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Separation and Preconcentration of Cesium from Acidic Media by Extraction Chromatography

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Abstract: A novel extraction chromatographic resin for the separation and preconcentration of cesium from acidic nitrate media comprising an inert polymeric substrate impregnated with 1,3-calix[4]bis-*o*-benzo-crown-6 ("BC6B") in a chlorinated diluent is described. Cesium is shown to be both strongly and selectively retained by the resin at low (<1 M) acid concentrations and readily eluted from it using 6 M HNO_3. Only potassium ion (at concentrations exceeding ca. 0.01 M) exerts a significant adverse impact on cesium retention. Unexpectedly, cesium uptake by the resin does not exhibit the acid dependency anticipated from liquid-liquid extraction data. This is also the case for a resin employing a related macrocyclic extractant, calix[4]arene-*bis*-(t-octylbenzocrown-6) ("BobCalix"), prepared and partly characterized in an effort to overcome certain limitations of the BC6B-based material. Despite this, the resin is shown to be well suited to the isolation of radiocesium from acidic solution for subsequent determination or for the removal of cesium intereference in the quantitation of other radionuclides.

Keywords: Cesium, separation, preconcentration, extraction chromatography, calixarene

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INTRODUCTION

The development of improved methods for the separation of cesium from other metal ions in aqueous solution has long been of interest in a number of areas, ranging from nuclear fuel reprocessing and waste treatment (1–3) to radiochemical analysis (4, 5) and nuclear medicine (6). Over the past four decades, numerous approaches to effecting this separation have been described, among them liquid-liquid (l–l) extraction (7), ion exchange (8, 9), fixation on inorganic sorbents (10–12), precipitation (13), and various forms of chromatography (6, 13, 14). Among analytical-scale methods for cesium (particularly Cs-137) separation and preconcentration, sorption on any of a variety of inorganic ion-exchange materials (e.g., ammonium molybdophosphate (15, 16), potassium hexanitratocobaltate (17), ammonium hexacyanocobaltferrate (18)) has probably received the most attention. Although effective, inorganic sorbents are not without drawbacks. Their fine powder form, for example, hinders their use in a column mode without prior fixation in a supporting matrix (19). The preparation of these supported sorbents is frequently cumbersome, however. Moreover, the reproducibility of the results obtained with them is often unsatisfactory (19). Also, inorganic ion exchangers are not always efficient (i.e., cesium recovery is incomplete (20).) Finally, although generally selective, they are not immune from interference. Not insignificant sorption of Am(III) and Eu(III) on alumina-supported ammonium molybdophosphate (AMP) from nitric acid solution has been noted, for example (19). For these reasons, there continues to be interest in the development of alternative approaches to cesium separation.

A number of studies have been concerned with the application of extraction chromatography, a form of liquid-liquid chromatography in which the stationary phase comprises an extractant or extractant solution sorbed in a porous polymeric (e.g., PTFE) or inorganic (e.g., silica) substrate, to the separation and preconcentration of cesium (6, 21–28). Early work by Cesarano et al. (21) demonstrated that cesium could be separated from certain fission product elements (e.g., Ru-106, Zr-95, Nb-95) for subsequent determination on a chromatographic colum packed with sodium tetraphenyl boron (TPB) in amyl acetate supported on Kel-F (polytrifluoro-chloroethylene) powder. The significant water solubility of TPB, however, led to a material exhibiting poor physical stability. Several subsequent investigators (24), (25, 27, 28) have evaluated extraction chromatographic materials based on various acyclic polyethers or related macrocyclic polyethers ("crown ethers"), including dibenzo-18-crown-6, benzo-15-crown-5, dicyclohexano-18-crown-6, diamino-dibenzo-18-crown-6, and 12-crown-4, typically dissolved in a chlorinated diluent (e.g., chloroform). In most instances, however, cesium retention by the materials is very poor. Better results have been obtained by employing Kel-F beads loaded with cobalt dicarbolide or its chloro- derivative dissolved in nitrobenzene. Column reuse is precluded by the need to elute sorbed cesium with acetone, however (26).

