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RECENT ADVANCES IN THE DEVELOPMENT OF EXTRACTION CHROMATOGRAPHIC MATERIALS FOR THE ISOLATION OF RADIONUCLIDES FROM BIOLOGICAL AND ENVIRONMENTAL SAMPLES

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ABSTRACT

The determination of low levels of radionuclides in environmental and biological samples is often hampered by the complex and variable nature of the samples. One approach to circumventing this problem is to incorporate into the analytical scheme a separation and preconcentration step by which the species of interest can be isolated from the major constituents of the sample. Extraction chromatography (EXC), a form of liquid chromatography in which the stationary phase comprises an extractant or a solution of an extractant in an appropriate diluent coated onto an inert support, provides a simple and efficient means of performing a wide variety of metal ion separations. Recent advances in extractant design, in particular the development of extractants capable of metal ion recognition or of strong complex formation even in acidic media, have substantially improved the utility of the method. For the preconcentration of actinides, for example, an EXC resin consisting of a liquid diphosphonic acid supported on a polymeric substrate has been shown to exhibit extraordinarily strong retention of these elements from acidic chloride media. This resin, together with other related materials, can provide the basis of a number of efficient and flexible schemes for the separation and preconcentration of radionuclides form a variety of samples for subsequent determination.

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The determination of low levels of radionuclides in environmental and biological samples is often hampered by the complex and variable nature of the samples. One approach to circumventing this problem is to incorporate into the analytical scheme a separation and preconcentration step by which the species of interest can be isolated from the major constituents of the sample. Extraction chromatography (EXC), a form of liquid chromatography in which the stationary phase comprises an extractant or a solution of an extractant in an appropriate diluent coated onto an inert support, provides a simple and efficient means of performing a wide variety of metal ion separations. Recent advances in extractant design, in particular the development of extractants capable of metal ion recognition or of strong complex formation even in acidic media, have substantially improved the utility of the method. For the preconcentration of actinides, for example, an EXC resin consisting of a liquid diphosphonic acid supported on a polymeric substrate has been shown to exhibit extraordinarily strong retention of these elements from acidic chloride media. This resin, together with other related materials, can provide the basis of a number of efficient and flexible schemes for the separation and preconcentration of radionuclides form a variety of samples for subsequent determination.

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INTRODUCTION

Extraction chromatography (EXC) is a type of liquid-liquid chromatography in which the stationary phase consists of an extractant or a solution of an extractant in an appropriate diluent supported on an inert substrate. The technique thus couples the selectivity of solvent extraction with the multi-stage character of a chromatographic process and the ease of handling of an ion-exchange resin (1). Since its introduction by Siekierski in 1959 (2), extraction chromatography has been extensively studied (1), and it is now widely recognized that it provides a simple and effective means by which the separation and preconcentration of any of a variety of metal ions can be accomplished. In the determination of radionuclides in environmental or biological samples, for example, the low levels of the nuclides typically encountered and the complexity of the sample matrix often preclude a direct determination of the species of interest. Rather, a preliminary separation and preconcentration step is a prerequisite to quantitation. Although numerous approaches have been described by which this can be accomplished (e.g., solvent extraction, ion exchange), none is entirely satisfactory. Solvent extraction, for example, is unsuitable for routine use on large numbers of samples, since it is cumbersome and generates large volumes of organic waste. Similarly, ion-exchange methods are frequently complicated by the lack of specificity of conventional ion-exchange resins. Extraction chromatography overcomes all of these shortcomings, and provides a selective and facile separation of the radionuclide of interest from complex sample matrices.

In an earlier report (3), we described the development of several new EXC resins based on TRUEX and SREX Process chemistries and related extractant design studies, and outlined the application of these materials in the separation and preconcentration of actinides and/or radiostrontium for subsequent determination. Since this time, certain limitations of these materials and thus, the need for improved EXC materials, have become evident. For example, although one of these materials, referred to as TRU•resin, has been found to be useful in the selective recovery of actinides from complex sample matrices, actinide retention on it has been found to be not particularly strong when high concentrations of complexing anions (e.g., fluoride, phosphate, or oxalate) are present in the sample (4). This poses a significant problem in attempts to isolate actinides from soil samples, as hydrofluoric acid is generally added to dissolve any silica present. In addition, americium retention on the TRU•resin, while better than that seen with many previous EXC materials, has been found to be inadequate for certain applications (e.g., large volume natural water samples) where acidification of the sample to ≥ 1 M nitric acid is not feasible.

