one, due to the longer diffusion path in the former case. This slow diffusion contributes to the band broadening observed in the elution curves of metal ions. In this study, an effort has been made to block the relatively inaccessible (“stagnant”) pores of the support by use of a suitable filler, thus enabling one to load the extractant only into the readily accessible pores. The results show that this “stagnant pore plugging” approach can yield EXC materials (hereafter referred as SPP material) providing narrower elution bands (*i.e.*, higher efficiency) than are achievable with conventional resins.

4.2 Experimental

4.2.1 Materials

The 4,4',(5')-di-(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6) was obtained from EichroM Technologies, Inc. (Darian, IL) and used as received. Polystyrene (MW: 1300, 13000, 123000), polypropylene glycol (PPG) and 1-octanol (99%) were obtained from Alfa Aesar (Heysham, UK). HDEHP was obtained from Sigma Aldrich and purified as described below before use. All solvents (*e.g.*, methanol, acetone, dichloromethane (DCM), propanol, butanol, isopropyl alcohol, toluene, acetonitrile, dimethyl formamide, diethyl ether), used were reagent grade. All water was obtained from a Milli-Q2 system and exhibited a specific resistance of at least 18 MΩ-cm. Radiostrontium (Sr-85) was purchase from PerkinElmer (Shelton, CT), while Europium-152/4 was a generously donation from Argonne National Laboratory.

4.2.2 Instrumentation

The radiotracers were assayed using a Perkin-Elmer Model 2480 Automatic Gamma counter. All thermograms were obtained using a TA Instruments Model Q50 thermogravimetric analyzer. The physical appearance and the phosphorous profile of the materials were determined by Hitachi Model S 4800 field emission scanning electron microscopy (SEM). SEM-EDX experiments were performed on a 20% (w/w) HDEHP-loaded SPP sorbent and commercial 40% HDEHP loaded Ln-resin. To mount the sorbents in the SEM column, a pair of cylindrical graphite poles were used. One of the ends of the pole was cut to make a shape of trapezium, on which two ton adhesive from Devcon (Danvers, MA) was applied and allowed to dry for ~30 minutes. The resin was then spread on top of the trapezium and allowed to settle overnight. The following day, a resin bead was cut in half to expose its interior, thereby permitting examination of the cross-section of the bead under SEM.

4.2.3 Methods

4.2.3.1 Preparation of stagnant pore-plugged EXC materials

Purification of HDEHP. A 1M solution of crude HDEHP was prepared by diluting 200 mL of HDEHP to 600 mL with diethyl ether. A 170 gram portion of $CuSO_4$.5H2O was dissolved in 500 mL of ultra-pure water to yield a 1M solution. The two (immiscible) solutions were then contacted in a 2-liter separation funnel, and 50 grams of NaOH was slowly added. (Twice the stoichiometric amount of $CuSO_4$ was used to ensure a complete reaction). The mixture was shaken vigorously for 15 minutes. When the reaction was complete, the organic phase had acquired a dark blue color, while the aqueous phase was light blue and contained traces of a brown precipitate (excess $Cu(OH)_2$). Because the phases were cloudy and poorly defined, the entire mixture was divided into four bottles and centrifuged at 1800 rpm for 30 minutes. When the two phases separated, the organic phase was carefully decanted and the aqueous phase discarded. To remove particulate matter from the organic phase (containing $Cu(DEHP)_{2)}$, it solution was filtered using Whatman glass microfiber paper (GF/F with a 0.7 micron particle size retention) in a vacuum filtration system.

The filtered $Cu(DEHP)_2$ solution was transferred to a 4 liter beaker and stirred rapidly using a large magnetic stirrer. A 2-L separatory funnel filled with acetone was positioned above the stirring solution and dripped into the solution at a rate of about 2L/hour. As the concentration of acetone increased, blue crystals began to precipitate out of the solution. When approximately 1.5 L of acetone had been added, the excess solution was decanted, and the crystals were filtered and washed 5 times with 20-mL portions of acetone. The crystals (160 grams) were air dried and then re-dissolved in 500 mL of diethyl ether. The purification procedure was then repeated.

The $Cu(DEHP)_2$ was converted back to the acid form by contacting the purified complex in diethyl ether(~150 mL) twice with a 500 mL portion of 0.5 M HCl. To remove any HCl from the ether, the HCl treatment was followed by three 500-mL washings of the organic phase with ultra-pure water. The HDEHP was isolated from the washed organic phase by rotary evaporation at 50˚C under vacuum for 2 hours. About 150 mL of clear and colorless HDEHP was recovered from the original 200 mL of impure amber-colored HDEHP.

Evaluation of Polystyrene as a filler material. In an effort to prepare an EXC material whose stagnant pores were plugged with polystyrene, a commercially available polymeric support, Amberchrom CG-71, was impregnated with polystyrene of various molecular weights using the same type of procedure normally employed to load the support with extractant ("dry impregnation"). Prior to impregnation, portions of the crude (*i.e.*, unpurified, as received) Amberchrom CG-71m resin (Rohm & Haas, Philadelphia, PA) were contacted with water for 30 minutes with occasional swirling. The resulting slurry was transferred to a coarse-fritted glass funnel and the water was removed by vacuum filtration. Methanol was poured over the wet resin and allowed to percolate through the bed under gravity. The remaining methanol was removed by evaporation under vacuum. This process was repeated two additional times or until the methanol washings were clear and colorless. Finally, the resin was water washed until the pH of the washings was ≤7. Beads of this pretreated resin were then mixed with a polystyrene solution prepared by dissolving a known mass of the polymer (corresponding to ~40% (w/w) of the impregnated final materials) in dichloromethane. The mixture was then subjected to vortex mixing and sonication for varying lengths of time to obtain polystyrene-impregnated EXC materials, which were recovered by rotary evaporation under vacuum. Because this process was expected to fill all pores in the support, it was next necessary to partly strip the support of the filler, thereby creating room for extractant loading. This was accomplished by slowly flowing dichloromethane through a known mass of the polystyrene-laden sorbent. The strip solution (*i.e.*, DCM) was collected and the mass of the polystyrene removed was determined both gravimetrically after evaporation of the solvent and by UV-VIS spectrophotometry. Polystyrene not recovered was assumed to remain in the less accessible regions of the support.

Polypropylene glycol (PPG) as filler. Beads of Amberchrom CG-71 were impregnated with polypropylene glycol (PPG) in the same manner described above for polystyrene. Following partial removal of the PPG by stripping with *n*-hexane, the beads were loaded with the extractant of interest by slurrying them in a minimal amount of n-hexane solution of the extractant, followed by slow removal of the hexane by rotary evaporation at room temperature under vacuum. A schematic diagram of the procedure followed is shown in Figure 4.1.

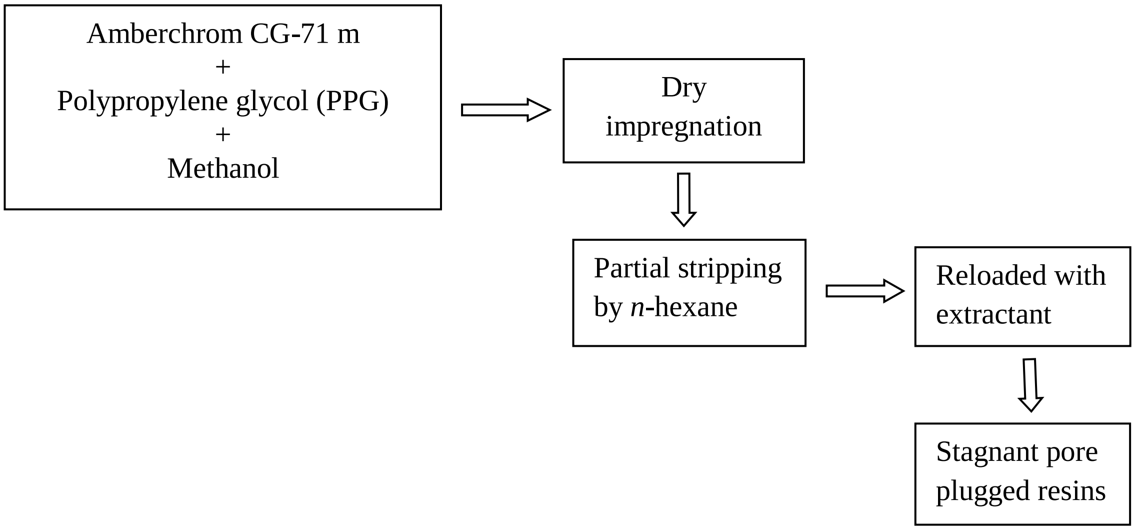


Figure 4.1: Schematic diagram for the preparation of stagnant pore plugged materials.

By changing the quantity of solvent (here, *n*-hexane) used for stripping, the mass of the PPG-filled material taken, and the contact time employed, supports impregnated to various degrees could be obtained. In a typical run, ~4 gm of the PPG-filled resin was placed in a fritted funnel (65 mm porosity C filter disc) and spread uniformly. A 40-mL aliquot of *n*-hexane was then added. The mixture was then subjected to occasional swirling and stirring for 10 minutes. After this, the stripping solution was allowed to discharge and collected in a round-bottom flask. The removal of the *n*-hexane by evaporation under vacuum left a residue, which was then weighed to determine the amount of filler (PPG) stripped from the resin. Following this procedure, a sorbent containing ~50% filler was obtained. By reducing the volume of the strip solution to 20 mL, sorbent incorporating ~75% filler was obtained. Impregnation of these sorbents with the extractant yielded materials containing ~10% and ~20% (w/w) of HDEHP or DtBuCH18C6 (CE) hereafter referred to as HDEHP/CE-SPP (simply SPP) materials.

4.2.3.2 Determination of weight distribution ratios

Solid-liquid (weight) distribution ratios (D_w) for the metal ions of interest (Sr^{2+} and Eu^{3+}) were measured radiometrically using commercial ^{85}Sr and ^{152}Eu radiotracers. Specifically, the uptake of the tracer from a series of nitric acid solutions by the sorbents was measured by contacting a known volume (typically 1.0 mL) of ^{85}Sr or ^{152}Eu-spiked acid solution of appropriate concentration with a known quantity of the sorbent. The ratio of the aqueous phase volume (mL) to the weight of the EXC material (g) typically ranged from 40-50. (This ratio is determined by the need to produce a readily measureable decrease in the aqueous activity by contact with the sorbent). A contact time of ~1 hour (with occasional swirling) was employed for equilibration. Following equilibration, an aliquot of aqueous phase was withdrawn from each culture tube and the activity counted. On the basis of the initial and final activity of a measured aliquot of this aqueous phase (determined *via* gamma spectroscopy according to standard procedures on a Perkin-Elmer 2480 Automatic Gamma Counter), the weight distribution ratio (D_w) of strontium was calculated from the following equation:

$$D_w = [(A_0 - A_f)/A_f]\ (V/w) \qquad (4.1)$$

Here, A_0 and A_f represent the aqueous phase activity (cpm) before and after equilibration, respectively, w is the mass of the resin taken (g), and V is the volume of the aqueous phase (mL).

4.2.3.3 Capacity of the sorbents

For this experiment, a highly concentrated solution (each mL. of solution containing 5 times the stoichiometric amount of the extractant present) of inactive strontium nitrate or europium nitrate (as appropriate) in ~5.8 M nitric acid was made and labeled (spiked) using a Sr-85 or Eu-152 radiotracer. A known quantity the sorbent (typically 20-25 mg) was then placed in a 2 mL plastic disposable column and contacted with 1 mL of the radiotracer-spiked solution. Contact was maintained for ~2 hours, well beyond the period required for equilibrium to be reached. The acidity of the aqueous phase was chosen to provide a distribution ratio for the strontium ion of *ca.* 120-150, corresponding to >99% uptake. Following equilibration, the aqueous phase was withdrawn from the column and its activity determined. From the initial and final (residual) activity of the aqueous phase, the D_w value was determined as described above. If it is assumed that the fraction of non-radioactive strontium taken up corresponds to the fraction of Sr-85 sorbed, then the capacity of the sorbent (mg Sr/g of sorbent) is easily calculated. Similar capacity experiments were conducted for the conventional Ln-resin to permit ready comparison of the performance of the new SPP sorbents to the commercial material.

4.2.3.4 Column preparation and characterization

To pack a column, a small quantity of the SPP material was slurried in deionized water, and aliquots of the slurry were transferred into a Bio-Rad Econocolumn (5.0 mm i.d. by 5 cm in length). Packing was carried out under gravity flow. When the column bed reached the desired height, a small plug of glass wool was placed atop it so that it would not be disturbed by the introduction of a sample. The packed sorbent was then rinsed with several free column volumes of deionized water. Prior to introduction of a sample, the column was preconditioned with 5-10 free column volumes of an appropriate nitric acid solution. Flow rates of ~2-3 mL cm^{-2} min^{-1} were typically employed.

Column parameters such as the bed density, the volume of stationary phase, (v_s, the volume of liquid extractant solution contained in the pores of the support), and the volume of mobile phase (v_m, also known as free column volume (FCV)) were either measured or calculate using the characteristics of the sorbents and the column listed in Table 4.1. In particular, the bed density was determined from the weight of the chromatographic material required to prepare a bed of known volume.

The density of the conventional EXC materials was determined by two different methods. In the first, the volume of water displaced by a known mass of sorbent suspended in water in a volumetric flask was measured. In the second, a portion of the

EXC material was added to solutions containing varying concentrations of nitric acid until a concentration was found in which the sorbent remained suspended after centrifugation. At this point, the density of the EXC material is the same as the density of the acid solution. The average of the two values was used in all calculations.

The volume of mobile phase (*i.e.*, the free column volume, v_m) was calculated from the difference in the bed volume and the volume of resin in the bed. The latter volume was determined from the weight of the EXC material in the bed and its density. The volume of stationary phase, v_s, was determined from the weight of EXC material in the column, the resin loading (*i.e.*, the weight percent of extractant or extractant diluent solution present in the resin), and the density of the extractant or its solution. Table 4.1 summarizes the characteristics of the 20% HDEHP loaded stagnant pore plugged sorbent and compared with conventional Ln-resin.