In the early 1980's, Izatt et al. showed that calixarenes, cyclic oligomers obtained by condensation of formaldehyde with p-alkyl phenols, will selectively and efficiently transport cesium ion through bulk liquid membranes (29). Because these compounds are only poorly soluble in most conventional organic solvents and because significant ion transport occurs only at very high pH (> 12), recent work in this area has sought to identify calixarene derivatives combining the high selectivity of the parent compound with improved physicochemical properties and effectiveness at lower pH (30). Of considerable interest in this context have been calix[*n*]crown-*m* ($n = 4$, 6, or 8) compounds and the analogous calix[*n*]arene-*bis*-(crown-*m*) derivatives, particularly those in which a calix[4]arene framework is maintained in a 1,3-alternate conformation by one or two polyoxyethylene bridges, respectively (31–33). (Any remaining phenolic units are typically replaced with alkyl chains.) Over the last decade, a variety of such compounds have been prepared and their performance as extractants for cesium from aqueous media assessed (30). Work by Asfari et al. (33) has identified 1,3-calix[4]bis-*o*-benzo-crown-6 (Fig. 1) as being especially effective for the selective extraction of cesium from high salinity media such as acidic radioactive liquid wastes, and a supported liquid membrane system employing *o*-nitrophenyl hexyl ether as the diluent has been described. Despite studies demonstrating the utility of such "calixcrown ethers" in cesium separations (34) and the growing interest in extraction chromatography as a facile approach to the separation and preconcentration of a variety of radionuclides for subsequent determination (35), no effort has been made to date to evaluate

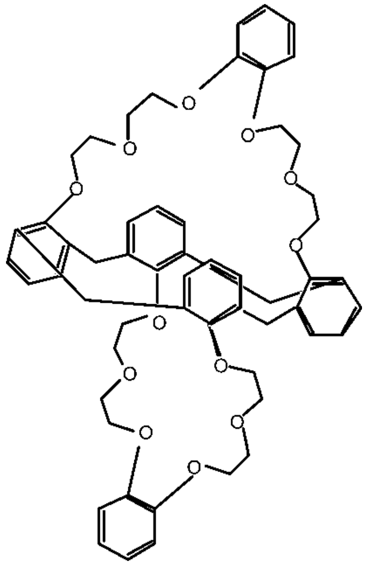

Figure 1. Structure of 1,3-calix[4]bis-*o*-benzo-crown-6 ("BC6B").

these compounds as the basis for an extraction chromatographic (EXC) material for cesium.

In this report, we describe the preparation and characterization of a novel extraction chromatographic resin incorporating a calixcrown ether. Despite unexpected differences in the behavior of the resin-supported compound *versus* the analogous liquid-liquid systems, the calixcrown ether is shown to provide a chromatographic material exhibiting efficient and selective uptake of cesium ion over a range of conditions.

EXPERIMENTAL

Materials

The 1,3-calix[4]bis-*o*-benzo-crown-6 ("BC6B") was a generous gift from Oak Ridge National Laboratory and was used as received. Calix[4]arene-*bis*-(t-octylbenzocrown-6) ("BobCalix") was obtained from IBC Advanced Technologies (American Fork, UT) and used without further purification. Nitric acid solutions were prepared from the Ultrex reagent (J. T. Baker Chemical Co., Phillipsburg, NJ). All water was obtained from a Milli-Q2 water purification system (Millipore, Bedford, MA). All other materials were ACS reagent grade and were used as received. Radiochemical experiments were performed using isotopes obtained from either ANL stocks (e.g., Cs-137, Am-241, Pb-210) or Isotope Products Laboratories (e.g., Sr-85, Ca-45) (Valencia, CA).

Procedures

Liquid-Liquid Extraction Studies

Cesium distribution ratios (D_{Cs} values) between solutions of aqueous nitric acid and 1,2-DCE solutions of the calixcrown ethers were measured radiometrically using a Cs-137 tracer. Prior to a distribution experiment, the organic phase was preconditioned *via* two contacts with twice its volume of an appropriate acid solution. An aliquot of this pre-equilibrated organic phase and an equal volume of fresh, tracer-spiked acid solution were then vigorously agitated for several minutes using a vortex mixer, then centrifuged until phase separation was complete. Two aliquots (100-200 μL) of each phase were then removed for analysis. The Cs-137 activity in all samples was then measured by gamma spectroscopy using a "Cobra II Auto-Gamma" counter (Packard Instruments, Downers Grove, IL). Standard radiometric assay and counting procedures were used throughout. Distribution ratios were typically reproducible to within $\pm 5\%$. All measurements were performed at 23 ± 2 °C.

Preparation of Extraction Chromatographic Resins

The extraction chromatographic resins were prepared by impregnating Amberchrom CG-71 m resin (Rohm and Haas Co., Philadelphia, PA) with a solution of the appropriate calixcrown ether in 1,2-dichloroethane (1,2-DCE). Using procedures described previously (36), modified only by the substitution of dichloromethane for methanol as the carrier solvent, materials comprising 40% w/w of the extractant solution ($\geq$0.05 M calixcrown in 1,2-DCE) on the support were obtained.

Column Preparation and Characterization

Columns were slurry packed (in water) under nitrogen pressure as previously described (37). Unless otherwise noted, column experiments were carried out using 7.9 mm i.d. disposable plastic columns (Isolab, Akron, Ohio). Detailed column characterization studies (i.e., determination of bed density, stationary phase volume, and free column volume (FCV)), the results of which are summarized in Table 1, were performed with a precision-bore glass column of known dimensions using procedures detailed in a prior report (38).