Earlier work in this laboratory on the design of improved water-soluble complexants for use as masking or stripping agents has led to the development of a series of substituted methanediphosphonic acid derivatives capable of forming highly stable complexes in acidic media with a variety of metal ions in the tri-, tetra- and hexavalent oxidation states (5). It has since been shown that by replacing two of the four hydrogen atoms with an alkyl group, lipophilic dialkyl-substituted diphosphonic acids can be prepared that are powerful actinide extractants from highly acidic solutions (6). Recently, we have demonstrated that if an inert polymeric support is impregnated with one such compound, di-(2-ethylhexyl) methanediphosphonic acid (H_2DEH[MDP]), an extraction chromatographic resin (referred to hereafter as "Actinide Resin") capable of extremely strong retention of actinides is obtained (7). In this report, we summarize our recent work with this material, and describe our preliminary investigations of a new configuration for EXC, the resin disc format, which promises to significantly improve sample throughput.

EXPERIMENTAL

The sources of all reagents and methods for the preparation and characterization of the EXC resins have been given previously (7-9). Determination of the metal ion uptake properties of the EXC resins was performed as previously described (7-9).

RESULTS AND DISCUSSION

Characterization of the Actinide Resin. Figure 1A depicts the acid dependency of the uptake of several representative actinides from 0.01 to 10 M HCl, while Figure 1B presents analogous results for various non-actinide metal ions commonly encountered in analytical procedures involving environmental or bioassay samples. (Bi(III) and Ti(IV), for example, are common and troublesome constituents of fecal and soil samples.) As can be seen, retention of actinides by the resin is extraordinarily high, a result anticipated from prior studies of the extraction behavior of H_2DEH[MDP] in o-xylene (6). Especially noteworthy is the strong retention of Am(III). Its k' values, in fact, exceed those of the other actinides up to 0.5 M HCl. Although k'_{Am} falls off rapidly at higher acidity, it nonetheless remains above 1000 over nearly the entire range of acidities examined. Of the non-actinides, Eu(III) and Fe(III) exhibit the highest k' values, as expected from the known affinity of the diphosphonic acid ligand for trivalent lanthanides and iron. (Note, however, that if Fe(III) is reduced to Fe(II), its k' values become much smaller.) The behavior of alkaline earth cations on the Dipex resin is consistent with the results of solvent extraction studies using o-xylene solutions of the extractant. Specifically, little selectivity is observed among the various alkaline earths.

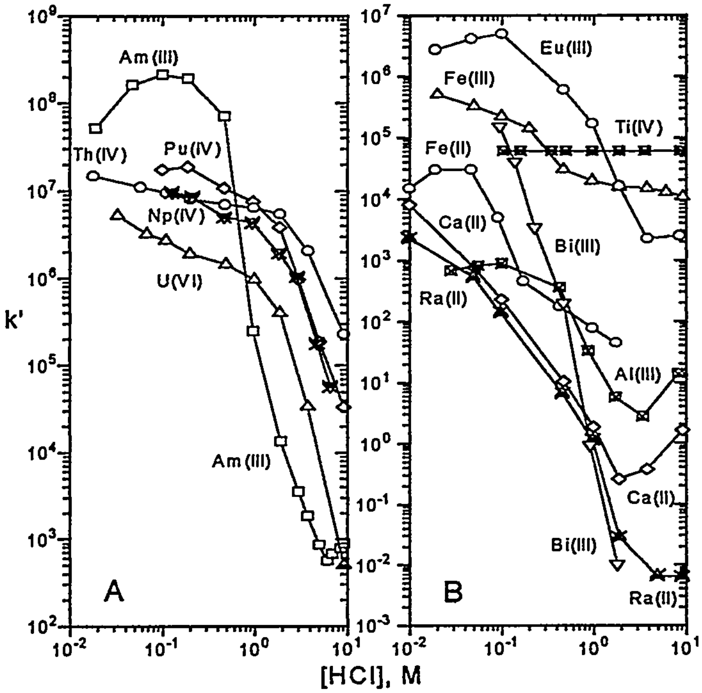

Figure 1. Hydrochloric acid dependency of k' for selected ions on the Actinide Resin.