Table 4.1 Characteristics of 20% HDEHP-loaded SPP sorbent and conventional Ln-resins and packed columns

Bulk materials	**20% HDEHP loaded SPP sorbents**	**40% HDEHP loaded conventional sorbents**
Stationary phase	HDEHP	HDEHP
Support	Amberchrom CG-71m	Amberchrom CG-71m
Particle diameter	75 µm	75 µm
Extractant loading	~20%	~40%
Density of extractant-loaded beads	1.16 g/mL	1.14 g/mL
Packed columns		
V_s, mL/mL of bed	0.07	0.15
Bed density (g/mL)	0.35	0.36
V_m, mL/mL of bed (also FCV)	0.70	0.69
V_s/V_m	0.10	0.22
Capacity, mg Eu/mL of bed	2.68	11.04

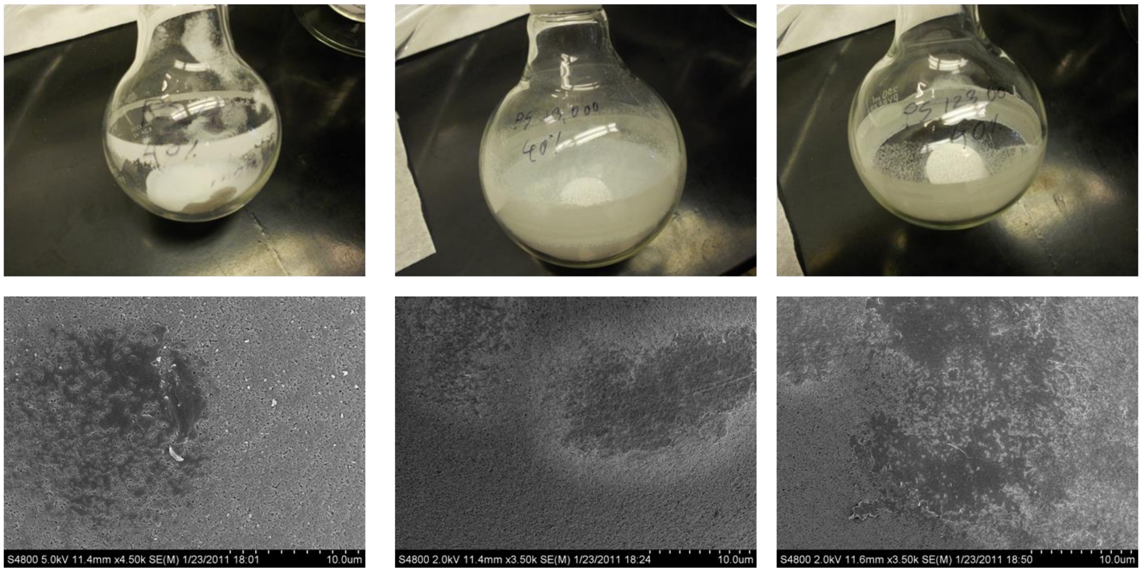
4.2.3.5 Elution curves for europium

The elution profile of europium on packed beds of both 20% (w/w) HDHEP-SPP materal and 40% (w/w) HDEHP-loaded conventional Ln-resin was determined employing Bio-Rad Econocolumns using HNO_3 as the eluent. The characteristics of the packed columns were determined prior to the experiment following the procedures outlined above. For SPP materials, a solution 0.16 M HNO_3 was used as the eluent, while a solution of 0.30 M HNO_3 was used with the conventional material. After conditioning the columns with the appropriate eluents, a small quantity (~10 μL) of ^{152}Eu in 0.05 M HNO_3 was introduced at the top of the bed and then eluted with appropriate nitric acids. Samples of the eluent were collected at various intervals and γ counted. The columns were subjected to slight pressure applied using the bulb of a Pasteur pipette, yielding a flow rate of ~2-3 ml/cm^{2}min. All runs were carried out at ambient temperature (23-25°C).

4.3 Results and Discussion

4.3.1 Development of a method for plugging stagnant pores in an EXC support

The concept of stagnant pore plugging is based on the idea that if a porous bead is filled with an inert material and then stripped, the peripheral filler will be removed first, yielding a sorbent whose inner pores are plugged with the filler. In our initial studies, polystyrene, a widely used solid support for EXC materials available in a wide range of molecular weights was employed to plug the stagnant pores. Polymers of three different molecular weights (1300, 13000, and 123000) were used to prepare sorbents with two different degrees of extractant loading (20% and 40% (w/w)). Figure 4.2 shows typical results, and indicates that the impregnation process was not complete. That is, as can readily be seen (upper panels), some of the polystyrene adheres to walls of the flask. In addition, scanning electron microscopy reveals (lower panels) the presence of patches of polystyrene on the surface of the beads. Clearly then, much of the polymer initially added does not end up in the bead interior as intended. Nonetheless, some polystyrene was incorporated. Unfortunately, this was not found to be reproducible, indicating that SPP sorbents cannot be prepared using polystyrene as a filler. The apparent unsuitability of polystyrene as a filler is likely related to its high molecular weight, high viscosity and hydrophobicity, all of which could serve to render it difficult for polystyrene molecules to penetrate the interior of the Amberchrom beads.



Polystyrene: MW-1,300 Polystyrene: MW-13,000 Polystyrene: MW-123,000

Figure 4.2: Stagnant pore plugging using polystyrene as filler. (Top panel). Photographs demonstrating incomplete impregnation of the beads. (Bottom panel). Scanning electron micrographs showing patches of polystyrene on the surface of the beads.

As an alternative to polystyrene, polypropylene glycol (PPG), a hydrophilic liquid polymer, with low molecular weight (M.W. 400), was evaluated as a filler material. PPG-impregnated materials (40% (w/w)) were easily obtained by physical impregnation using methanol as the volatile solvent. The partial removal of PPG from the impregnated beads was not straightforward, however. In principle, any of a variety of solvents could be used to accomplish this removal, among them methanol, propanol, butanol, isopropyl alcohol, dichloromethane, toluene, acetonitrile, dimethyl formamide, diethyl ethyl and *n*-hexane), but with many of these, control of the rate/extent of PPG removal proved difficult. Eventually, isopropyl alcohol, acetonitrile and n-hexane were found to dissolve PPG relatively slowly. In this study, n-hexane was chosen to strip PPG from the resin. Following partial PPG removal, the beads were impregnated with an appropriate extractant.

4.3.2 Phosphorus profile

SPP materials impregnated with HDEHP were examined by energy dispersive X-ray analysis (SEM-EDX) to determine the distribution of the phosphorus (and thus, extractant) in the bead. It was anticipated that filler removed in the stripping step would come from the periphery of the beads, so that the HDEHP would reside in the near-surface regions. Figure 4.3 shows the phosphorus profiles for a conventional Amberchrom CG-71 resin loaded to 40% (w/w) with HDEHP (left panel) and 20% HDEHP-loaded SPP materials (right panel). As hoped, phosphorus (and thus, HDEHP) is present throughout the entirety of the conventional resin, but is confined to the outer edges in the SPP material.

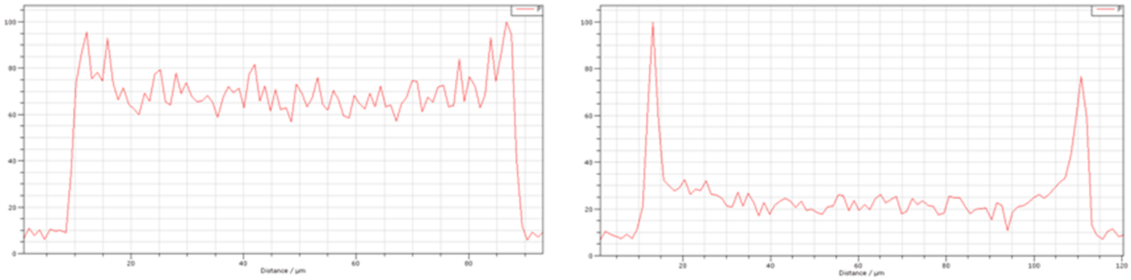


Figure 4.3 Phosphorus profiles obtained using SEM-EDX for conventional Ln resin (left panel) and a stagnant pore plugged (right panel) sorbent containing HDEHP.

4.3.3 Elution profiles for europium-152/4

To determine the effect of the differing distribution of the extractant within the beads on the chromatographic efficiency of the two sorbents (conventional Ln resin and the SPP material) the elution profile of Eu^{3+}-152/4 was obtained for columns of both resins. The characteristics of the materials and the packed columns are summarized in Table 4.1. So that the band spreading of the elution curves could be compared at similar values of k' (*i.e.*, the number of free column volumes to peak maximum), the acidity of the eluents used was adjusted. Figure 4.4 depicts the elution profiles obtained using the two sorbents. As can be seen, the elution band is clearly narrower for the SPP resin, consistent with higher column efficiency. The number of theoretical plates (N), a quantitative measure of this efficiency (4.18), is 17 and 43, respectively, for the Ln-resin and the SPP resin. From N, another measure of efficiency, the height equivalent of a theoretical plate (HETP), can be calculated as 2.35 mm and 0.93 mm, respectively, for the Ln-resin and the SPP material. These parameters imply that the efficiency of the SPP material is *ca.* 2.5 times that of the regular Ln-resin.

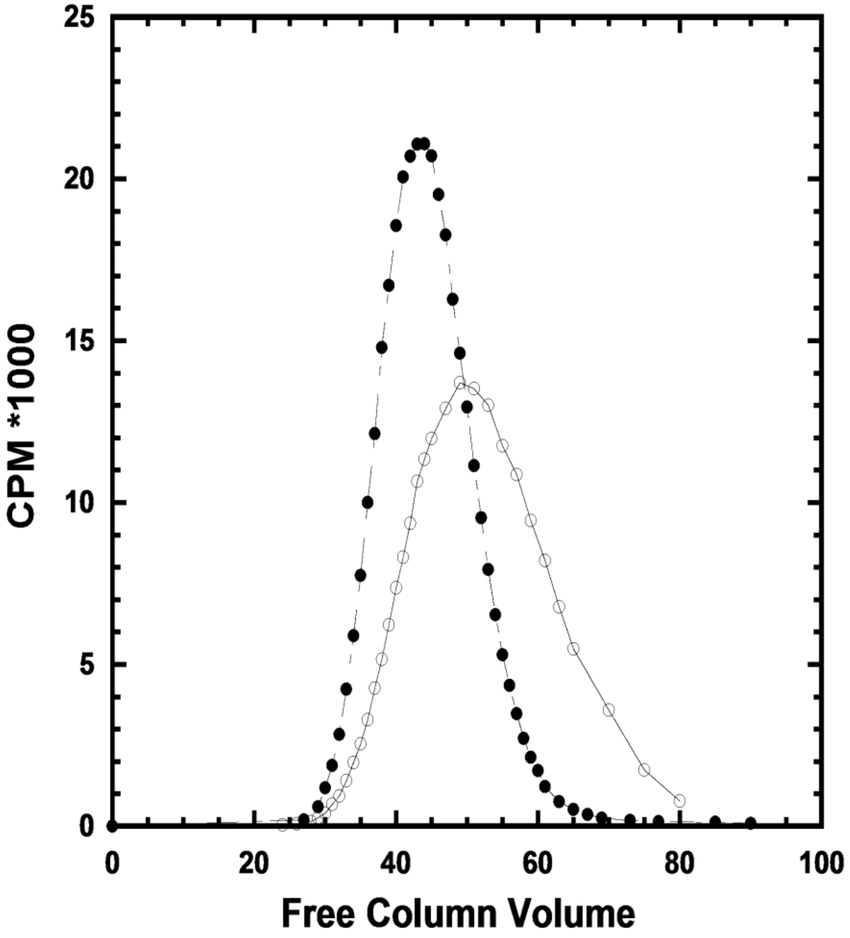


Figure 4.4 Europium (as $^{152/4}Eu^{3+}$) elution profiles on conventional Ln-resin and on the analogous SPP material. (Eluent : 0.30 M HNO_3 for Ln-resin and 0.16 M HNO_3 for SPP resin; flow rate : 2-3 mL/cm^2/minute; temperature: ~23°C; open circle: regular Ln-resin; filled circles: SPP resin). (The smooth curves are intended only as a guide to the eye.)

4.3.4 Metal ion uptake studies on conventional and stagnant pore plugged materials

It was expected that the SPP materials could exhibit lesser metal ion uptake than conventional EXC materials due to the reduced level of extractant loading (20% *vs.* 40% employed for the SPP resins. Indeed, both the SPP Ln-resin and SPP Sr-resin showed lower metal ion uptake at a given acidity (as reflected in the values of D_w) than the corresponding conventional sorbents (Figure 4.5). If we assume that the reduction in HDEHP loading for the SPP resin is equivalent to reducing its concentration by a factor of two and we assume that the extraction (*i.e.*, uptake) of europium will exhibit a third-power dependence on HDEHP concentration (4.19), a factor of 8 decline in $D_{w, Eu}$ should be observed, and the uptake results (left panel), which differ by a factor of ~8, are consistent with this. Along these same lines, the *ca.* 50% reduction in crown ether loading, along with the first power dependence of D_{Sr} on DtBuCH18C6 concentration (4.20), indicate that $D_{w,Sr}$ values on the SPP resin should be approximately half those observed under the same conditions. In fact, this is observed until high aqueous acidities are reached (Figure 4.5; right panel). Thus, the improved efficiency of the SPP sorbents appears to come at the expense of reduced uptake. Except at high acidities for SPP-Sr resin, however, this problem can be reduced simply by changing the aqueous acidity to boost retention.

As expected, the stagnant pore-plugged materials showed faster kinetics in case of SPP Ln-resin compare to those of conventional Ln-resin (Figure 4.6- left panel). Unexpectedly, for the Sr-resins (plugged or conventional) the differences in the rate of Sr uptake are not significant, as both resins equilibrate quickly (Figure 4.6-right panel).

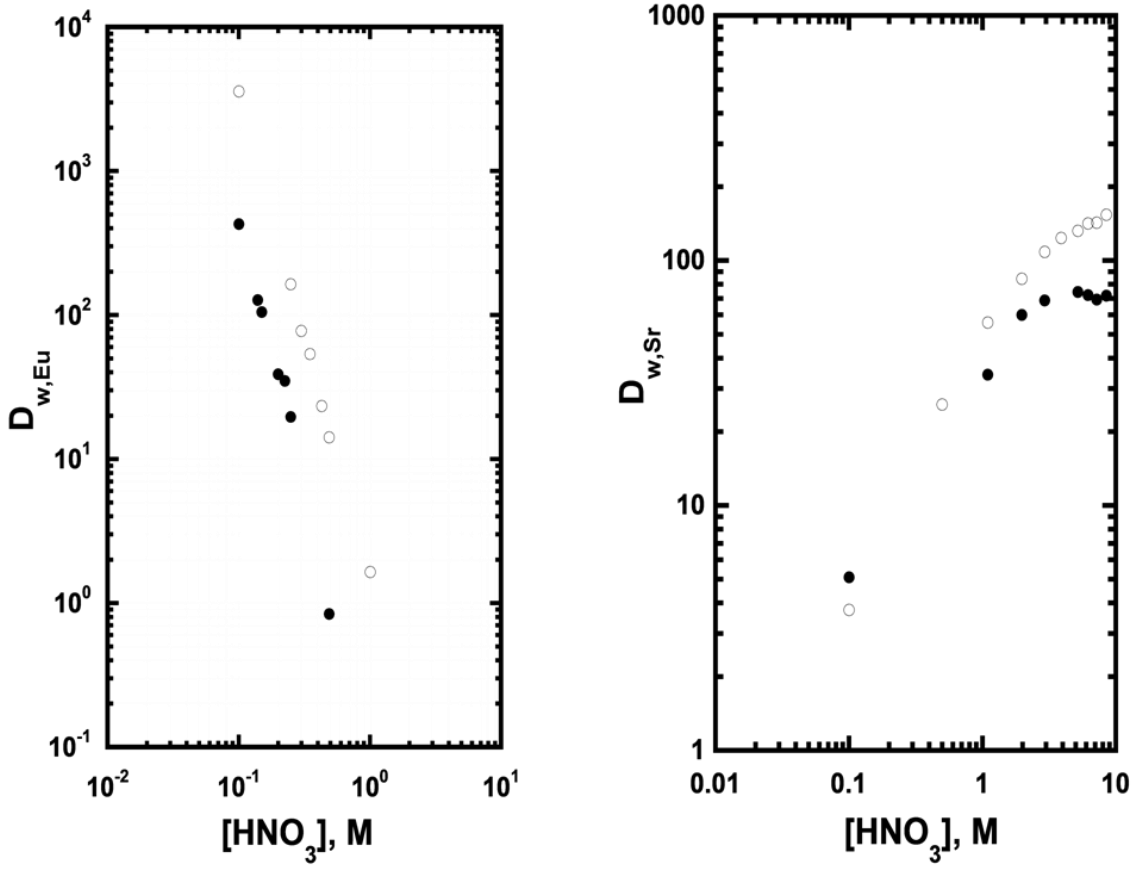


Figure 4.5 Effect of nitric acid concentrations on europium (left panel) and strontium (right panel) sorption by SPP resins (filled circle) and conventional resins (open circle). (SPP resins are loaded with 20% (w/w) HDEHP or DtBuCH18C6 for Eu and Sr, respectively. Conventional resins incorporated 40% (w/w) of the same extractants).