Elution Profile for Radiocesium

The elution behavior of Cs-137 on a column of the BC6B-based resin was determined using 0.5 M HNO_3 as the eluent. Specifically, a small (10 μL) aliquot of a Cs-137 tracer solution in 0.1 M acid was introduced to the top

Table 1. Characteristics of the Cs-selective extraction chromatographic material and packed columns

Bulk material	
Stationary phase	0.05 M "BC6B" in 1,2-DCE
Support	Amberchrom™ CG-71 m
Particle diameter	50–100 micron
Extractant loading	40% (w/w)
Density of extractant-loaded beads	1.27 g/mL[a]
Packed Columns	
V_s, mL/mL of bed	0.102
Bed density (g/mL)	0.305
V_m, mL/mL of bed (also FCV)	0.688
V_s / V_m	0.148
Capacity calculated, mg Cs^+ / mL of bed	0.68[b]

[a] Picnometric density and flotation density values were 1.23 and 1.31 g/mL, respectively.

[b] Assumes 1 : 1 stoichiometry between the extractant and cesium ion.

of the resin bed, then eluted with 0.5 M HNO_3. Aliquots of the column effluent were collected throughout the elution, and measured volumes of each gamma counted. Gravity flow rates (1–2 mL cm^{-2} min^{-1}) were employed throughout. All runs were performed at ambient temperature (23 ± 2 °C).

Elution Behavior of Selected Elements

A 1-FCV (0.69 mL) aliquot of a multi-element stock solution containing more than two dozen metal cations (selected because of their possible presence in a variety of environmental, biological, or nuclear waste samples) was introduced to a column of the Cs-selective resin (bed volume = 1.0 mL; bed height = 2.0 cm) and eluted with 0.5 M HNO_3. The eluate was collected in a series of 5 FCV aliquots until 35 FCV had been collected, at which point the eluent was changed to 6 M HNO_3, an acidity at which cesium ion is not retained. A total of 20 additional FCV were collected. Portions of each sample were then subjected to analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Gravity flow rates (1–2 mL cm^{-2} min^{-1}) were employed throughout.

Determination of Weight Distribution Ratios and Column Capacity Factors

The sorption of cesium and other radionuclides (e.g., Na-22, Ba-133) from nitric acid was measured by contacting a known volume (typically 1.00 mL) of a spiked acid solution of appropriate concentration with a known weight of extraction chromatographic resin in a culture tube. The exact ratio of aqueous phase volume (mL) to resin weight (g) was chosen to yield a readily measurable decrease in the initial aqueous activity upon a single contact with the resin. A vortex mixer was employed to ensure efficient contact of the resin and aqueous phase. Under the experimental conditions, equilibrium is generally achieved very rapidly (ca 5 min). Nonetheless, for convenience, longer contact times (ca 15 minutes) were normally employed. Following equilibration, the samples were centrifuged and the aqueous phase carefully withdrawn from the test tube. To ensure that the aqueous phase was free of dispersed resin, it was filtered through either a porous plastic frit (Isolab) or a 0.45 μm syringe filter (Whatman, Inc., Florham Park, NJ).

Weight distribution ratios were calculated from the following equation:

$$D_w = (A_0 - A_s)/W\big/(A_s/V)$$

where A_o and A_s are the aqueous phase activities (cpm) before and after equilibration, respectively, W is the weight of resin (g), and V is the volume of aqueous phase (mL). This distribution ratio may be converted to the number of free column volumes to peak maximum, k′ (i.e., the resin capacity factor) by dividing by 2.21. This factor includes conversion of D_w to D, a volume distribution ratio, through the extractant density and the ratio of V_s to V_m typically observed for columns packed with the Cs-selective resin, 0.148.

The effect of macro concentrations of selected ions on cesium uptake by the resin was evaluated by measuring the sorption of Cs-137 from 0.5 M HNO_3 containing various concentrations of the ion of interest.

Resin Stability

The resistance of the Cs-selective resin to extractant loss induced by acid washing (i.e., by dissolution and shear effects) was evaluated by comparing the elution profile of Cs-137 on a column of fresh resin to that observed following washing of the resin with 200 FCV of water.