The kinetics of metal ion uptake by the Actinide Resin are somewhat slower than those previously observed for U/TEVA or TRU resins, with the time required to achieve equilibrium uptake of a metal ion approaching 20 minutes (vs. 10 minutes for the U/TEVA or TRU resins). This is not unexpected given the greater viscosity of the $H_2DEH[MDP]$ stationary phase. One aspect of the resin behavior that is not readily predictable from the properties of the extractant is that the experimental capacity for metal ion uptake is typically much smaller than that calculated on the basis of the metal:extractant stoichiometric ratios required for charge neutralization, a possible consequence of extractant aggregation, polymerization of the complex at high metal ion loadings, or slow diffusion of metal ions in the viscous extractant film. Note, however, that the capacity values are sufficiently high to permit efficient actinide uptake by the resin.

Figure 2 shows the effect of HF on the retention of representative actinides in the tri-, tetra-, and hexavalent oxidation states on the Actinide Resin. Although the k' values for U(VI) and Np(IV) fall rapidly at the highest acid concentrations, up to ~2M HF can be tolerated without serious adverse impact on actinide retention. This is significant for two reasons. First, several potential interfering cations, among them Ti(IV), Zr(IV), and Al(III), form strong anionic fluoride complexes; as a result, their sorption on the actinide resin is significantly reduced (and thus, their intereference minimized) by addition of fluoride. In addition, these results, taken together with those of similar studies with other complexing anions (e.g., PO_4^{3-}) and common cations (e.g., Ca^{2+}), illustrate the relative insensitivity of actinide uptake to matrix composition, a property that considerably simplifies the application of the resin in the analysis of environmental and biological samples, and that represents a significant advantage of the Actinide Resin over previously described EXC materials.

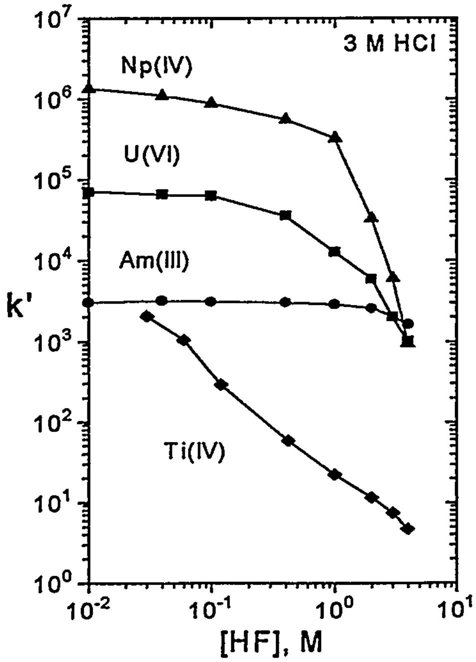

Figure 2. Effect of HF on the retention of selected metal ions on the Actinide Resin.

Applications of the Actinide Resin. Analysis of large-volume water samples. The properties of the Actinide Resin that have been described here, in particular its extremely strong retention of actinides even in the presence of high concentrations of a variety of matrix constituents, make it well-suited to the preconcentration of actinides from soils or large-volume water samples for subsequent determination. In a simple experiment that nicely illustrates the potential usefulness of the resin in such applications, aliquots of acidified (HNO_3) river water were spiked with Am-241 and contacted with various amounts of the Actinide Resin in a batch mode. After a fixed time, the supernatant solution was counted to determine the extent of Am sorption by the resin. The results indicate that a single gram of the resin can sorb Am quantitatively from as much as 3.5 L of water. Under the same conditions, approximately 90% recovery of tetra- and hexavalent actinides is observed.