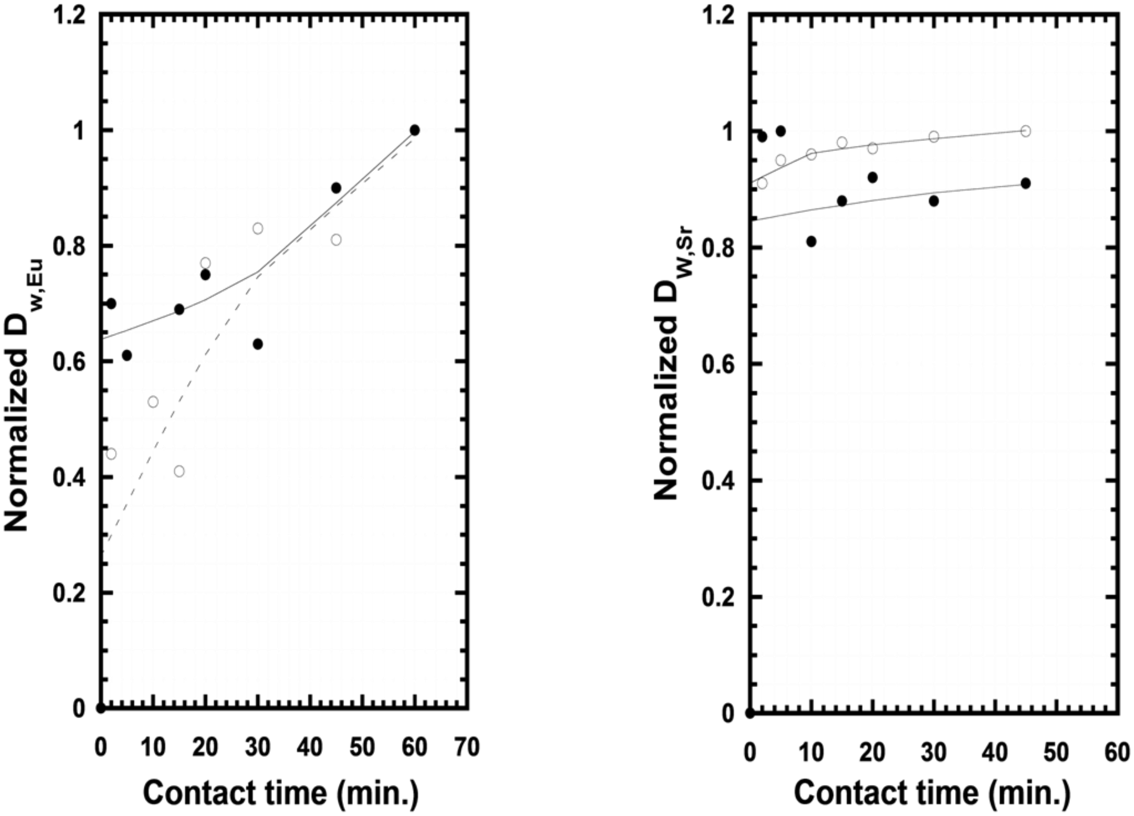


Figure 4.6: Left panel: Uptake kinetics for Eu-152/4 on SPP Ln resin (●), and conventional Ln resin (○) from ~0.1 M nitric acid; Right panel: Uptake kinetics for Sr-85 on SSP Sr resin (●) and conventional Sr resin (○) ~3 M nitric acid. ((The smooth curves are intended only as a guide to the eye.)

4.3.5 Capacity of the stagnant pore plugged resins

The theoretical and experimental capacities for the SPP Ln and Sr resins and their conventional counterparts are listed in Table 4.2. The experimental capacity for the regular Ln-resin shows almost complete utilization of the theoretical capacity, whereas the experimental capacities for the SPP Ln-resins are unexpectedly (and inexplicably) significantly lower than the theoretical capacity of the sorbents. In case of Sr-resin interpretation of the percent utilization of the theoretical capacity is more problematic, given that DtBuCH18C6 exists in a multitude of isomeric forms, not all of which extract strontium well.

Table 4.2: Capacity of the stagnant pore plugged and corresponding regular sorbents

Sorbents	Capacity (mg/g)	
Ln-resins	Theoretical	Experimental
~10% HDEHP loaded SPP	5.66	0.9
~20% HDEHP loaded SPP	13.83	7.67
~40% HDEHP regular resins	31.42	30.67
Sr-resins		
~20% CE loaded SPP	15.18	9.82
~40% CE loaded regular resins	36.15	26.78

4.5 Conclusions

Extraction chromatographic materials exhibiting improved column efficiency can be prepared by blocking the deep pores of a conventional EXC support with an appropriate filler such as polypropylene glycol. Studies of one such material, SPP Ln-resin, using SEM-EDX confirms the hypothesis that extractant loaded into the SPP beads remains on the periphery, while the core of the beads is plugged by the filler. The elution profile of europium on this new material showed that the SPP Ln-resin provides a narrower elution band than does conventional Ln-resin. In fact, based on the plate number (N) and plate height (H), the efficiency of a packed column of the SPP Ln-resin is more than twice that of a conventional Ln-resins column. Because of the reduced amount of extractant in the support, the metal ion uptake is reduced, and unexpectedly, the percent utilization of the theoretical capacity of the SPP sorbents also declines. For the SPP Sr-resin, the uptake efficiency and percent utilization of the theoretical capacity are greater than that of SPP Ln resin. Additional study is needed to determine the cause(s) of the incomplete capacity utilization and the effect of various types of filters on the SPP resin performance.

4.6 References

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CHAPTER 5:

DEVELOPMENT OF HIGH CAPACITY EXTRACTION CHROMATOGRAPHIC MATERIALS BASED ON POLYSULFONE CAPSULES

5.1 Introduction

Because of the ability of commercially available supports to hold and retain an extractant is limited and because extractants are frequently diluted with an organic solvent to improve the kinetics of metal ion uptake (by reducing the stationary phase viscosity), the metal ion sorption capacity (*i.e.,* the maximum loading of metal ion possible) of conventional EXC materials is typically low, often only a few mg per mL of bed volume. As a result, in many applications, inconveniently large columns may be required to avoid extractant saturation (*i.e*., column overload). To overcome this problem, higher capacity EXC materials are clearly required. Previous work indicates that polymer microencapsulation techniques may yield materials containing much more extractant per unit mass than is found in any conventional material (5.1-5.3). In one study, for example, applying a modified dry-impregnation technique (described below) yielded microcapsules capable of holding up to 11.8 mL solvent per gram of (polysulfone) capsules (5.1). This enormous capacity for solvents clearly opens up the possibility of producing very high capacity (*i.e.,* high extractant content) EXC materials.

Microencapsulation is a process in which small solid particles, liquid droplets, or gas bubbles are enveloped by a coating. Depending on the conditions used for preparation, the capsules produced can vary widely in size, from less than 1μm to several thousand microns. Those smaller than 1μm are known as nanocapsules , while those between 1 and 1000 μm are termed microcapsules (5.4). Capsules greater than 1000 μm are referred to as macrocapsules (5.4). Encapsulation offers a number of potential advantages as an approach to preparing EXC materials, including simplicity and the ability to produce materials exhibiting high porosity, active component content, and mechanical strength (5.5). Since its beginnings in the 1950s as a means to prepare capsules containing dyes for carbonless copy paper, the use of encapsulation technology has increased considerably (5.6). Today the technology is employed in numerous fields, among them metal ion (5.7-5.16) and organic acid separations (5.1, 5.3, 5.17, 5.18), protection of food ingredients (5.19), controlled release of perfumes (5.2, 5.20) and drugs (5.4), and the isolation of solvents (5.3). In these applications, a variety of materials, including polysaccharides, proteins, cellulose ether, synthetic and bio-polymers, carbohydrates, and glycerides have been employed to synthesize capsules (5.4).

Microcapsules are prepared in one of three ways: coacervation methods (phase inversion), physical/mechanical methods such as solvent evaporation or a spray-drying, and polymerization methods. In this study, polysulfone (PS) was used to prepare the microcapsules. PS is a well-known and widely-used polymer that offers high chemical and physical stability, excellent thermal, electrical and creep resistance over a wide range of temperatures, and low toxicity (5.21). Both the phase inversion and solvent evaporation methods were used to synthesize the capsules. The microcapsules prepared were then impregnated with 4,4',(5')-di-(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6) in an effort to prepare a strontium-selective sorbent. This novel, polysulfone capsule-based strontium sorbent has been characterized and its properties compared to those of a commercially available EXC resin for strontium.

5.2 Experimental

5.2.1 Materials

The 4,4',(5')-di-(*tert*-butylcyclohexano)-18-crown-6 (DtBuCH18C6) was obtained from EichroM Technologies, Inc. (Darian, IL) and used as received. 1-octanol (99%) was obtained from Alfa Aesar (Heysham, UK). Polysulfone (PS) average M_n (number average molecular weight) ~22,000 by MO (monomer molecular weight) beads were purchased from Sigma Aldrich (St. Louis, MO) and used as received. Optima™ grade nitric acid and HPLC grade methanol were obtained from Fisher Scientific (Waltham, MA). Dimethyl formamide (DMF) (99.8%) was obtained from BDH (Philadelphia, PA) and used as received. All water was obtained from a Milli-Q2 system and exhibited a specific resistance of at least 18 MΩ-cm. Amberchrom CG-71m was obtained from Rohm and Haas Company (Philadelphia, PA) and preconditioned before use as described previously (5.26). Gelatin was obtained from Ward's Science (Rochester, NY) and used as received. Radiostrontium isotope (Sr-85) and radiocalcium (Ca-45) were received from PerkinElmer (Shelton, CT) and radiotracers of Na-22 and Ba-133 were purchased from Eckert and Ziegler Isotope Products, Inc. (Valencia, CA).

5.2.2 Instrumentation

Gamma emitting isotopes were assayed using a Perkin-Elmer 2480 Automatic Gamma counter. All thermograms were obtained using a TA Instruments Model Q50 thermogravimetric analyzer. Scanning electron microscopy (SEM) was carried out on a Hitachi Model S 4800 field-emission scanning electron microscope (SEM). The porosity of the materials was evaluated *via* BET measurements, specifically, the determination of

N_2 adsorption-desorption isotherms at 77 K using a Micromeritics ASAP 2020 instrument. Liquid scintillation counting was performed using a PerkinElmer Tri-Carb 2810 TR Series liquid scintillation counter equipped with QuantaSmart software.

5.2.3 Methods

5.2.3.1 Synthesis of polysulfone capsules

Phase inversion method. In the phase inversion method, a solution of a polymer in an organic solvent is contacted with a “non-solvent” (also known as “anti-solvent”) in which the polymer is insoluble to yield capsules. Here a solution of PS in DMF (PS : DMF = 1 : 10 (v/v)) (5.1, 5.18) obtained by overnight stirring at room temperature was dispersed into a non-solvent-containing bath consisting of 30% (v/v) ethanol in water. A burette equipped with a specially designed tip whose outer diameter is 1 mm was used to deliver the solution to the anti-solvent bath. A distance of 7 cm was maintained between the tip of the burette and the surface of the anti-solvent (5.1). The PS capsules obtained by this route consisted of *macro*capsules averaging ~2 mm in diameter. Figure 5.1 summarizes the phase inversion procedure and depicts the macrocapsules obtained by this approach.

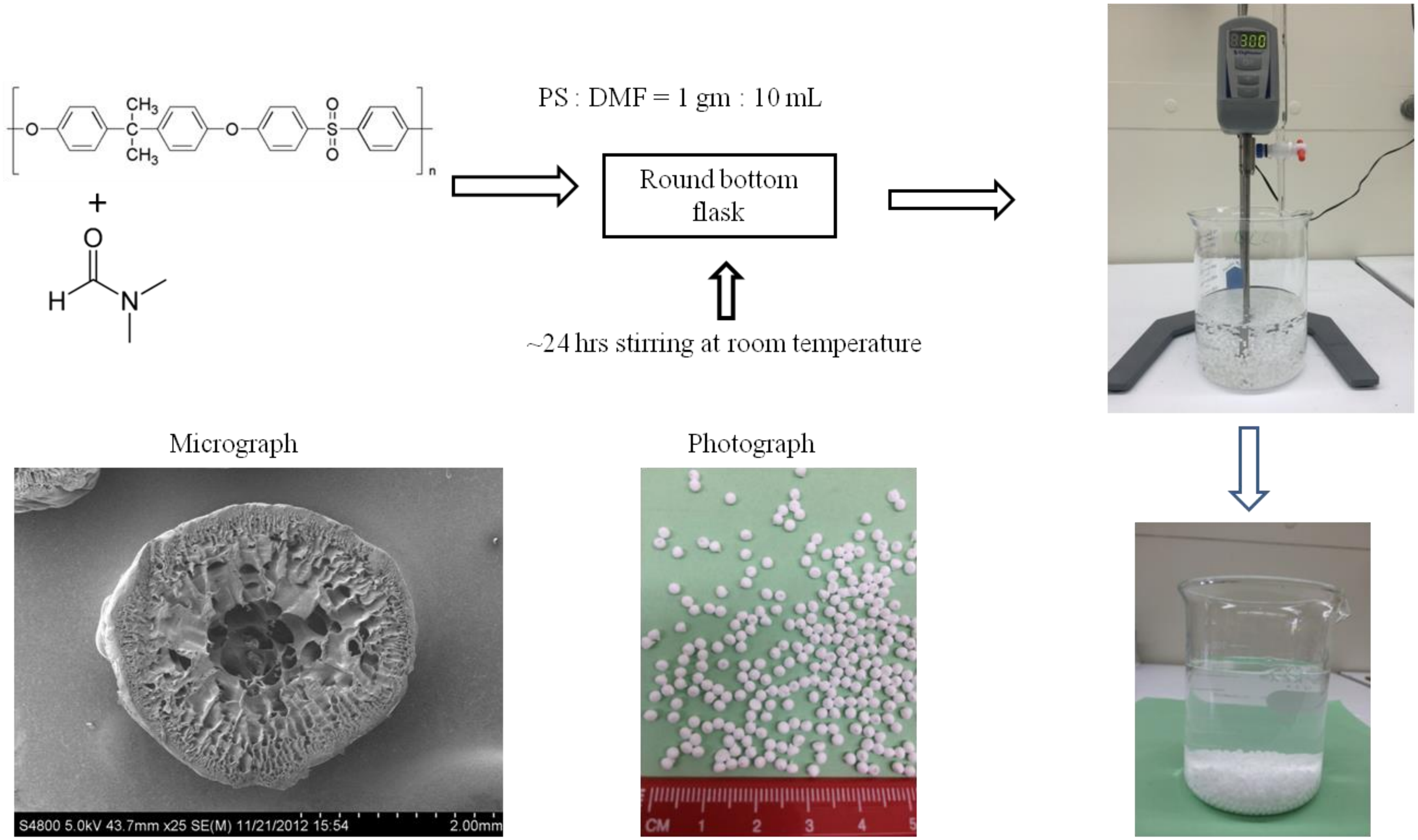

Figure 5.1: Synthesis of macrocapsules using phase inversion method

The preparation of *micro*capsules (size 1 μm to 1000 μm) was accomplished by employing an airbrush (Crescendo^{TM} Model 175^{TM} M Air-Brush) to disperse the polymer solution into the non-solvent, as shown in Figure 5.2 (5.2). Specifically, an airbrush was positioned 50 cm above the non-solvent surface and the polymer solution sprayed perpendicularly onto the surface of the bath. A wide range of microcapsule sizes (~20 to ~300 μm) were produced by this technique. As a result, it was necessary to carefully sieve (USA Standard Testing Sieves; 53 μm and 106 μm), the capsules to obtain materials in the desired size range. A light water jet was used to force the microcapsules through the sieves, thus allowing the separation of capsules of the size required for chromatographic applications (50-100 μm) without disrupting the spherical morphology of the capsules. The polysulfone capsules thus obtained predominantly in the 53-106 μm size range, were stored in the non-solvent solution until use.

