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Separation and Preconcentration of Uranium from Acidic Media by Extraction Chromatography*

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ABSTRACT

A novel extraction chromatographic resin for the separation and preconcentration of uranium from nitric and hydrochloric acid solutions comprised of diamyl amylphosphonate sorbed on an inert polymeric support (Amberlite XAD-7) is described. Uranium sorption by the resin is shown to be most efficient at high (> 1 M) acid concentrations. Sorbed uranium can be eluted using only dilute acid. The application of the material to the isolation of uranium from various environmental samples (e.g., groundwater and soil) is described. Uranium recoveries from these samples are shown to be consistently high (~ 95%).

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INTRODUCTION

Numerous methods have been described for the determination of uranium in a variety of matrices [1-5]. In many instances, the low concentrations of uranium encountered and the presence of high levels of potentially interfering matrix constituents preclude its direct determination. As a result, various separation and preconcentration techniques are often employed prior to analysis [6-8]. The separation of uranium is also frequently required for the characterization of various uranium-rich samples, among them certain minerals [9], waste solutions, and uranium metal itself [10], since high levels of uranium can interfere with the accurate quantitation of various trace elements (e.g., rare earths).

Many methods have been described for effecting the separation of uranium from mixtures of cations. Liquid-liquid extraction, for example, has been widely applied. Unfortunately, it is far too time-consuming for routine use on large numbers of samples. Many procedures based on ion-exchange have also been described [11]. The lack of specificity of conventional ion-exchange resins, however, often complicates sample treatment. Several previous workers have proposed the use of reversed-phase partition chromatography ("extraction chromatography"), in which an inert support is impregnated with a selective organic extractant to produce a solid sorbent, for the isolation of uranium from various samples [12]. Of the extractants studied to date, the neutral organophosphorus extractant tri-n-butyl phosphate (TBP) has probably received the most attention [13-18]. Hamlin et al. [13], for example, described a procedure for the analysis of uranium compounds incorporating a separation of uranium on a column of Kel-F moulding powder supporting TBP. This procedure was incorporated by Huff [14] into a combined anion exchange-extraction chromatographic method for the analysis of uranium alloys. More recently, Al-Ammar et al. have investigated the chromatographic behavior of TBP-impregnated macroporous Amberlite XAD-4 and have applied the material to the separation of uranium from impurities in nuclear grade uranium compounds prior to analysis by ICP-AES [15]. Other organophosphorus extractants, including bis-2-ethylhexyl phosphoric acid, HDEHP, (on kieselguhr) [19] and tri-n-octyl phosphine oxide (on Wofatit EP-60) [20], and various sulfur-based extractants (e.g., dioctyl sulfoxide, DOSO, [21]), have also been examined for use as stationary phases.

Without exception, the extraction chromatographic materials described to date suffer from limitations which make alternate materials desirable. With the DOSO-based resin, for example, best results are obtained when the extractant is dissolved in a chlorinated solvent and when the aqueous phase contains high concentrations of perchlorate ion. Waste disposal considerations, however, make both chlorinated solvents and perchlorate salts less than ideal. The HDEHP-based material is plagued by the formation of gel-like U(VI)-HDEHP inside the column body. In addition, because HDEHP is an acidic extractant, the resin is not suitable for samples containing

high concentrations of nitric or hydrochloric acids. Such solutions often result from the preliminary digestion or leaching of environmental or biological samples. Finally, because of the significant water solubility of TBP, the useful lifetime of a TBP-based resin is likely to be limited.

Earlier work in this laboratory [22] has shown that certain neutral, phosphorus-based extractants, structurally similar to TBP but differing in either the basicity of the phosphoryl group or the extent of branching of the alkyl chains, exhibit extraction properties superior to those of TBP. In this report, we examine the performance of an extraction chromatographic material based on one of these extractants, diamyl amylphosphonate (DAAP), and describe the application of the material to the isolation of uranium from environmental samples.

EXPERIMENTAL

Reagents.