Soil analysis. The Actinide Resin provides a means of simplifying complex sample matrices, thereby facilitating subsequent actinide determinations. For the determination of actinides in soils, for example, dissolution of the sample via NaOH fusion is followed by washing and dissolution of the iron hydroxide residue in HCl, removal or sequestration of the silica, and addition of ascorbic acid to reduce iron to the divalent state. At this point, the sample solution can be loaded onto a column of the Actinide Resin, where at 2 M HCl, actinides will be strongly sorbed. Following column rinsing to remove, for example, Ti(IV) and residual Si, the actinides can be eluted from the column with a small volume of isopropanol. This treatment, which also removes the stationary phase (i.e., extractant) from the resin, yields a small quantity of actinide-DPA complexes, which must be oxidized to convert the actinides to a form suitable for chemical separations. The oxidation product of this extractant is phosphoric acid, which upon addition of Ca^{2+}, can be made to precipitate basic calcium phosphate. At this point, a complex soil matrix has been converted to a much simpler form ($CaHPO_4$), thereby making subsequent separation schemes simpler and more predictable. A scheme consisting of columns of the U/TEVA and TRU resins operated in tandem have, for example, been shown to provide an effective method for the isolation of U and Th (U/TEVA•resin) or Am and Pu (TRU•resin) for subsequent quantitation.

Gross alpha activity. One of the most frequently requested radioanalytical analyses in environmental monitoring involves the determination of "gross alpha" activity. In standard protocols for this analysis (10), aqueous samples are evaporated onto a stainless steel planchet followed by counting in a gas flow proportional counter (GPC) after a prescribed period. This method suffers from a number of limitations, among them low counting efficiency, long counting times, large counting errors, and self-absorption problems (making coprecipitation necessary for radionuclide isolation from samples containing high levels of solids). These problems can be avoided by taking advantage of the nearly quantitative sorption of actinides and the very high (~80%) sorption of Ra-226 from acidified (pH 2) water samples. Specificially, the water sample is reacted in a batch mode with the Actinide Resin, after which the sample is filtered and the collected resin transferred to a scintillation vial containing liquid scintillation (LS) cocktail. The cocktail dissolves the extractant (and radionuclide-extractant complexes) from the support, leaving the inert, translucent beads at the bottom of the vial. Samples are then counted on an LS counter. Application of this technique to the analysis of ten natural water samples has demonstrated that it yields results that agree well with those obtained by the conventional GPC method. At the same time, counting efficiency, precision, sample throughput, and detection limits are significantly improved. Average recoveries from groundwater simulants range from 76.2% for Th-232 to 95.9% for U-234/238 (11).

Disc-format EXC. For the determination of the concentration of individual actinides in various samples, tandem EXC column arrangements , in which the effluent from one column becomes the influent for another (e.g., an Actinide Resin column followed by U/TEVA and TRU columns) have been suggested (9, 12). Passing large volume samples through multiple EXC columns, however, can be time-consuming. For this reason, there has been considerable recent interest in the development of new physical configurations for EXC by which the speed of a separation might be increased. Recently, an EXC resin consisting of Aliquat 336™ sorbed on silica has been incorporated into a glass fiber filter to yield an EXC disc (13). This "TEVA (for tetravalent actinide specific) Disc" can be positioned in a standard filtering funnel and the sample solution passed through it without applied pressure. Following appropriate rinsing, sorbed radionuclides (e.g., Tc-99) can be counted. This format has been found to permit flow rates of up to ~33 mL/min; thus, a 1 L water sample requires only 30 minutes for treatment. In tests of the TEVA Disc in the determination of Tc-99 in groundwater simulants, recoveries averaging 95.9% have been obtained. Higher volume samples (3-6 L) yield slightly lower recoveries (85-90%), but provide improved limits of detection (0.30 pCi/L for a 6 L sample). These results compare favorably with those of traditional TBP extraction methods, and suggest that the disc format offers many possibilities for the improvement of EXC methods.

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