Solvent evaporation method. A second method, the solvent evaporation technique, was also employed to prepare microcapsules. In this approach, a solution of PS and the extractant (DtBuCH18C6) in DCM was dispersed in a continuous phase consisting of a 0.5% (w/v) solution of gelatin in water. Using an overhead stirrer, an oil-in-water emulsion was generated from this mixture. In a typical run, 2 g of polymer and 1 g of CE dissolved in 25 mL of DCM were added to 500 mL of continuous phase in a 1 L beaker and then subjected to vigorous agitation (~650-800 rpm) under ambient conditions (5.8). The size of the capsules was manipulated by varying the speed, with higher speeds yielding smaller particles (5.8). After 2 hrs of stirring, the DCM was allowed to evaporate completely. The PS microcapsules produced settled at the bottom of the beaker and were collected. Here too, sieving was necessary to obtain capsules in the desired size range.

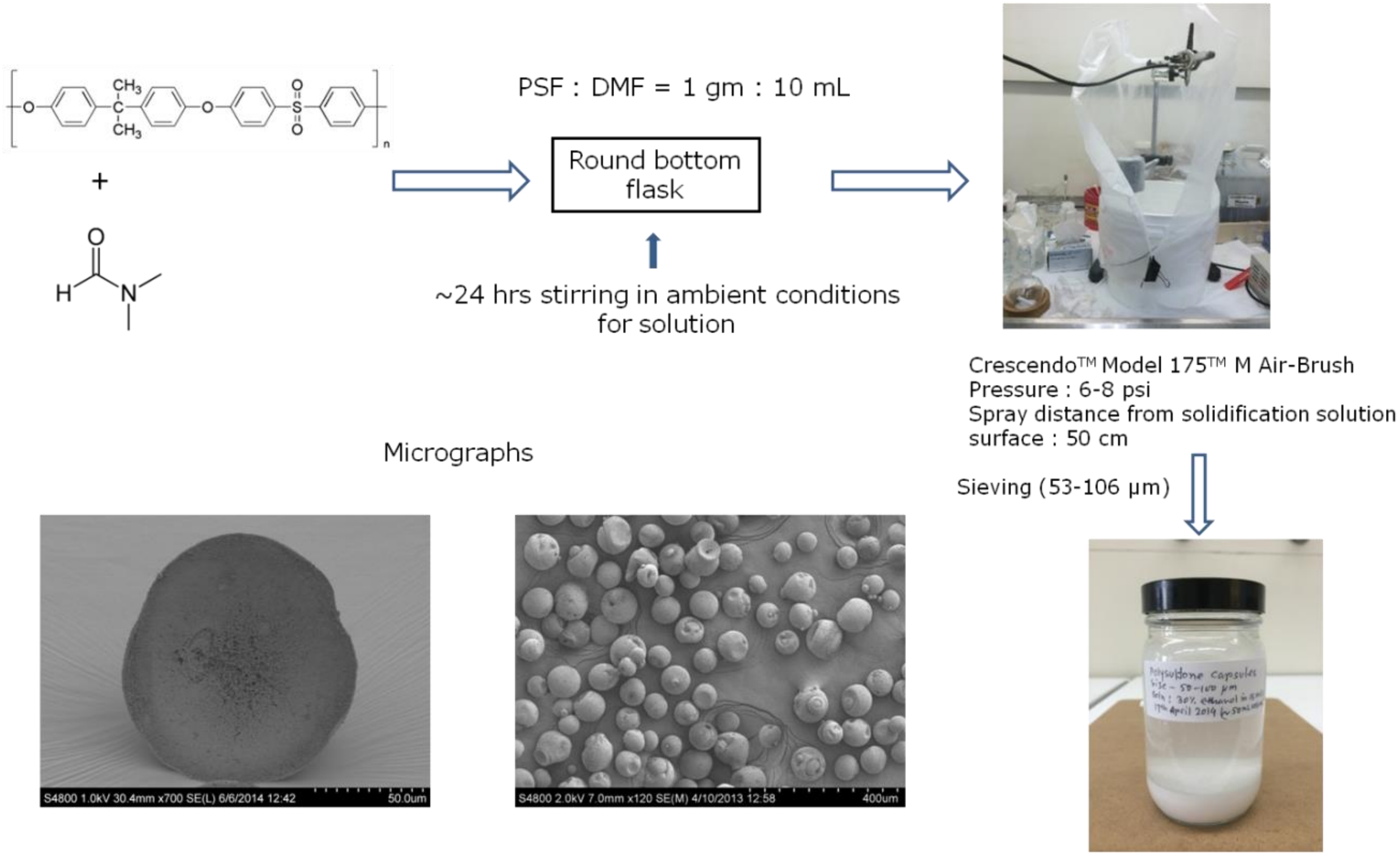

Figure 5.2: Synthesis of microcapsules using phase inversion method

The capsules were stored in water until characterization, which was performed after drying the capsules in a vacuum oven at 50ºC overnight. Microcapsules not loaded with extractant were made following the same general procedures.

5.2.3.2 Loading of extractants in polysulfone capsules and in conventional resin

Conventional EXC materials are prepared by the physical impregnation of a porous solid support with an extractant by any of several techniques (5.21, 5.26). Most commonly, the support material is contacted with a solution of the extractant (neat or with diluent) in a volatile solvent, which is slowly removed by evaporation under vacuum. Impregnation of dried capsules in this way is not feasible, as the pore structures of the capsules would be damaged or deformed during the drying process. Therefore, an alternative technique was employed. That is, a weighed amount of vacuum-filtered wet capsules was used for impregnation. The dried mass (skeletal mass) of this material was calculated from the dry mass of another sample of the same capsules measured separately. Water-containing capsules were employed to ensure that the capsule morphology remained undisturbed. These wet capsules were soaked in a solution of DtBuCH18C6 in methanol. To achieve maximum impregnation efficiency, the mixture was vortex mixed and subjected to sonication for one hour. Solvents (*i.e.,* methanol, water and residual DMF) were then removed by rotary evaporation under vacuum (23-25 in Hg) at 75°C. At times during this evaporation process, the capsules were observed to cling to the wall of the round bottom flask. At this point, the vacuum was lowered to ~15 in. Hg, which was found to improve the efficiency of impregnation. Using this general procedure, a series of extractant-loaded capsules were synthesized, including macrocapsules containing, for example, ~50% (w/w) neat DtBuCH18C6 or its 1 M solution in 1-octanol, macrocapsules containing ~40% (w/w) neat HDEHP, and microcapsules containing 28, 42, or 60% (w/w) DtBuCH18C6. Attempts to prepare capsules impregnated with more than ~60% (w/w) extractant did not yield satisfactory results, as evidenced by their sticky physical appearance.

In an effort to improve the impregnation technique, the water in the wet capsules was replaced with methanol before mixing the capsules with the extractant solution. For this modification, the capsules were first placed on a fritted funnel and washed with 18.2 MΩ water to remove ethanol and any residual DMF. Methanol was then used to wash the capsules, thereby replacing the water. The mass of the dried capsules was measured by using a one-milliliter volumetric flask. The mass after drying of this volume wet capsules was taken as the dry mass of that volume of wet capsules. The remaining procedures were the same as those described (above) for the dry impregnation technique, with the exception of carrying out the rotary evaporation at 50ºC. Using this modified method involving methanol for the preparation of extractant loaded capsules, microcapsules incorporating ~42% (w/w) neat DtBuCH18C6, and either ~45% or ~62% (w/w) 1 M DtBuCH18C6 in 1-octanol were prepared. Note that the microcapsules containing ~45% (w/w) of a 1 M solution of DtBuCH18C6 (here after referred to as "Sr-PSC") correspond closely to the conventional Sr-Spec resin, which contains 40% (w/w) of a 1 M solution of DtBuCH18C6. Along these same lines, microcapsules incorporating ~62% (w/w) of the 1 M solution DtBuCH18C6, which exploit the high loading capacity of the capsules are hereafter referred to as high capacity Sr-PSC ("HC Sr-PSC") capsules.

To determine the percentage of the extractant or its diluent in the microcapsules, a DSC T_{zero} pan capped with a T_{zero} lid into which 8 holes had been needle-bored was used.

The use of a capped pan minimized the noise of the thermogram and yielded extractant mass loss well resolved from that of the PS skeleton.

5.2.3.3 Determination of weight distribution ratios

Solid-liquid (weight) distribution ratios (D_w) for strontium were measured radiometrically using a commercial ^{85}Sr radiotracer. Specifically, the uptake of the tracer by the capsules from a series of nitric acid solutions was measured by contacting a known volume (typically 1.0 mL) of ^{85}Sr-spiked acid solution of appropriate concentration with a known quantity of capsules. Because the capsules float in aqueous solution, for these measurements, they were held between two porous plastic frits in a 2-mL disposable plastic column (Eichrom Technologies, Lisle, IL) to ensure adequate contact between the capsules and aqueous solution. The ratio of the aqueous phase volume (mL) to the weight of the solid sorbent (g) typically ranged from 40-50. (This ratio is determined by the need to produce a readily measureable decrease in the aqueous activity by contact with the sorbent.) Depending on the kinetics of tracer uptake by the sorbent, a contact time of 2-4 hours (with occasional swirling) was employed for equilibration. Following equilibration, the upper frit of the column was pushed down using a glass rod and an aliquot of the aqueous phase was withdrawn. On the basis of the initial and final activity of a measured aliquot of this aqueous phase (determined *via* gamma spectroscopy according to standard procedures on a Perkin-Elmer 2480 Automatic Gamma Counter), the weight distribution ratio (D_w) of strontium was calculated from the following equation:

$$D_w = [(A_0 - A_f)/A_f]\ (V/w) \qquad (5.1)$$

Here A_0 and A_f represent the aqueous phase activity (cpm) before and after equilibration with the sorbent, respectively, w is the mass of the resin taken (g), and V is the volume of the aqueous phase (mL).

5.2.3.4 Metal ion uptake kinetics

Into a series of 2-mL disposable plastic columns, each containing the same (± 10%) amount (20 mg) of extractant-loaded PS capsules, was introduced a known volume (typically 1 mL) of an appropriate nitric acid solution containing a Sr-85 radiotracer. As described above, the capsules were held between the frits ensure good contact with the aqueous solution. At various time intervals following the introduction of the tracer solution, during which the samples were periodically mixed using a vortex mixer to facilitate equilibration, the upper frit was pushed down by a glass rod and the aqueous phase withdrawn. The activity of this aliquot was determined and from the initial and final activity of the aqueous phase, D_w values were determined. A plot of the contact time dependence of D_w was then prepared.

5.2.3.5 Capacity of the sorbents

For this experiment, a highly concentrated (5 times the stoichiometric amount of the extractant present) solution of inactive strontium nitrate in 5.89 M nitric acid was prepared and labeled (spiked) using Sr-85 radiotracer. A known quantity of extractant-loaded capsules (typically 20-25 mg) was then placed in a 2-mL plastic disposable column and contacted with 1 mL of this solution. Contact was maintained well beyond (4x) the period required for equilibrium to be reached. The acidity of the aqueous phase was chosen to provide a distribution ratio for the strontium ion of *ca.* 120-150, corresponding to >99% uptake. Following equilibration, the aqueous phase was withdrawn from the column and its activity determined. From the initial and final (residual) activity of the aqueous phase, the D_w value was determined as described above. If it is assumed that the fraction of non-radioactive strontium taken up corresponds to the fraction of Sr-85 sorbed, then the capacity of the sorbent (mg Sr/g of solvent) is easily calculated. Similar capacity experiments were conducted for the conventional Sr-resin to permit ready comparison of the performance of the new sorbents to the commercial material.

5.2.3.6 Column preparation and characterization

To pack a column, a small quantity of sorbent was slurried in deionized water, and aliquots of this slurry were transferred into a Bio-Rad Econocolumn (5.0 mm i.d. by 5 cm in length). Packing was carried out under gravity for the conventional materials. For capsules, which tend to float in water, pressure (5-10 psi) was applied. When the bed reached the desired height, a small plug of glass wool was placed atop it so that it would not be disturbed by the introduction of a sample. The packed sorbent was then rinsed with several free column volumes of deionized water. Prior to introduction of a sample, the column was preconditioned with 5-10 free column volumes of an appropriate nitric acid solution. Flow rates of ~2-3 mL/ cm^2min were typically employed.

Column parameters such as the bed density, the volume of stationary phase, (v_s, the volume of liquid extractant solution contained in the pores of the support), and the volume of mobile phase (v_m, also known as free column volume (FCV)) were measured using the characteristics of the sorbents and the column dimensions. In particular, the bed density was determined from the weight of the chromatographic material required to prepare a bed of known volume.

The density of the conventional EXC materials was determined by two different methods. In the first, the volume of water displaced by a known mass of sorbent suspended in water in a volumetric flask was measured. In the second, a portion of EXC material was added to solutions containing varying concentrations of nitric acid until a concentration was found in which the sorbent remained suspended after centrifugation. At this point, the density of the EXC material is the same as the density of the acid solution. The average of the two values was used in all calculations. For the capsules, the density of the polysulfone, CE and 1-octanol was used to calculate the density of the loaded capsules.