RESULTS AND DISCUSSION

Nitric Acid Dependency of Cesium Partitioning in L-L and Extraction Chromatographic Systems

Measurements of the partitioning of a metal ion in liquid-liquid (l-l) systems have often been demonstrated to provide useful insights into the expected behavior of the ion in analogous extraction chromatographic systems (39). For this reason, our initial efforts to devise a chromatographic sorbent for cesium focused on its extraction by BC6B into 1, 2-DCE under various conditions. Figure 2a depicts the nitric acid dependency of D_{Cs} at constant (0.05 M) BC6B concentration. As can be seen, D_{Cs} increases with rising nitric acid (and therefore nitrate) concentration to a maximum at *ca.* 4 M acid. Such behavior is consistent with that reported by Asfari et al. for a closely related extractant, 1,3 calix[4]biscrown-6, in 1,2-nitrophenyl octylether, for which a maximum in the dependency was observed at *ca.* 2 M acid (33). The decline in cesium extraction at higher acidities was attributed both to activity effects and competitive extraction of acid by the calixcrown, and these effects likely also explain the dependency observed for BC6B. Figure 2b depicts the nitric acid dependency of $D_{w,Cs}$ on an extraction chromatographic resin prepared by simply dispersing the same extractant solution on a porous polymeric support. That the dependency is significantly different than that observed in the liquid-liquid system is immediately evident. That is, cesium sorption by the resin is essentially invariant from 0.01 to 1 M HNO_3, above which it falls precipitously. This disagreement is both unexpected and not readily explained. Although a few reports have suggested that even an ostensibly "inert" substrate can affect the physicochemical properties of a supported extractant (40–42), in most instances, l-l extraction studies have been shown to provide the basis for at least a qualitative prediction of the behavior of an analogous chromatographic system. Clearly, in the present system, the complexation properties of the extractant are being

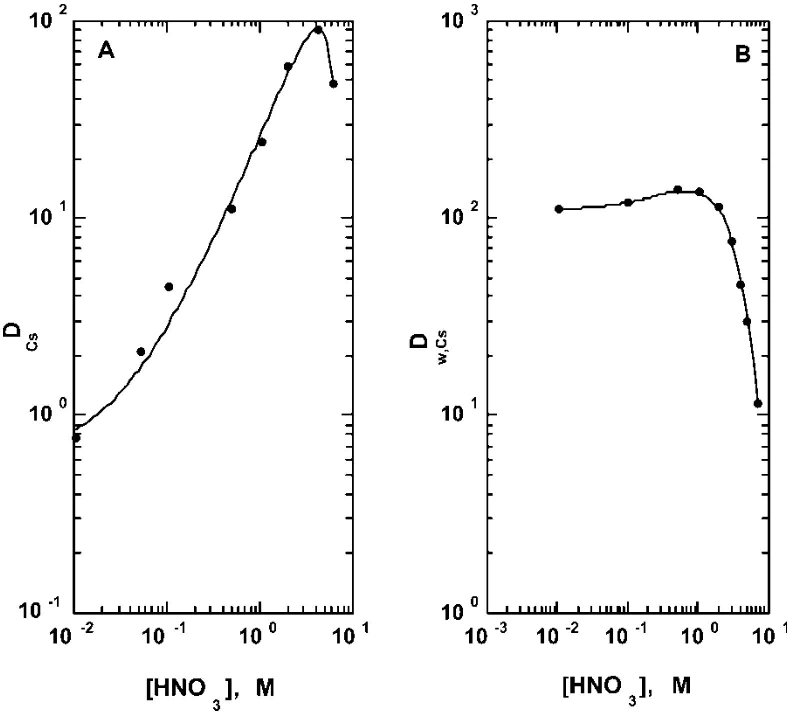

Figure 2. (A) Nitric acid dependency of cesium extraction into 1,2-DCE by "BC6B" (0.05 M). (B) Nitric acid dependency of cesium sorption on Cs-selective extraction chromatographic resin comprising 0.05 M BC6B in 1,2-DCE supported on Amberchrom CG-71 m.

significantly affected by its adsorption on the support. The precise nature of the effects and their relationship to the shape of the acid dependency observed for cesium uptake, however, remain unclear at present.

From a practical perspective, it must be noted, the disagreement between the l-l and chromatographic results poses no problem (although it clearly precludes the use of l-l extraction data as a basis for optimizing the composition of the extraction chromatographic material). In fact, that cesium is efficiently sorbed by the resin from solutions containing a wide range of nitric acid concentrations and not retained at high acidities (implying that cesium stripping/recovery should be facile under these conditions) actually represents a useful combination of resin properties.

Nitric Acid Dependency of D_w for Selected Elements

Figure 3 summarizes the results of measurements of the uptake of various alkali, alkaline earth, transition, and actinide elements by the Cs selective