Diamyl amylphosphonate was obtained from Albright & Wilson (Richmond, VA). The crude product was purified by distillation (T = 105 °C) at reduced pressure (0.1 mm). Nitric and hydrochloric acid solutions were prepared from the Ultrex reagents (J. T. Baker Chemical Co.). All water was obtained from a Milli-Q2 water purification system. All other materials were ACS reagent grade and were used as received. Radiochemical experiments were performed using ^{137}Cs, ^{230}Th, ^{233}U, ^{239}Np, ^{239}Pu and ^{241}Am. The ^{239}Np was obtained from ^{243}Am using a BioRad™ AG-MP1 anion-exchange column and 9 M hydrochloric acid.

Procedures.

Preparation of extraction chromatographic resin. The extraction chromatographic resins were prepared by impregnating either Amberchrom CG-71ms or Amberlite XAD-7 with undiluted DAAP to 40% (w/w) using procedures described previously [23]. Note that Amberchrom CG resin (Toso Haas Corp., Montgomeryville, PA) and Amberlite XAD-7 (Rohm and Haas, Philadelphia, PA) are essentially the same material, differing only in particle size (50-100 µm vs. 100-125 µm average diameter, respectively). The XAD-7 requires treatment to remove traces of preservatives and unreacted monomer prior to impregnation, however [23]. The resultant materials, referred to hereafter as U/TEVA•Spec resin (for uranium and tetravalent actinide specific) are now commercially available from EIChroM Industries, Inc. (Darien, IL).

Column preparation and characterization. Columns were packed as previously described [24]. The selectivity and radiochemical separation experiments were performed using either

disposable glass BioRad (Richmond, CA) Econocolumns (5.0 mm. i.d.) or disposable plastic Isolab (Akron, OH) columns (7.9 mm. i.d.). The bed density (i.e., the weight of resin per unit bed volume), the volume of stationary phase, Vs (referring here to the volume of extractant contained in the pores of the support), and the mobile phase or free column volume, Vm, were measured as described previously [25]. The column capacity was determined as described earlier [25], except that a solution of uranyl nitrate in 2 M nitric acid was used for all measurements. Table 1 summarizes the characteristics of the U/TEVA•Spec materials.

Elution profiles for uranium and thorium. The elution profiles of uranium and thorium with 2 M nitric acid as the eluent were measured using a precision bore glass column of known dimensions. Small (10 µL) aliquots of ^{233}U or ^{230}Th tracer solution in 2 M nitric acid were introduced at the top of the bed and eluted with 2 M nitric acid. The effluent was sampled at intervals during the elution and counted via liquid scintillation. A flow rate of ~2 mL/min/cm^2 was employed throughout. All runs were carried out at ambient temperature (23-25 °C).

Elution behavior of selected elements. A 600 µL portion of a multi-element stock solution containing more than 30 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 U/TEVA•Spec resin (bed volume = 1.0 mL; bed height = 5.0 cm) and eluted with 2 M nitric acid. The concentration of each constituent was chosen so as not to exceed 10% of the capacity of the column. The eluate was collected in a series of 3-mL aliquots until 18 mL (30 FCV) had been collected. The elutrient was then changed to 0.02 M nitric acid (to strip sorbed uranium from the column). A total of 6 mL (~10 FCV) were collected. Portions of each fraction were then subjected to analysis by ICP-AES [26], atomic absorption (Cs), or flame atomic emission (Rb). The flow rate was maintained at 1-2 mL/cm^2/min throughout.