The volume of mobile phase (*i.e.,* the free column volume, v_m) was calculated from the difference in the bed volume and the volume of resin in the bed. The latter volume was determined by the weight of the EXC material in the bed divided by its density. The free column volume was also obtained by measuring the volume of eluent corresponding to breakthrough of an unretained solute, ^{137}Cs. The average of these two methods was taken to be the free column volume. The volume of stationary phase, v_s, was determined from the weight of EXC material in the column, the resin loading (*i.e.*, the weight percent of extractant or extractant diluent solution present in the resin), and the density of the extractant or extractant solution. Table 1 summarizes the characteristics of the PS capsule based sorbent (Sr-PSC) and the conventional Sr-Spec sorbent.

Table 5.1 Characteristics of the polysulfone capsule-based sorbent and conventional Sr-Spec EXC material and packed columns

Bulk materials	**Sr-PSC**	**Sr-Spec**
Stationary phase	1 M DtBuCH18C6 in 1-octanol	1 M DtBuCH18C6 in 1-octanol
Support	Polysulfone capsules	Amberchrom CG-71m
Particle diameter	53-106 µm	75 µm
Extractant loading	~45%	40%
Density of extractant-loaded beads	1.12 g/mL	1.08 g/mL
Packed columns		
V_s, mL/mL of bed	0.11	0.17
Bed density (g/mL)	0.23	0.39
V_m, mL/mL of bed (also FCV)	0.79	0.64
V_s/V_m	0.14	0.27
Capacity, mg Sr/mL of bed	5.83	10.52
Capacity, mg Sr/g of sorbent	25.33	26.78

5.2.3.7 Elution curves for strontium and the stability of the sorbents

The elution profile of strontium on packed columns of both Sr-PSC and conventional Sr-Spec resin using 3M HNO_3 as the eluent was determined employing a Bio-Rad Econocolumn column as mentioned earlier. The parameters of the packed columns were determined prior to the experiment following the procedures outlined above. After conditioning the column with the eluent (3 M HNO_3), a small quantity (~10 μL) of ^{85}Sr in 0.05 M HNO_3 was introduced at the top of the bed and then eluted with 3 M nitric acid. Samples of the eluent were collected at various intervals and γ counted. The column was subjected to slight pressure applied by a rubber pasteur pipette bulb fitted with a 100 μL pipette tip, thus yielding a flow rate of ~2-3 ml/cm^{2}min. All runs were carried out at ambient temperature (23-25ºC). After the first elution curve was obtained for each column, ~250 FCV of deionized water was passed through each to wash the sorbents. A second elution curve was then obtained, thus providing an indication of the physical stability of the sorbents.

5.2.3.8 Strontium recovery determination

Columns containing Sr-PSC or Sr-Spec were prepared for the strontium ion recovery experiments according to the general procedures for packing and preconditioning outlined above. The column conditioning and strontium radotracer loading were performed using 5.2 M HNO_3 for Sr-PSC, however, while 3 M HNO_3 was used for the Sr-Spec column. Following conditioning, a small aliquot (~100 µL) of ^{85}Sr was introduced at the top of the bed. This was followed with a ~1 FCV aliquot of an appropriate HNO_3 solution to complete the load step and a 5 FCV portion of the same acid as a column rinse. Stripping of the column was carried out with dilute (0.01 or 0.05 M) HNO_3 acid. The stripping was continued until the ^{85}Sr count rate approached the background level. The total ^{85}Sr activity introduced and the ^{85}Sr activity found in combined strip fractions was used to calculate the strontium recovery.

5.3 Results and Discussion

5.3.1 Methods for the preparation of polysulfone microcapsules: phase inversion vs. solvent evaporation

As already noted, microcapsules can be synthesized by either the phase inversion (5.1-5.3, 5.14) or solvent evaporation method (5.8-5.10, 5.22). Of these, the latter would appear to offer greater promise. That is, by incorporating the extractant during the synthesis of the capsules, the number of synthetic steps is reduced. In addition, it would be expected that highly stable (*i.e.,* resistant to extractant loss) materials would result. In this work, we have followed a procedure employed by Yang *et al.* for the preparation of HDEHP-loaded PS microcapsules (5.8) to produce microcapsules incorporating DtBuCH18C6. Unexpectedly the results proved to be unsatisfactory. That is, rather than yielding free flowing powder, the procedure provided only a sticky solid prone to the formation of clumps. In addition, the material exhibited very poor strontium ion uptake (D_w ~4 at 2 M HNO_3). These problems may have their origins in the high viscosity of the crown ether. That is, because of this viscosity, evaporation of the solvent leaves a significant amount of the DtBuCH18C6 on the surface of the capsules, thus rendering them sticky. In addition, this would increase the hydrophobicity of the capsules, decreasing their wettability and making encapsulated extractant inaccessible to the metal ion. Another limitation of the solvent evaporation method is the modest encapsulation efficiency. Yang (5.8) reported encapsulation efficiency of ~60% or less, with maximum incorporation occurring when the ratio of PS to extractant was 2:3(w/w). Similarly poor encapsulation efficiency was observed for DtBuCH18C6. For all these reasons, capsules taken for further evaluation in our studies (described below) were prepared by the phase inversion method.

5.3.2 Morphological characterization

Morphological characterization of the polysulfone capsules prepared *via* phase inversion (both with and without encapsulated crown ether) was carried out by scanning electron microscopy (SEM). For comparison, SEM characterization was also performed on conventional strontium resin (Sr-resin/ Sr-spec). SEM micrographs obtained show that the polysulfone microcapsules are isolated predominantly as well-defined spherical particle (Figure 5.2). As shown in Figure 5.3, magnification of surface features of these particles indicates that the pore sizes of the capsules are larger than those observed for conventional resin. The micrographs reveal the presence of a number of small protuberances on the surface of the capsules. Similar observation has also been reported in the literature (5.8, 5.23). The SEM image of a cross section of a macrocapsule (Figure 5.1) clearly shows that the capsule interior contains significant hollow regions, particularly at the center of the capsule. It has been suggested that macrovoids form due to differences in the rate of DMF and water diffusion during capsule formation (5.18). That is, when a mixture of PS in DMF contacts water, DMF diffuses into water. At the same time, water diffuses into the DMF. The rate of diffusion of DMF into water is much higher than the diffusion of water into the polymer solution, however. As a result, a microvoid grows as PS separates from the mixture. Specifically, upon contact of the PS-DMF mixture with water, a layer of PS forms around droplets of the PS-DMF solution. Despite the presence of this layer, DMF in the center of the droplet continues to diffuse outward, eventually passing through the PS layer. As this process proceeds, PS is drawn outward and away from the droplet center, thus generating the structure evident in the macrocapsule cross-sectional micrograph shown in Figure 5.1.

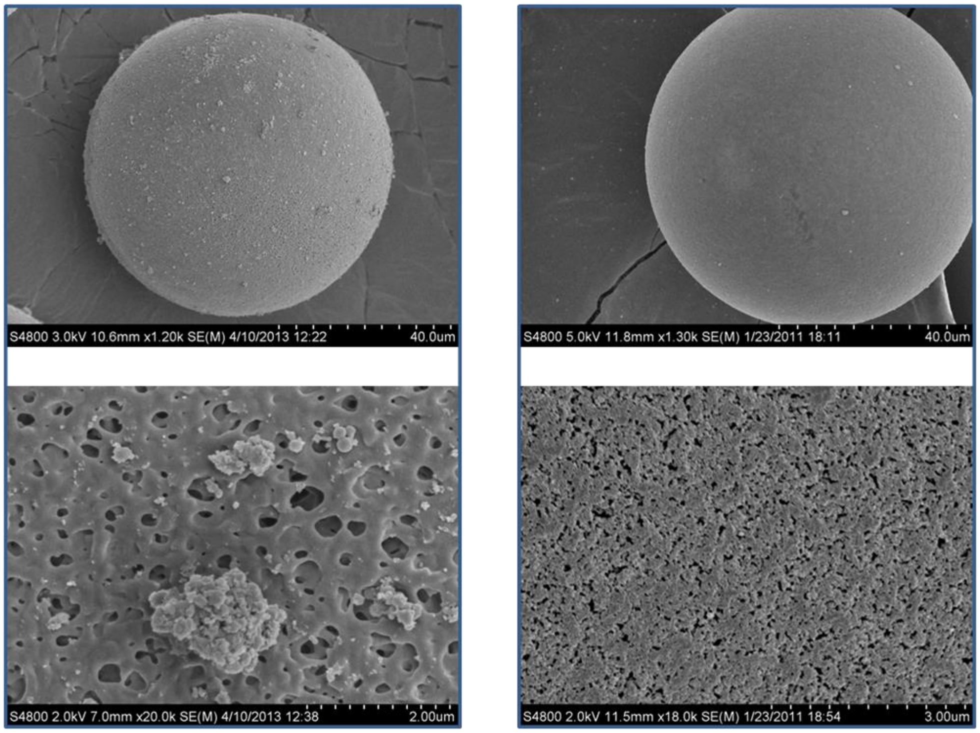

Figure 5.3: SEM micrographs of polysulfone capsule skeleton and convention polymer bead skeleton. Left: Top-whole image of a microcapsules; Bottom- surface structure of a microcapsules. Right: Top-whole image of an Amberchrom CG-71m bead; Bottom- surface structure of an Amberchrom CG-71m bead.

The SEM images of the crown-ether impregnated capsules shown in Figure 5.4 (left) demonstrate that the capsules morphology remains unaffected upon extractant loading. The physical appearance of the capsules also indicates that the surface has been smeared by the extractant, which is evident from the comparison of the capsule skeleton micrograph shown in Figure 5.3 left-top. The interior of the capsules (right) shows significant void volume, with sponge-like PS skeletons comprising the remainder of the capsule interior.

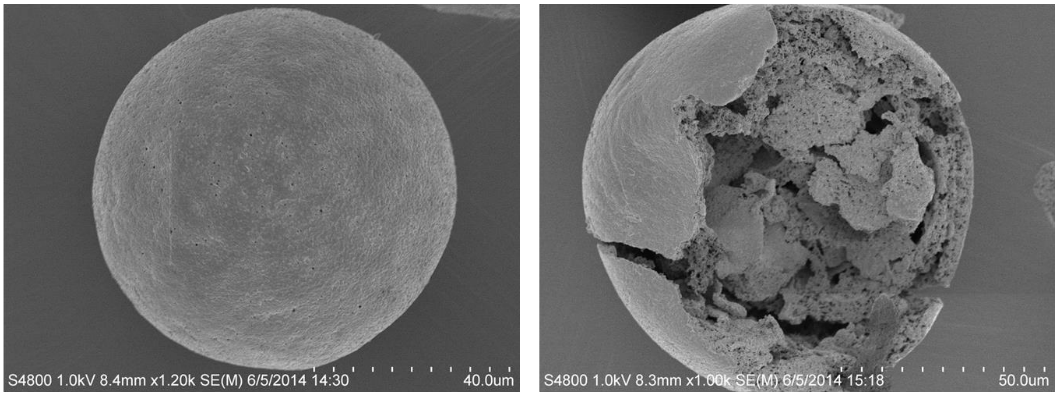

Figure 5.4: SEM micrographs of DtBuCH18C6-loaded polysulfone capsules. Left: exterior of the impregnated capsules; Right: interior of the microcapsules.

5.3.3 Physical properties of polysulfone macro- and microcapsules

Table 5.2 summarizes the physical properties of the micro- and macrocapsules prepared from polysulfone, along with those of the support employed to prepare conventional Sr-Spec resin, Amberchrom CG-71m. Interestingly, the skeletal mass of the PS capsules turns out to be only half of that of the conventional resin, which is consistent with the observation that the capsules tend to float in water unless subjected to lengthy sonication and vortex mixing. The water regain experiments provide information about the specific pore volume of the sorbents (5.25). The efficiency of supports in general depends on their specific pore volume and on their pore size distribution, as well as on their specific internal surface area (5.29). For the microcapsules, the water regain found in this study matches the literature value (5.25) and is approximately double that of the conventional material, which indicates that the capsules have the potential to perform well as support materials. The BET experiment, which provides information on such characteristics as pore volume, pore size and surface area, appear to show substantial differences between the microcapsules and the conventional Amberchrom resin. BET measurements, however, do not take into account the presence of macropores, which are evident from the micrographs of the capsules shown above. BET determinations, in fact, encompass only micropores and mesopores, which are the predominant in case of the Amberchrom materials. Clearly then, the presence of micropores and mesopores in the PS capsules are insignificant, indicating that the internal pore structure of the capsules is completely different from that of the conventional support considered.

Table 5.2: Comparison of physical properties of macrocapsules, microcapsules and amberchrom CG-71 beads backbone

Property	Macrocapsules	Microcapsules	Amberchrom CG-71m
Material	Polysulfone	Polysulfone	Methylmethacrylate
Skeleton mass (g/mL wet sorbent)	ND	0.0985	0.2128
Particle diameter (μm)	~2000	~50-100	~75
Water regain[a] (g/g)	6.12	4.41	2.38
Pore volume[b] (mL/g)	ND	0.07	1.27
Surface area[b] (m^2/g)	ND	22.26	577.53
Average pore diameter[b] (Å)	ND	126	87

[a] based on difference between amount of water inside capsule during formation and capsule dry weight (by blotting the wet resin between sheets of filter paper)

[b] BET measurement

ND- not determined

5.3.4 Thermogravimetric analysis

As noted above, the impregnation of dried capsules is not feasible due to the possibility of collapse of the pore structure of the capsules during the drying process. A weighed amount of wet capsules was therefore used for impregnation. The process of obtaining wet mass of capsules is not precisely reproducible. As a result, it is not possible to determine exact the amount of extractant loaded in the capsules directly from the amounts of support and extractant taken, as is the case for conventional materials. Therefore, thermogravimetric analysis was employed to determine the percent composition of the extractant-loaded capsules. As shown in Figure 5.5, the loss of mass for polysulfone occurs above 500°C. In contrast, both the extractant (DtBuCH18C6) and 1-octanol begin to lose mass well below this temperature (T_{onset} = ~118°C and ~ 280°C for the crown ether and alcohol, respectively). These differences enable one to use TGA to determine the level of extractant loading achieved in the preparation of a given batch of capsules. As shown in Figure 5.6, the onset temperature for mass loss is ~280°C for the undiluted crown ether in a microcapsule. The boiling point for 1-octanol is 195°C, which allows us to ensure the complete loss of 1-octanol prior to loss of CE by employing a 20 minute hold time at 200°C. Similarly, holding the temperature at 420°C for 20 minutes ensures the complete loss of the crown ether.