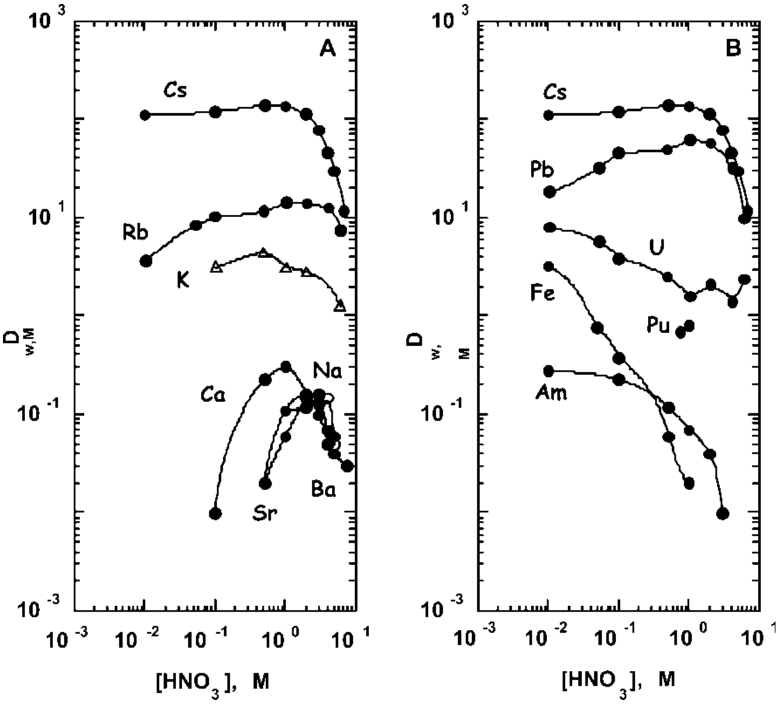

Figure 3. Nitric acid dependency of the uptake of selected alkali, alkaline earth, transition metal, and actinide ions on the Cs-selective extraction chromatographic resin.

resin. (For ease of viewing, the data are presented in two panels. To facilitate comparisons, the results for cesium are presented in both.) Several features of the data are noteworthy. First, the uptake of cesium is significantly greater than that of any of the alkaline earth or other alkali metal cations over a wide range of acidities. The magnitude of the D_w values for these ions, in fact, is such that they would be essentially unretained on a column of the Cs resin under most conditions. (The behavior of rubidium at high (*ca.* 1-3 M) acidities represents a notable exception.) From the perspective of the possible application of this resin in environmental analysis, its excellent selectivity for cesium over sodium, calcium, and iron, all of which are ubiquitous in environmental samples, is particularly worthy of mention. Next, the uptake of tri-, tetra-, and hexavalent actinides, as represented by Am(III), Pu(IV), and U(VI), respectively, is also poor, indicating that the Cs resin may be applicable in coupled-column schemes, in which multiple radionuclides (e.g., Cs-137 and actinides) are isolated sequentially from a single sample solution (43). Also, the retention of lead on the resin is nearly as great as that of cesium at certain acidities (ca 2 M HNO_3), a not entirely unexpected result given the high affinity of 18-crown-6-based macrocycles for lead ion (44, 45). Finally, it is interesting to note that the selectivity exhibited by the Cs resin compares quite favorably with that reported for commercial (Empore^{TM}, 3M Corp.) "Cesium Rad Disks" (comprising potassium cobalthexacyanoferrate particles embedded in a PTFE membrane), for which capture of strontium-90, barium-133, and uranium-238 (all potential interferents in the low-background gas proportional counting of cesium-137) has been reported (46).

Elution Profile of Cs-137

Figure 4 depicts the elution behavior of Cs-137 on a column of the Cs-selective resin using 0.5 M HNO_3 as the eluent. The value of the column capacity factor, k', obtained from this curve (V_{max} − 1), 60, is in excellent agreement with the value obtained from batch uptake (D_w) measurements ($k' = D_w/2.21$), 64. The number of theoretical plates (a measure of column efficiency) calculated from the elution curve, 40, is somewhat lower, however, than the plate numbers typically reported for Amberchrom-based extraction chromatographic materials of this particle size (38, 47, 48). Determination of the predominant factor underlying the modest column efficiency in this system (i.e., flow phenomena, stationary phase diffusion, or extraction kinetics) would

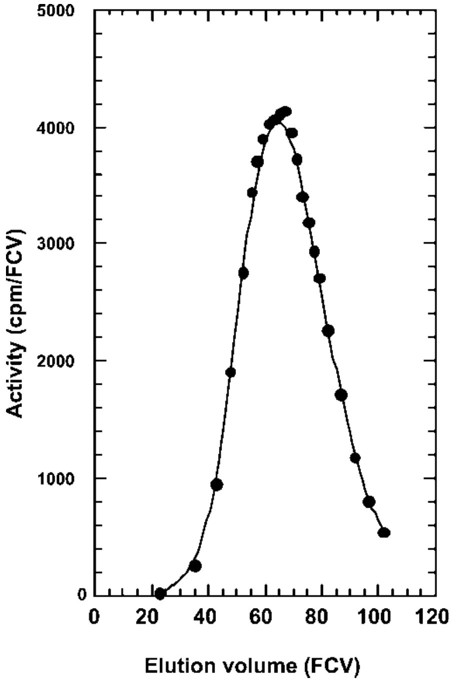

Figure 4. Elution behavior of Cs-137 on a column of Cs-selective extraction chromatographic resin. (Eluent = 0.5 M HNO_3).

require the measurement of the number of theoretical plates as a function of mobile phase velocity and temperature for a series of resins comprising different particle sizes and extractant loadings (39), measurements beyond the scope of the present work. It should be noted, however, that because the rate of cesium uptake by the resin (Fig. 5) is comparable to that of other cations on related chromatographic materials, the lower column efficiency appears unlikely to have its origins in slow extraction kinetics.

Elution Behavior of Selected Cations

The magnitude of the k′ value obtained for cesium ion from 0.5 M HNO_3 (Fig. 4) and the excellent selectivity exhibited by the resin over various potential interferents (Fig. 3) suggests that it should be possible to elute many commonly encountered sample constituents from the Cs resin prior to cesium breakthrough. Table 2 summarizes the elution behavior of more than two dozen elements using 0.5 M HNO_3 as the mobile phase. As can be seen, nearly all of the test elements are quantitatively removed in the first 5 FCV of eluent. (Ru and Pd require 10-15 FCV.) Especially noteworthy is the

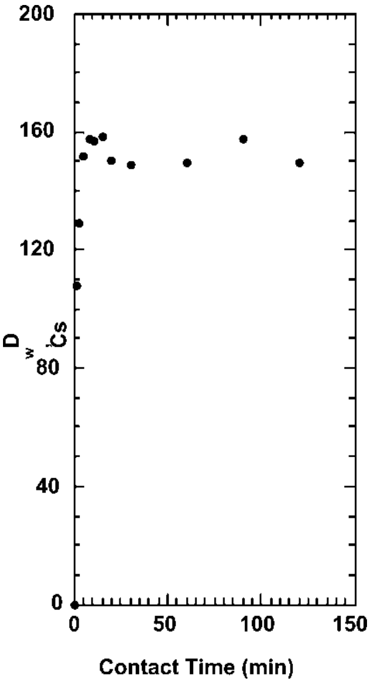

Figure 5. Kinetics of cesium uptake from nitric acid solution (0.5 M) by the Cs-selective extraction chromatographic resin.

Table 2. Elution behavior of selected elements on a column of cs-selective extraction chromatographic resin

	Number of free column volumes[a] Portion eluting (%)[b] 0.5 M nitric acid							6 M nitric acid		
Element	1–5	6–10	11–15	16–20	21–25	26–30	31–35	36–40	41–45	46–50
Na	94.5	0.9	0.6	0.5	0.4	0.3	0.4	–	–	–
Mg	100	–	–	–	–	–	–	–	–	–
Al	98.6	0.4	0.1	0.1	0.1	0.1	0.1	–	–	–
Ca	100	–	–	–	–	–	–	–	–	–
Cr	99.3	0.4	–	–	–	–	–	–	–	–
Mn	100	–	–	–	–	–	–	–	–	–
Fe	100	–	–	–	–	–	–	–	–	–
Ni	99.1	–	–	–	–	–	–	–	–	–
Cu	98.4	–	–	–	–	–	–	–	–	–
Sr	99.4	–	–	–	–	–	–	–	–	–
Y	97.3	–	–	–	–	–	–	–	–	–
Zr	95.7	–	–	–	–	–	–	–	–	–
Mo	96.9	–	–	–	–	–	–	–	–	–
Ru	83.2	9.3	2.5	1.0	–	–	–	–	–	–

Rh	95.5	–	–	–	–	–	–	–	–	–
Pd	84.7 4.1	–	–	–	–	–	–	–	–	–
Cd	93.8	–	–	–	–	–	–	–	–	–
Ba	100	–	–	–	–	–	–	–	–	–
La	98.5	–	–	–	–	–	–	–	–	–
Ce	98.7	–	–	–	–	–	–	–	–	–
Pr	99.5	–	–	–	–	–	–	–	–	–
Nd	99.5	–	–	–	–	–	–	–	–	–
Sm	97.1	–	–	–	–	–	–	–	–	–
Eu	87.4	–	–	–	–	–	–	–	–	–
Cs	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.12	28.4	61.9	7.5

[a] 1 FCV = 0.69 mL here.

[b] Because of uncertainties inherent in the ICP-AES method used for analysis, the fractions shown for a given element may not total 100%.

facile elution of zirconium, which has been reported as a significant interferent in the estimation of cesium-137 in urine (15). As expected from Fig. 4, no trace of cesium is observed up to ca. 35 FCV of the 0.5 M acid. Once the eluent is changed to 6 M HNO_3, however, cesium removal is complete in only 15 FCV.