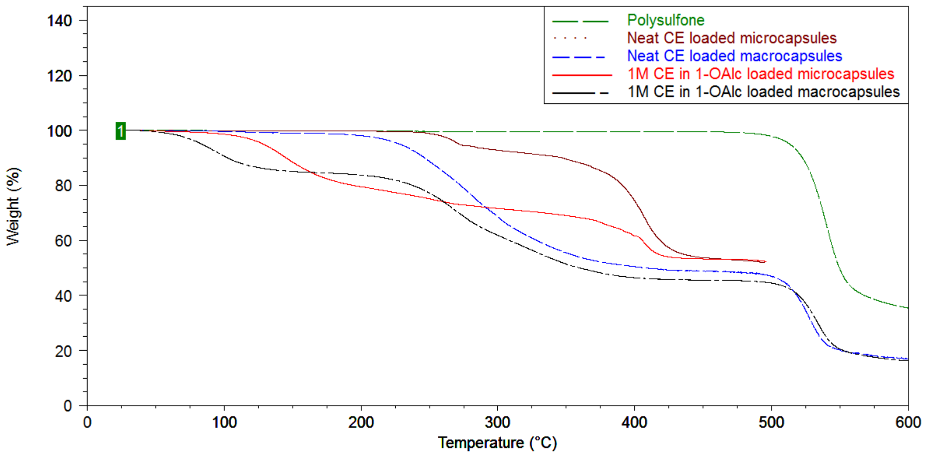

Figure 5.5: TGA thermograms of crown ether-loaded PS capsules (top to bottom at 400°C): polysylfone; microcapsules loaded with undiluted (neat) DtBuCH18C6; microcapsules loaded with 1 M DtBuCH18C6 in 1-octanol (Sr-PSC); macrocapsules loaded with neat DtBuCH18C6; macrocapsules loaded with 1 M DtBuCH18C6 in 1-octanol).

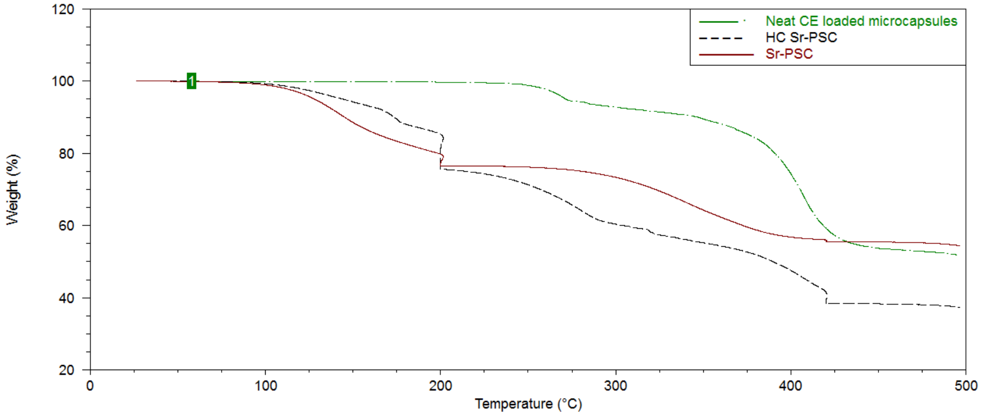

Figure 5.6: TGA thermograms of the microcapsules to determine percent extractant loading (top to bottom: 47% neat dtBuCH18C6 loaded microcapsules, Sr-PSC, HC Sr-PSC)

5.3.5 Acid dependency of metal ion uptake

According to published studies (5.26, 5.27) the conventional resins "Sr-Spec" and "Super Sr-Spec", in which DtBuCH18C6 is dispersed on a polymeric support as a 1 M solution in 1-octanol or as a neat DtBuCH18C6 extractant, respectively, exhibit similar performance as EXC materials. The indistinguishable elution behavior of Sr-85 on these resins (5.21) indicates that the role of diluent is not significant if an appropriate extractant (here, DtBuCH18C6) is chosen. Following these observation, we prepared macrocapsules containing ~50% (w/w) undiluted DtBuCH18C6 (*i.e.,* neat) and characterized them. In contrast to the behavior observed when Amberchrom CG-71m/XAD-7 is employed as a support, PS microcapsules unexpectedly show no strontium ion uptake. When the macrocapsules were loaded instead with a 1 M solution of DtBuCH18C6 in 1-octanol, yielding material containing an amount of DtBuCH18C6 comparable to that of the macrocapsules loaded with undiluted crown ether, some strontium uptake is observed, but the $D_{w,Sr}$ values are low (Table 5.3), too low to be of practical value. To determine if unsatisfactory metal ion retention is a peculiarity of this particular extractant-capsule combination or a general observation, PS macrocapsules were also impregnated with HDEHP and the suitability of the resultant material for europium sorption was determined. Europium ion sorption (as reflected in the values of $D_{w,Eu}$), while significant, is much lower than that expected on the basis of the behavior of the analogous XAD-7 based materials. These uptake studies thus suggest that the PS macrocapsules are not well-suited as a support for the extractant(s) of interest in this work. This unexpected result may be a consequence of either the nature of the polymer (*i.e.,* polysulfone) itself or the morphology of the capsules.

Table 5.3: Effect of nitric acid concentration on metal ions extraction by polysulfone macrocapsules

$[HNO_3]$, M	Dw, 20% HDEHP	Commercial Ln-resin	Dw, 1M CE in 1-OAlc	Commercial Sr-resin
0.01	289.39	ND	ND	ND
0.10	102.65	3578.05	ND	3.75
1.00	3.10	1.64	3.96	55.78
3.00	ND	ND	25.56	188.37
6.00	ND	ND	43.17	135.01

ND – Not determined

As noted above, polysulfone macrocapsules exhibit an interior characterized by a number of substantial voids. As a result, much of the extractant (or its solution) will be present in the capsule interior as a collection of “droplets”. It might be anticipated that in such a case, particularly when the extractant is highly viscous, metal ion interaction with the extractant could be restricted, resulting in poor uptake. An obvious way to determine the role played by morphology is to prepare microcapsules loaded with the same extractant. In contrast to macrocapsules, these capsules lack substantial interior voids, suggesting that extractant present is found not as large droplets, but as a thin film. As already stated, microcapsules can be prepared with either water or methanol as a filler to maintain the integrity of the capsules prior to extractant loading. As a first step in the evaluation of microcapsules then, strontium uptake by water-containing microcapsules (WWMCs) loaded with neat CE was measured. Uptake was significant (Figure 5.7, left panel), with $D_{w,Sr}$ exceeding 100 for all loading levels at some acidities. Thus, the behavior of the extractant is dependent on the capsule size, consistent with the notion that the smaller voids and pores in the microcapsules provide a thinner and thus more accessible layer of extractant.

Microcapsules prepared using methanol (methanol-containing microcapsules, MCMCs) extracted strontium even more efficiently. As a result, all subsequent studies of microcapsule-based sorbents employed MCMCs. Figure 5.7 (right panel) summarizes the results for measurements of the nitric acid dependency of $D_{w,Sr}$ for three different microcapsule-based sorbents. The first contains ~47% (w/w) neat CE. The second, which utilized the maximum loading capacity of the microcapsules, contains ~62% (w/w) of a 1 M solution of the DtBuCH18C6 in 1-octanol ("HC Sr-PSC"), while the third, which contains ~45% of a 1 M solution of the DtBuCH18C6 in 1-octanol (Sr-PSC), is comparable to "conventional" (*i.e.,* Amberchrom-based) Sr resin. As can be seen, the metal ion uptake observed for microcapsules loaded with a 1 M solution of DtBuCH18C6 in 1-octanol is comparable to that observed for capsules prepared with the undiluted extractant. Not unexpectedly, higher strontium ion retention at any given acidity is generally observed for microcapsules containing the maximum loading of extractant.

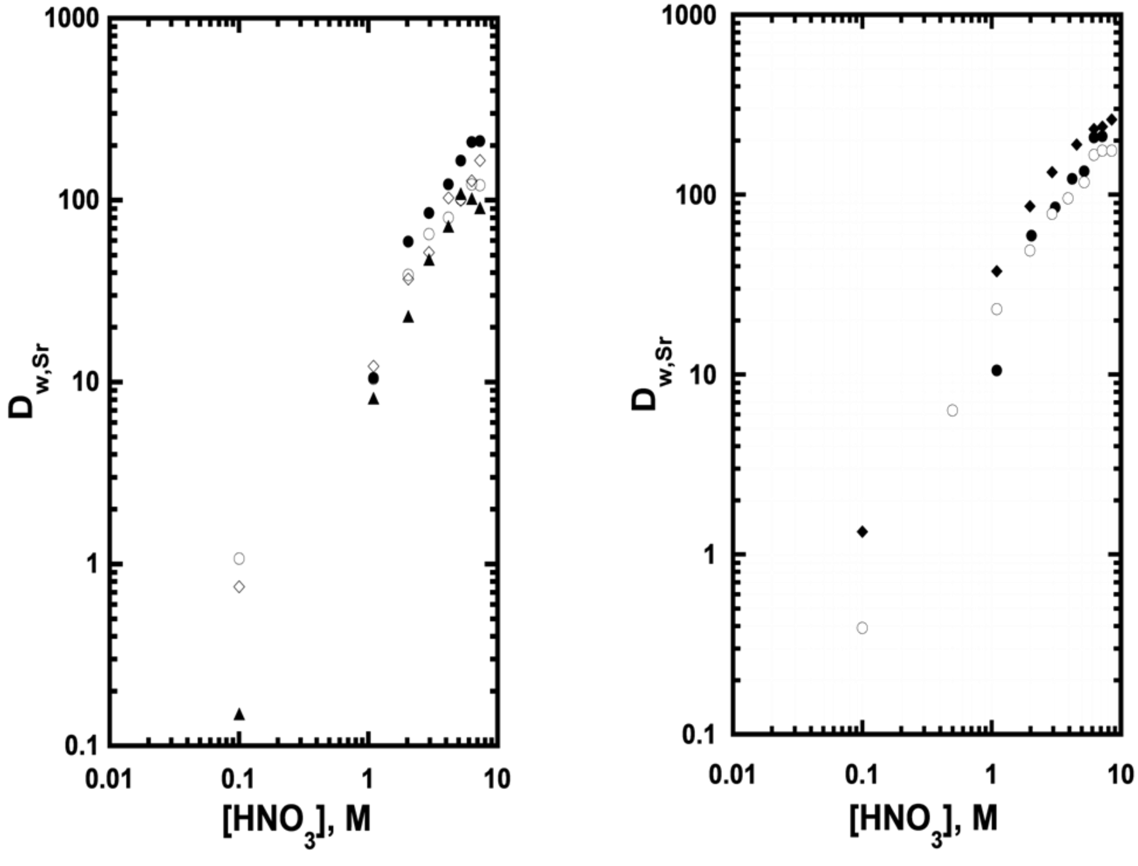

Figure 5.7: Effect of nitric acid concentration on the extraction of strontium ion by polysulfone capsule-based sorbents. Left panel: WCMCs containing ~28% (w/w) neat CE (o); ~42% (w/w) neat CE (◊); ~60% (w/w) neat CE (▲); and MCMCs containing ~47% (w/w) neat CE (●); Right panel: MCMCs containing ~47% (w/w) neat CE (●); Sr-PSC (o); and HC Sr-PSC (♦).

Figure 5.8 compares the acid dependency of strontium ion uptake by the Sr-PSC microcapsules to that obtained with the commercially available Sr-Spec (5.26) and Super Sr-Spec sorbents (5.27). As can be seen, up to ~5 M HNO_3, the $D_{w,Sr}$ values for Sr-PSC are lower than those obtained with the commercial resins. Above this acidity, however, its $D_{w,Sr}$ values exceed those of Sr-Spec and are comparable to those of the Super Sr-Spec sorbent. Taken together, these results indicate that the Sr-PSC sorbent should provide adequate strontium retention at high acidity (≥ 5 M HNO_3) and facile stripping of the sorbed strontium with dilute acid. Ideally, however, retention should be high at more modest acidities (1-3 M HNO_3). For this reason, an effort was made to increase the $D_{w,Sr}$ values of Sr-PSC by diluting the DtBuCH18C6 with 1-pentanol rather than 1-octanol. Previous solvent extraction studies have shown strontium ion extraction into oxygenated aliphatic solvents (*e.g.*, alcohols, ketones) increases as the alkyl chain length of the solvent decreases (5.28). As shown in Figure 5.9, however, dilution of crown ether with 1-pentanol did not yield the expected increase in $D_{w,Sr}$. In fact, lower strontium ion retention was observed over a range of acidities (*ca.* ≥ 4 M HNO_3). It is important to note here that disagreement between the results obtained in liquid-liquid extraction and extraction chromatography is not without precedented (5.30). In fact at best, solvent extraction behavior is regarded as a qualitative indicator of EXC performnace (5.31).

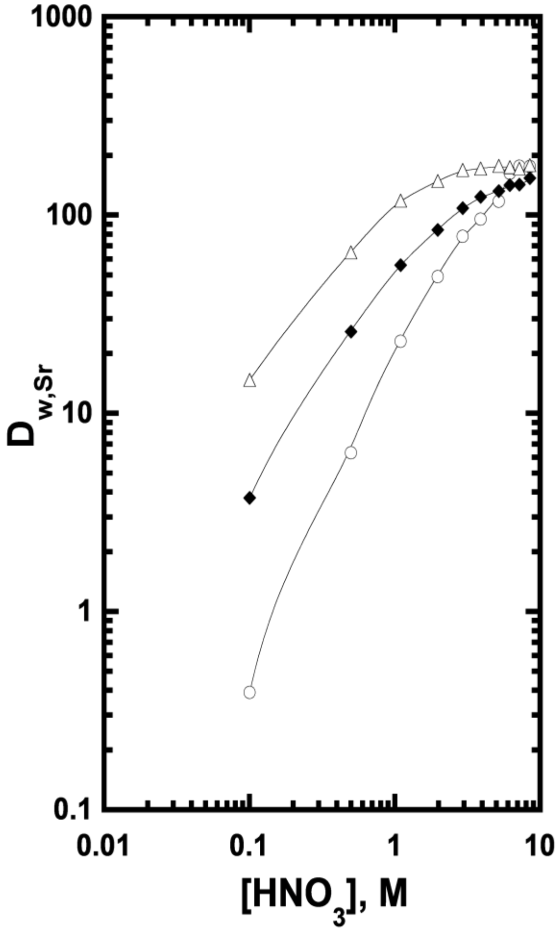

Figure 5.8: Comparison of the acid dependency of strontium uptake by Sr-PSC (o), Sr-Spec (♦) and Super Sr-Spec (Δ). (The smooth curves are intended only as a guide to the eye.)

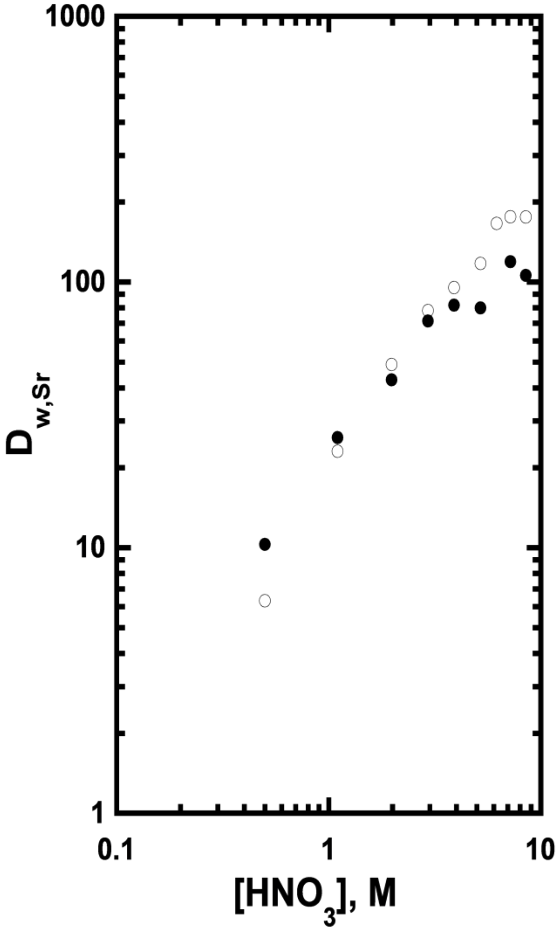

Figure 5.9: Effect of nitric acid concentration on the uptake of strontium by Sr-PSC incorporating 1 M CE in 1-octanol (o), or in 1-pentanol (●).