Physical Stability

Because extraction chromatography inevitably involves the contact of a comparatively small volume of a highly dispersed organic extractant exhibiting some finite water solubility with a much larger volume of aqueous phase, the possibility of extractant loss from the resin, along with the accompanying deterioration in column performance, must be considered in evaluating any new chromatographic material. In fact, insufficient physical stability has long been recognized as being among the most important factors limiting the more widespread application of extraction chromatography (39). Figure 6 depicts the effect of column washing on the elution behavior of Cs-137 on the Cs-selective resin. As can be seen, the elution profile observed following washing of the column with 200 FCV of water (which corresponds to approximately 1350 times the volume of extractant solution present) is essentially indistinguishable from that observed on a column of unwashed resin. From the perspective of possible analytical applications, this is significant for two reasons. First, it indicates that the resin could cope with a substantial load volume in a given run. In addition, it indicates that a given column could be used more than once, assuming of course, that adequate care is taken to avoid cross-contamination between samples.

Matrix Effects

The nitric acid dependency data presented in Fig. 3 and the elution data in Table 2 are important not only because they show conditions that are suitable for the separation of cesium from other cations, but also because they indicate which elements may cause a significant decrease in the retention of cesium if present at sufficiently high concentrations (i.e., exceeding 20% of column capacity). The uptake of lead and rubidium, for example, would be expected to compete with cesium sorption under certain conditions (Fig. 3). These elements are not, however, typically found in high concentrations in “real world” (i.e., environmental, biological, or geological) samples. Rather, significant quantities of such elements as sodium, iron, and calcium are present in these materials, and it is for this reason that their influence on the retention of cesium by the new resin has been evaluated (Fig. 7). Of the elements tested, potassium clearly has the most pronounced effect, with concentrations as low as 0.01 M reducing $D_{w,\ Cs}$ (and thus, k') by nearly a factor of 2. The presence of only 0.05 M K^+, in fact,

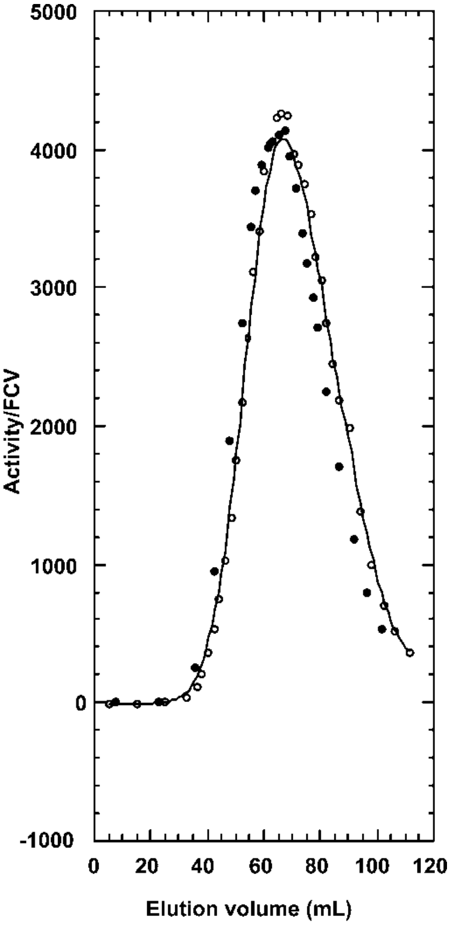

Figure 6. Effect of column washing on the elution behavior of Cs-137 on the Cs-selective extraction chromatographic resin. (Eluent = 0.5 M HNO_3; Open circles: unwashed column; Filled circles: washed (200 FCV) column).

would likely render the resin unusable for cesium separations, as cesium breakthrough would occur during the column rinsing to remove other ions present. In contrast, the effect of sodium, calcium, and iron is negligible, even at high (*ca.* 0.5–1 M) concentrations.

Alternate Resin Formulation

Although the good physical stability of the Cs selective resin suggests that it would be well suited for even relatively large sample volumes, cesium

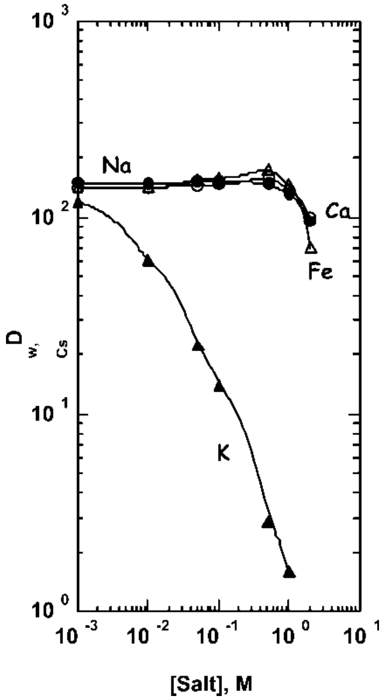

Figure 7. Effect of increasing concentrations of various matrix elements on the sorption of cesium ion by the Cs-selective extraction chromatographic resin from 0.5 M nitric acid.