5.3.6 Interferences effects

Sodium, potassium, calcium, iron, and aluminum are the major constituents of many environmental and biological samples (5.26). Accordingly, the selectivity of the Sr-PSC sorbent for strontium ion over these ions, especially Na^+ and Ca^{2+}, is an important parameter in assessing the performance of the sorbent. As can be seen from Figure 5.10, in which the behavior of the microcapsule-based sorbent is compared to that of conventional Sr-Spec resin, the two materials exhibit similar behavior. Specifically, for sodium, Sr-PSC shows no measurable uptake, while that of Sr-Spec is low. For calcium ion, the uptake by the two resins is nearly indistinguishable. Although Ba sorption by the Sr-PSC resin is generally higher than that of Sr-spec (and thus, the Sr/Ba selectivity is poorer), the difference is greatest at low acidity, not at the high acidities ($\geq$ 3M HNO_3) that would typically be employed for sample loading.

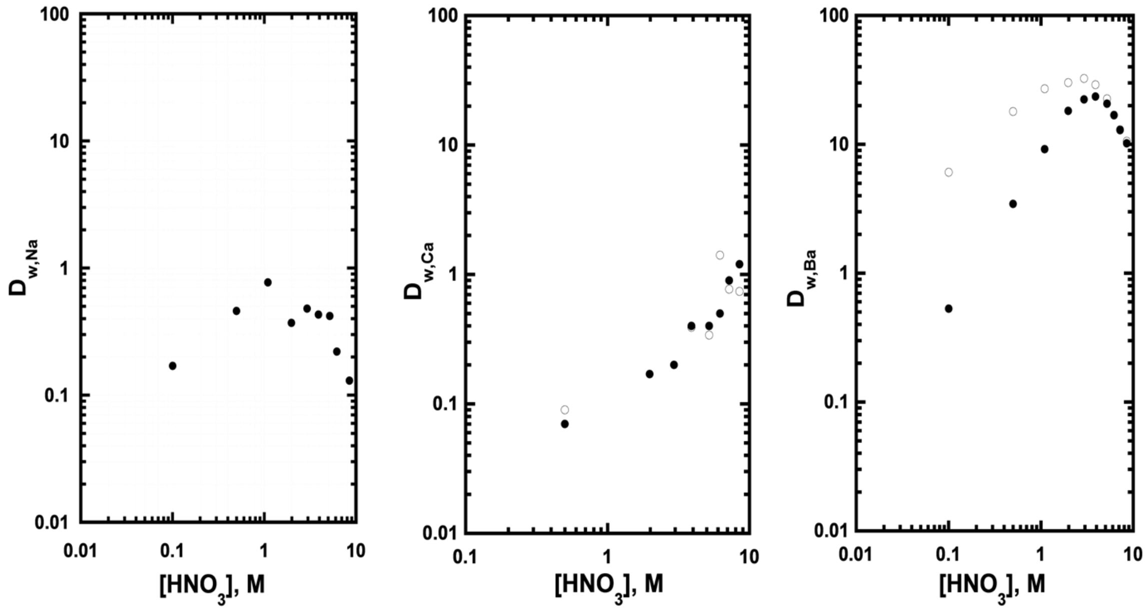

Figure 5.10: Effect of nitric acid concentration on the extraction of sodium (left panel), calcium (middle panel) and barium (right panel) by Sr-PSC (o) and Sr-Spec (●).

5.3.7 Metal ion uptake kinetics

A rapid rate of metal ion uptake is an important characteristic of practical EXC materials. The kinetics of conventional Sr-resin are very fast, with 91% of equilibrium uptake being reached in only 2 minutes (P_{2min}). Super Sr-Spec, another conventional material, exhibits somewhat slower kinetics, but its p_{2min} is still 81%. Figure 5.11 (left panel) summarizes the results of studies of the kinetics of strontium ion uptake by PS microcapsules containing DtBuCH18C6, either neat or as a solution (1 M) in 1-octanol. As can be seen, the sorbent containing the undiluted extractant yields a much lower rate of uptake (requiring ~2 hrs to reach equilibrium) than the does the material incorporating a solution of the extractant (Sr-PSC), as might be expected from the lower viscosity of the solution *vs.* the extractant. For the highly-loaded sorbent (HC Sr-PSC), the kinetics are somewhat slower (P_{2min} = 46%) than Sr-PSC (P_{2min} = 91%), but are nonetheless faster than for the neat CE-loaded microcapsules. Figure 5.11 (right panel) compares the kinetics of Sr^{2+} uptake of Sr-PSC to the two commercial resins, Sr-Spec and Super Sr-Spec. As is evident, the uptake kinetics for the Sr-PSC and Sr-Spec sorbents are similar, and both are faster than for the Super Sr-Spec resin, a not unexpected result given the absence of a diluent from the latter resin.

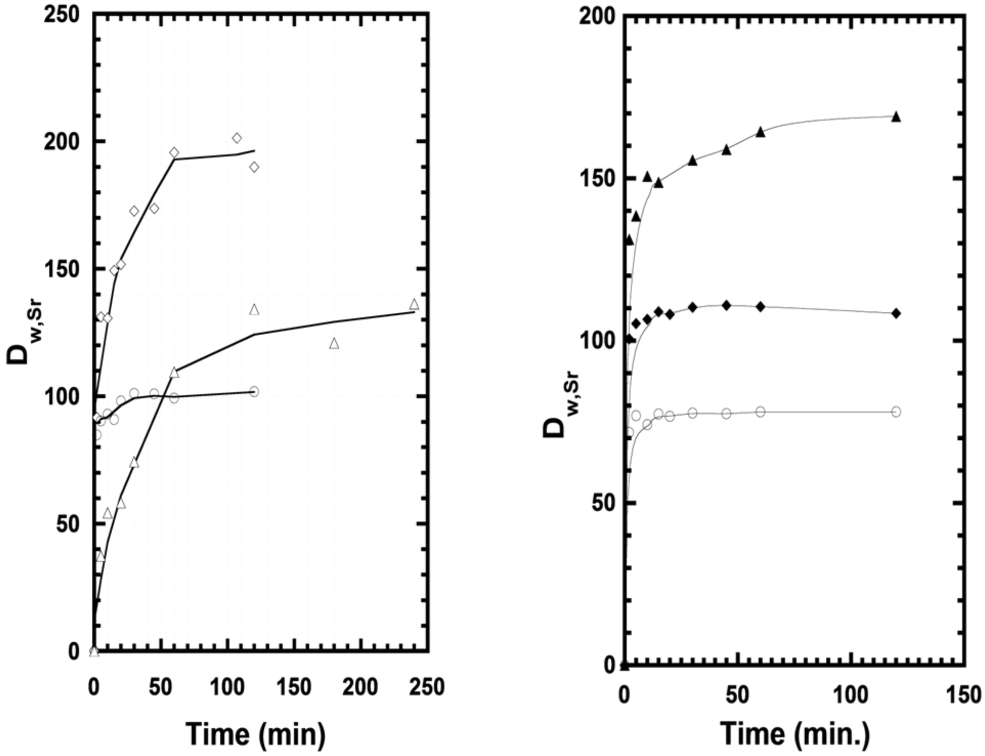

Figure 5.11: Left panel-uptake kinetics for Sr-85 on Sr-PSC (o), HC Sr-PSC (◊) and ~47% neat CE loaded microcapsules (∆) from ~5 M nitric acid; Right panel-uptake kinetics for Sr-85 on Sr-PSC(o), Sr-Spec (♦) and Super Sr-Spec (▲) resins from ~3 M nitric acid. (The smooth curves are intended only as guides to the eye.)

5.3.8 Elution profiles for strontium/sorbent stability

The elution profile of a metal ion on an EXC material provides information on both metal ion retention behavior (*i.e.,* the number of free column volumes to peak maximum, k') and the efficiency of the column, both important parameters in designing a separation. In addition, the profile provides a means to assess the column stability (another important characteristic of an EXC material) simply by acquiring an elution profile curves before and after extensive washing of the column. Figure 5.12 shows the elution for strontium obtained on a pair of identical columns packed with two different sorbents: the commercial Sr resin (left panel) and Sr-PSC resin (right panel). All of the elution curves show reasonable symmetry, but some tailing is evident. Breakthrough occurs at a smaller number of bed volumes (~8 bed volume) on the Sr-PSC column than on the Sr-Spec column (~20 bed volume). This differences can be understood from the characteristics of the two resins presented in Table 5.1, in particular, the values of v_s/v_m, bed density, and the column capacity. As can be seen from the Table, v_s/v_m (which is related to elution volume through the equation $k' = Dv_s/v_m$) is a factor of two smaller for Sr-PSC than for Sr-Spec. Not unexpectedly then, the breakthrough volume for Sr-PSC resin column is half that of the corresponding column filled with Sr-Spec. Because PS capsules can accommodate more extractant (up to ~65% (w/w)), increasing the loading of CE in the capsules could resolve the problem of early breakthrough for the Sr-PSC column.

Alternatively, one could simply use a larger bed volume column. In fact, because of the lower density of the Sr-PSC resin, a given mass of it occupies approximately twice the volume occupied by the conventional resin. The number of theoretical plates (N) calculated from the elution curves (5.32), which indicates the efficiency of the column, is 8 and 22 for Sr-Spec and the Sr-PSC sorbent, respectively. From N, the height equivalent of a theoretical plate (HETP), another measure of efficiency can be calculated as 5 mm and 1.8 mm for Sr-Spec and Sr-PSC, respectively. These parameters indicate, unexpectedly, that the efficiency of the Sr-PSC column is higher than that of the commercial Sr-Spec column by *ca.* a factor of 3.

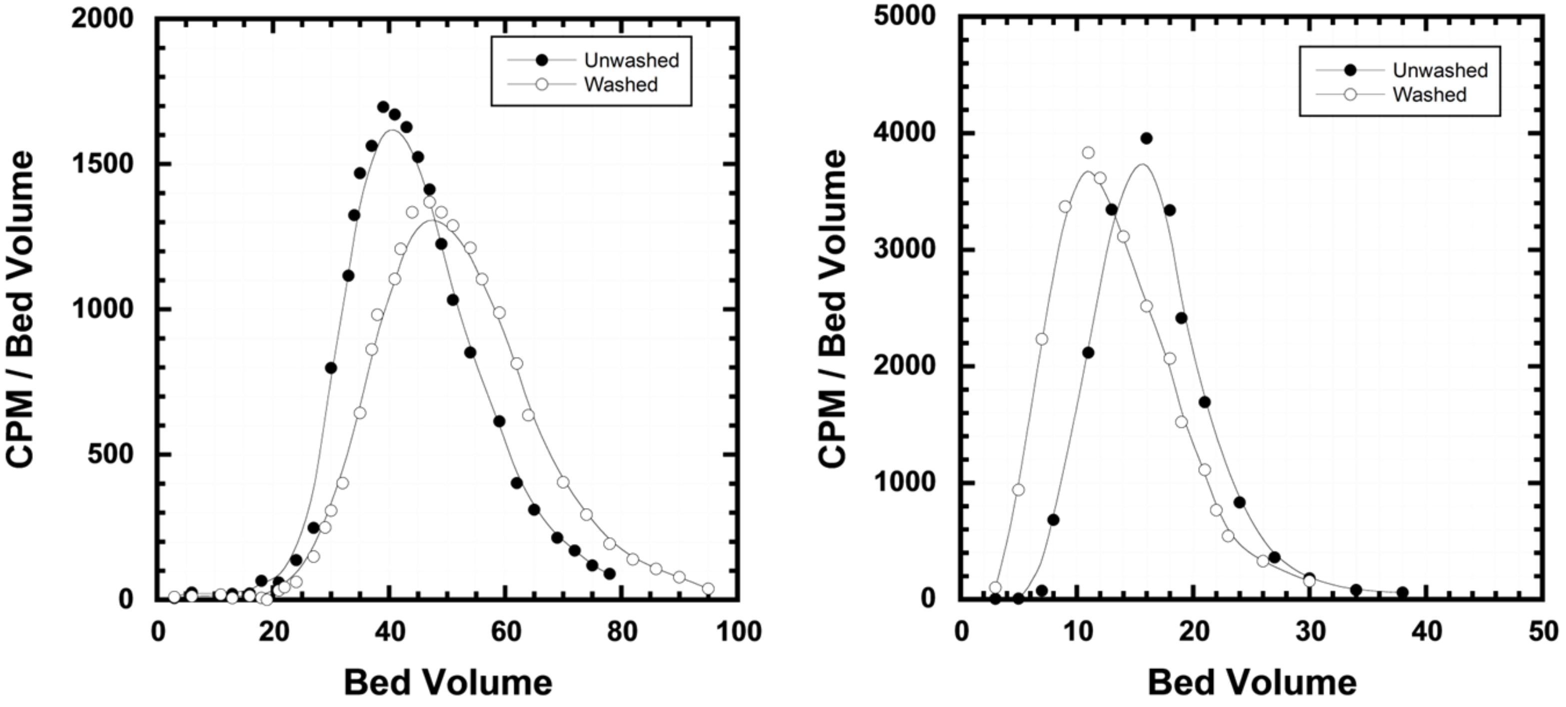

Figure 5.12: Effect of column washing on the elution behavior of Sr-85 on Sr-Spec (left) and Sr-PSC (right) EXC materials (eluent: 3 M HNO_3; flow rate: 2-3 mL/cm^2/minutes; temperature: ~23˚C; filled circles: unwashed resin; open circle: washed resin [25 FCV])

Because extraction chromatography involves contacting a small volume of a highly dispersed organic extractant with a much larger volume of aqueous phase, the possibility of extractant (stationary phase) loss is of particular concern with any new sorbent. To investigate the stability of the Sr-PSC resin, the column employed to obtain the strontium elution curves (above) was subjected to washing with 250 FCV of water, after which another elution curve measured (Figure 5.13). For purposes of comparison, the Sr-Spec column was subjected to the same treatment. In both cases, the elution behavior of strontium is affected by washing, consistent with some degradation of the sorbents. Strangely, however, the shift of the elution band for the two materials is in opposite. The reason behind this observation remains unclear at present.

5.3.9 Recovery of strontium ion

To determine the effect of the apparent change in the behavior of the sorbents upon washing on the recovery of sorbed strontium, a column of Sr-PSC resin was used for a series of experiment involving strontium loading, a column rinse, and stripping of sorbed strontium. The recovery of loaded strontium was determine in each case and compared to that seen for an analogous Sr-Spec column. Table 5.3 summarizes the results obtained. As can be seen, the two sorbents behave similarly. That is, the strontium recovery is consistently high and essentially complete.