retention on the resin is not sufficient to make such volumes practical. Given the low levels of Cs-137 typically encountered in environmental analyses and the not infrequent need for its concentration from a significant volume of sample, it would clearly be desirable to have available an extraction chromatographic resin exhibiting stronger retention of cesium while maintaining facile stripping. Although in principle, such a material might be obtained simply by raising the concentration of BC6B in the stationary phase, in actual practice, this is not feasible, both because 0.05 M represents the limit of the extractant solubility in 1,2-DCE and 40% (w/w) loading corresponds to complete filling of the pores of the support. Thus, if k'_{Cs} is to be increased, an alternate extractant will be required. With this in mind, a preliminary evaluation of the di-*t*-octyl derivative of BC6B, "BobCalix" (49), whose solubility in 1,2-DCE is significantly greater than that of BC6B, was undertaken.

Figure 8 depicts the nitric acid dependency of cesium retention on a resin comprising 40% (w/w) of either a 0.05 M or a 0.1 M solution of BobCalix in 1,2-DCE sorbed on Amberchrom CG-71 m. Also shown for purposes of comparison is the dependency for the BC6B-based resin. As is readily apparent, the

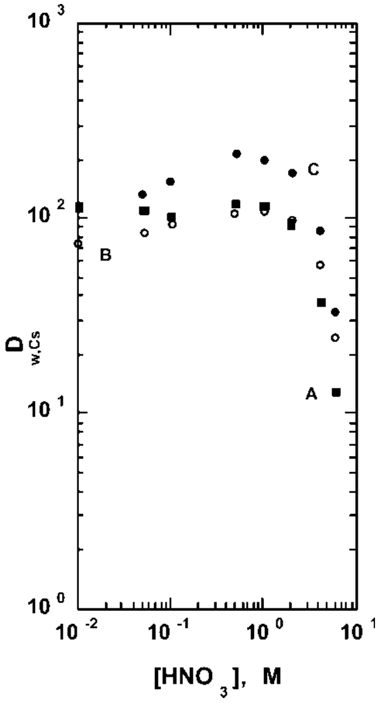

Figure 8. Nitric acid dependency of cesium retention on extraction chromatographic resins comprising various concentrations of BC6B or BobCalix in 1,2-DCE on Amberchrom CG-71 m. (A. 0.05 M BC6B; B. 0.05 M BobCalix; C. 0.10 M BobCalix.)

behavior of the BobCalix resin employing the lower extractant concentration is virtually identical to that of the BC6B-based material, indicating that the incorporation of alkyl side chains into the calixcrown ether has no adverse impact on its cesium complexation/extraction properties. As expected, increasing the stationary phase concentration of the BobCalix does boost the retention of cesium over the entire range of acidities considered. This increase is not consistently a factor of two, however, as would be expected for a doubling of the extractant concentration by assuming a first-power dependence of $D_{w,Cs}$ on BobCalix concentration. Similar behavior (i.e., a lack of direct proportionality between stationary phase extractant concentration and metal ion retention) has been noted in the sorption of radiostrontium by a series of EXC resins incorporating increasing amounts of di-*t*-butylcyclohexano-18-crown-6, for which 20% and 40% (w/w) extractant loading of the support yield nearly the same $D_{w,\ Sr}$ values (48). Such results suggest that not all of the additional extractant is accessible to the mobile phase, thus indicating that attempts to improve the performance of the Cs-selective resin may also require the investigation of alternative supports. Work addressing these opportunities is now underway in this laboratory.

CONCLUSIONS

The results of this study clearly demonstrate that cesium can be rapidly, efficiently, and selectively sorbed from aqueous solution by an extraction chromatographic resin comprising BC6B in a chlorinated diluent supported on a porous polymeric substrate. Unlike commonly employed inorganic sorbents, the EXC resin is readily applied in a chromatographic mode. As is the case for these sorbents, the capacity of the new resin is modest, but this characteristic is unlikely to represent a limitation in most analytical-scale applications of the material.

A number of uses for a Cs-selective EXC material can be readily envisioned. For example, although the readily measurable gamma emission associated with the decay of Cs-137 frequently obviates the need for its preconcentration prior to counting, the low levels of cesium typically encountered in natural waters (5), marine samples (16), milk (20), and soils (4) can make preconcentration necessary or desirable. Just as important is that the presence of radiocesium sometimes complicates the determination of other radionuclides. For example, ^{137}Cs has been shown to interfere in both the determination of ^{63}Ni by coupled liquid chromatography/ on-line scintillation counting (14) and the quantitation of ^{151}Sm in radioactive wastes (50). In such cases, a simple method for cesium removal would greatly facilitate the desired determination. The unique combination of properties exhibited by the Cs-selective EXC resin suggests that it would be well suited to such applications.

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