Table 5.4: Recovery of strontium ion from the Sr-PSC and Sr-Spec resins.

Load-rinse-strip cycle	Sr-PSC materials	Sr-Spec materials
1	100	101
2	102	103
3	99.5	97.8
4	102	98.8
5	102	99

5.3.10 Capacity of the capsules

There has long been a demand for high-capacity sorbents. In fact, as noted above, the present study of PS capsules was initiated in an attempt to devise a high capacity Sr sorbent. The conventional Sr resins (*i.e.*, Sr-Spec and Super Sr-spec) have been reported (5.26, 5.27) to use less than their full capacity, implying that some of the extractant is inaccessible to metal ions. Our measurements show that ~71% of the theoretical capacity of Sr resin used. Because no additional pore volume is available in the support, the amount of extractant and thus, the capacity cannot be increased. Measurements on the Sr-PSC sorbent indicate that its experimentally determined capacity is virtually the same as of the Sr resin (Table 5.5). Thus, for reasons that are unclear at present, the vastly different morphology/porosity of the two supports yields no difference in resin capacity. Not unexpectedly, the HC Sr-PSC capsules show higher capacity than either the conventional sorbent or the Sr-PSC resin, the result of the higher amount extractant present in the sorbent. Although the utilization of the theoretical capacity is somewhat greater (77% *vs.* 67%), it remains well under 100%. Moreover, this higher capacity comes at the price of slower strontium uptake kinetics.

Table 5.5: Capacity of the capsules

Support	Loading (%)	Theoretical Capacity (mg/g)	Exp'l Capacity[a] (mg/g)	% of theoretical capacity used
Sr-psc	~45 (1M CE in 1-OAlc)	37.96	25.33	66.72
HC Sr-PSC	~62 (1M CE in 1-OAlc)	66.88	51.36	76.79
Sr-Spec	~40% (1M CE in 1-OAlc)	37.96	26.78	70.54

[a]measured radiometically

[b]Percent attainment of equilibrium in 2 min

5.4 Conclusions

Polysulfone capsules-based extraction chromatographic materials have been successfully prepared by the phase inversion precipitation technique. A simple modification of a widely practiced physical impregnation method (*i.e.*, using methanol-containing microcapsules instead of water-containing microcapsules for the impregnation) results in satisfactory EXC materials. Unlike polysulfone macrocapsules, microcapsules loaded with neat crown ether show significant metal ion extraction, but the uptake kinetics of strontium for these microcapsules are slow. This limitation can overcome, however, by loading the capsules instead with a 1 M solution of DtBuCH18C6 in 1-octanol. These extractant-loaded polysulfone capsules (Sr-PSC) show metal ion uptake efficiency and kinetics comparable to commercial Sr-Spec resin. The capacity limitation of the conventional materials (~40% (w/w) pore volume), which prompted our search for alternative materials with higher capacity, has been overcome using polysulfone microcapsules. These capsules can contain up to ~65% (w/w) extractant, which is significantly higher than the conventional materials, and the capacity utilization of the highly extractant loaded capsules (HC Sr-PSC) is similar to that of conventional materials. The only drawback of the high-capacity Sr-PSC material is its slightly slower metal ion uptake kinetics.

The breakthrough of strontium from a Sr-PSC column occurs at a lower elution volume compared to a conventional Sr-Spec packed column. This can be understood from the characteristics of the EXC materials and packed columns, in particular, the different ratios of v_s/v_m. This means that the mass of extractant in a given volume of PS capsules is only half that of conventional Sr resin. This limitation can be overcome using HC Sr-PSC materials to pack the column or by simply employing a larger bed of Sr-PSC. Stability studies of the Sr-PSC column involving significant water washing show some peak drift. Curiously, this drift is opposite in direction to that seen for a Sr-Spec column. The recovery of strontium using a Sr-PSC column is complete for at least 5 load-rinse-strip cycles, which is consistent with observations made for a Sr-Spec column. All these results suggest that polysulfone capsules have the potential to address some long standing limitations of existing EXC materials.

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CHAPTER 6:

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

In this work, an effort has been made to improve several important performance characteristics of extraction chromatographic materials, including their metal ion retention, stability, column efficiency and sorption capacity. Four different approaches have been pursued; ionic liquid-based sorbents for improved retention, extractant encapsulation in silica sol-gel glasses for improved stability, stagnant pore plugging to improve efficiency, and polysulfone capsule-based materials for improved capacity. A series of materials prepared using each of the four approaches have been characterized made and their properties compared to those of the conventional materials.

To improve the retention of metal ions, various ionic liquids have been incorporated into extraction chromatographic materials, as they had previously shown extraordinary performance in the solvent extraction of strontium ion using crown ethers (6.1). In solvent extraction, the ILs $C_{10}mimTf_2N$ and $C_{12}OHbimTf_2N$ yielded higher strontium ion extraction than the conventional solvent 1-octanol. In extraction chromatography, however, the strontium ion uptake by the IL-based materials was unexpectedly found to be lower than for the conventional octanol-based sorbent. This result indicates that the performance of an ionic liquid as an extractant solvent will not always translate in a straightforward manner into extraction chromatography. In this instance, this may be attributable to factors such as precipitation of the extractant in support, solvent molar volume considerations, high stationary phase viscosity (and the accompanying slow uptake kinetics), and the peculiarities of the extraction mechanism.

Acid catalyzed sol-gel chemistry was employed to synthesize silica-based EXC materials. Extractant loading experiments showed that the silica network can retain up to ~50% (w/w) of the crown ether DtBuCH18C6, and a series of materials containing extractant loadings ranging from ~10-~50% (w/w) were prepared and characterized. Although the rate and extent of metal ion uptake and the physical stability of these materials were not found to be satisfactory, these limitations could be easily overcome by using a porogen to increase the porosity of the silica network. A series of porogen-treated materials were synthesized to optimize their composition and the optimized material characterized. This sorbent was found to provide both higher metal ion uptake and better resistance to water or acid washing than conventional Sr-resin. Although the metal ion uptake kinetics of the optimized material are somewhat slower than the conventional Sr-resin, uptake rates comparable to another conventional strontium resin, Super Sr-resin, are observed. Thus silica encapsulation may provide a route to the preparation of new and useful sorbents for metal ions.

Among the long-standing significant problems of separation science is the separation metal ions of the same charge and comparable size. In extraction chromatography, such ions normally either co-elute or yield elution bands exhibiting significant overlap. By plugging the stagnant pores of the support, metal ion elution band can be narrowed considerably, the present work has shown. In particular, comparison of two different stagnant pore-plugged materials, SPP Ln-resin and SPP Sr-resin, to analogous conventional EXC resins showed that the column efficiency, as expressed by either the plate number (N) or plate height (H), is more than factor of 2 higher for the SPP resins than for the conventional materials. The metal ion uptake and the percent utilization of the theoretical capacity of the SPP sorbents are unexpectedly low, however.

The limited capacity of commercial EXC materials and the problem associated with this lower capacity (*i.e.,* the requirement for a large column to avoid extractant saturation) make necessary efforts to increase the capacity of EXC materials. In this study, polymer microencapsulation techniques have been shown to provide sorbents exhibiting the ability of retaining much more extractant per unit mass than conventional materials (6.2-6.4). In particular, polysulfone microcapsule-based extraction chromatographic materials prepared by the phase inversion precipitation technique and loaded with a 1 M solution of the crown ether DtBuCH18C6 showed significant metal ion uptake and good uptake kinetics. The metal ion uptake efficiency and kinetics of these extractant-loaded polysulfone microcapsules (Sr-PSC) were found to be comparable to the conventional Sr-resin, while as expected, the capacity was found to be higher (up to twice) than that of the commercial material on the high capacity microcapsule-based resin.

The chromatographic characterization of the capsules showed the early breakthrough of strontium compared to a conventional Sr-Spec packed column, but this observation can be understood on the basis of the characteristics of the EXC materials and packed columns, (in particular, the different ratios of v_s/v_m) and can be easily overcome by loading the column using HC Sr-PSC. Stability studies (involving water washing) of Sr-PSC and Sr-Spec columns have demonstrated shifts in the position of elution bands in both instances, but curiously, the shift is opposite in direction. Despite this, the recovery of loaded strontium is complete for both washed and unwashed resin. Taken together, these results suggest that the long-standing limitations of existing EXC materials may be overcome by the use polysulfone capsules as a chromatographic substitute.

While the studies presented in this work have provided a better understanding of the behavior of extraction chromatographic materials, many important questions remain unanswered. It is hoped that the knowledge and techniques provided in this work will facilitate the continued development of this understanding and assist in the generation of improved extraction chromatographic materials for separation and preconcentration of metal ion from various sample types.

6.2 Recommendations

In the following section, several recommendations are made to guide future efforts to improve the performance of extraction chromatographic materials. Although these do not represent a comprehensive list of possible areas of interest, they do include both ongoing studies in this laboratory and future experiments that may lead to significant progress in this field.

6.2.1 Overview

In this work, the approaches described were pursued to improve the metal ion retention, physical stability, column efficiency, and capacity of extraction chromatographic materials. In these studies, only a limited number of extractants and solid supports were considered. In fact, however, a wide variety of solid supports are available for examination as potential substrate for novel and improved EXC materials.

Similarly, a wide range of extractants and diluents are available for consideration. Clearly then, the work described hare represents only a first step towards realizing the potential of approaches.

6.2.2 Incorporating ionic liquids in extraction chromatographic materials

The findings of these and other studies have demonstrated the difficulty of preparing practical radioanalytical separations media simply by replacing a conventional solvent with an IL, even one that behaves well in solvent extraction studies. The reasons behind this, including such IL characteristics as high molar volume and viscosity, have already been discussed here. Overcoming these problems will undoubtedly require newer ILs exhibiting lower viscosity (6.5, 6.6), and reduced molar volume or the use of IL mixture (6.7) to achieve the desired properties. Also, it will be important to consider the optimum level of extractant-diluent loading on the support, the preferred support hydrophobicity and porosity, and the characteristics of both the extractant and the IL yielding the most satisfactory stationary phase behavior.

6.2.3 Silica sol-gel encapsulated extractants

Although significant progress has been made in this study in exploiting the physical properties of silica (*e.g.*, especially the surface area and the pore width), much remains to be accomplished before materials comprising a silica-encapsulated extractant can be regarded as a viable alternative to existing extraction chromatographic resins. For example, the current route to preparation yields an assortment of irregular particles (resembling shards of glass) whose chromatographic properties are not entirely satisfactory. It has been shown that the porogen-treated optimized silica-based EXC materials yield better metal ion uptake and comparable uptake kinetics *vs.* conventional materials. The irregular particle shape of the silica materials makes it impossible to carry out a satisfactory comparison of their chromatographic characteristics with the conventional materials, however. Some studies have reported (6.8, 6.9) the preparation of spherical silica materials in the desired size range, but none of them have involved encapsulating extractant in the particles. Clearly then, a facile means to prepare uniform, porous, spherical glass particles containing an extractant is required.

Along these same lines, in this study, only a crown ether has been encapsulated in a silica matrix. It is worthy attempting to encapsulate other extractants and to optimize extractant and porogen (if needed) content of the matrix to determine if silica sol-gel glasses can serve as a "generic" support for extraction chromatography.

6.2.4 Stagnant pore plugging for an efficient EXC materials

Despite a more than two-fold efficiency enhancement resulting from stagnant pore plugging, the EXC materials suffer from the unexpected drawback of lower than anticipated utilization of the theoretical capacity *vs.* conventional materials. The origin of this problem is unclear at present, but identifying its origin requires investigation of other support-filler-extractant combinations. A wide variety of filler materials are available that can be explored for this application. For example, the stagnant pores could be filled with a manner, which is then polymerized to create the "plug". Success in this effort could facilitate the resolution of a long-standing difficulty in EXC, the separation of metal ions of similar charge/size ratios.

6.2.5 Polysulfone capsules for high-capacity EXC materials

Polysulfone capsule-based EXC materials demonstrated a very significant improvement in capacity *vs.* conventional EXC resin, more than a factor of 2. The light weight of the balloon-like capsules, however, makes it difficult to fully exploit this higher capacity, as the capsules tend to float. It is expected that this problem could be overcome by employing more hydrophilic capsule-producing polymers. Studies have shown that other materials can be used to produce capsules for metal ion separations (6.10-6.18). In this study, however, only polysulfone capsules have been investigated, leaving a wide variety of materials remaining to be evaluated for preparing high capacity sorbents.

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Cory A. Hawkins, M. A. Momen, Sarah L. Garvey, John Kestell, Michael D. Kaminski, and Mark L. Dietz, "Evaluation of Solid-Supported Room-Temperature Ionic Liquids Containing Crown Ethers as Media for Metal Ion Separation and Preconcentration", *Talanta*, 2015, 135, 115-123.

Presentations

M. A. Momen, Mark L. Dietz, "Improved Extraction Chromatographic Materials for the Separation and Preconcentration of Metal Ions" 249 ACS Meeting and Exposition, Denver, CO, March 2015.{oral presentation}

M. A. Momen, Mark L. Dietz, "Extraction Extraction Chromatographic Materials Based on Silica Sol-Gel-Encapsulated Crown Ethers for the Separation and Preconcentration of Sr^{2+} from Acidic Media" 18th Symposium on Separation Science and Technology for energy applications, Oak Ridge, TN, October 2014. {poster}

M. A. Momen, Mark L. Dietz, "Improved Extraction Chromatographic Materials for the Separation and Preconcentration of Metal Ions" Carroll University, Waukesha, WI, Sepatember 2014. {oral presentation}

M. A. Momen, Cory A. Hawkins, and Mark L. Dietz, "Evaluation of Solid-Supported Room-Temperature Ionic Liquids Containing a Crown Ether as Novel Media for Metal

Ion Separation and Preconcentration” Department of Chemistry & Biochemistry, University of Wisconsin-Milwaukee, WI (Spring 2014). {Poster}

M. A. Momen, Mark L. Dietz, “Silica Sol-Gel-Encapsulated Crown Ethers for Sr^{2+} Separation and Preconcentration”, Department of Chemistry & Biochemistry, University of Wisconsin-Milwaukee, WI (Fall 2013). {Poster}

M. A. Momen, Cory A. Hawkins, and Mark L. Dietz, “Evaluation of Solid-Supported Room-Temperature Ionic Liquids Containing a Crown Ether as Novel Media for Metal Ion Separation and Preconcentration” YCC symposium, Milwaukee, WI (Fall 2013) {poster}

M. A. Momen, Mark L. Dietz, “Microfluidic Paper-Based Analytical Devices (μPADs)”, Department of Chemistry & Biochemistry, University of Wisconsin-Milwaukee, WI (Fall 2010). {seminar}

Awards

University of Wisconsin-Milwaukee Graduate Students Travel Awards	2015
University of Wisconsin-Milwaukee Chancellor’s Award	2009-2014
National Science and Technology Fellowship, Ministry of Education, Bangladesh,	2000