Determination of weight distribution ratios and column capacity factors. The sorption of actinide ions by the U/TEVA•Spec resin from nitric and hydrochloric acid solutions was measured by contacting a known volume (usually 1.00 mL) of a spiked acid solution of appropriate concentration with a known weight of resin. In experiments involving Pu (IV), 0.01 M $NaNO_2$ was added to the aqueous phase to stabilize the +4 state. The valency of Np (IV) was stabilized by 0.01 M Fe(II) in the presence of 0.1 M NH_2OH and 0.01 M NH_2NH_2. The exact ratio of aqueous phase volume (mL) to resin weight (g) was varied as necessary to produce a measurable decrease in the aqueous activity by a single contact with the resin. The mixing of the resin and the aqueous phases was performed using small magnetic stirring bars. The stirring rate was chosen to produce a suspension of the resin in the aqueous phase. Although equilibrium is generally reached in less

than 15 minutes, a 2 hour mixing time was ordinarily employed. After equilibration, the phases were centrifuged and the aqueous phase withdrawn from the test tube. To ensure that the aqueous phase was free of dispersed resin, it was also filtered through Whatman #1 paper.

Weight distribution ratios were calculated from the following equation:

$$D_W = (\frac{A_o - A_s}{W})/(\frac{A_s}{V})$$

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). The distribution ratio values may be converted to the number of free column volumes to peak maximum, k' (i.e., the resin capacity factor) by dividing by 1.665. This factor includes the conversion of D_W to D, a volume distribution ratio, through the density of the extractant and the ratio V_s/V_m typically observed for columns packed with U/TEVA•Spec, 0.257.

The effect of macro concentrations of oxalic, sulfuric, or phosphoric acids upon uranium and neptunium (IV) uptake by the resin was evaluated by measuring the sorption of ^{233}U and ^{239}Np from 2 M nitric acid containing various concentrations of the acids.

Resin stability. The resistance of the U/ TEVA•Spec resin to extractant loss induced by acid washing was evaluated by passing aliquots of 2 M nitric acid through a 2 mL bed of the material and determining the phosphorus content of the column effluent by ICP-AES. For samples expected to contain the highest levels of phosphorus, the sample solution was simply diluted to a known volume and analyzed directly. The phosphorus found in samples containing lower levels was first concentrated by passing a measured volume of the column effluent through a bed of uncoated Amberlite XAD-7. (This material has been utilized previously for the sorption of organics from aqueous solution [27].) The sorbed organics were then stripped from the bed with 15-20 FCV of methanol. This solution was taken to dryness under a heat lamp and the residue remaining taken up in nitric acid. This process was repeated several times using aqua regia until all material present had been solubilized. The final residue was taken up in a few mL of concentrated nitric acid and diluted to a known volume with water for analysis.

Preparation of environmental samples for uranium isolation/Elution sequence. For water samples, two mL of concentrated nitric acid were added to an appropriate volume of sample (a volume corresponding to 0.5 - 50 μg of uranium). The solution was taken to dryness and the residue redissolved in 1-5 mL of 3 M nitric acid.

For ordinary soil samples, a 1-2 g portion was ignited in a platinum crucible at 600 °C in a muffle furnace to destroy any organic matter present. The residue was then transferred to a teflon beaker and digested with 2-4 mL each of concentrated hydrochloric, nitric, hydrofluoric, and perchloric acids. The digestate was then taken to dryness and redissolved in 1-5 mL of 3 M nitric acid. Any undissolved solids were removed from the solution prior to column treatment by passing the solution through either a small piece of filter paper or a disposable filter unit (0.22 - 0.8 μm pore size; 25 mm diameter) attached to a polyethylene syringe.

For high silica soils, a weighed portion of the material (typically 0.25 g) was placed in a teflon-lined pressure vessel (Parr Bomb, Model 4745, Parr Instrument Co., Moline, IL) with a mixture of 4 mL of concentrated nitric acid, 1 mL hydrofluoric acid, and 2 mL of water. The sealed vessel was then heated overnight at 150 °C. The solution resulting was evaporated to dryness to expel silicon (as SiF_4) and excess acid. The residue was then treated with three 0.5 mL portions of a 2% boric acid solution. Each treatment consists of adding the boric acid solution to the sample beaker and evaporating the mixture to dryness on a hot plate at ~145 °C. The boric acid, by forming volatile BF_3, eliminates fluoride retained in the sample as aluminum fluorides. (This treatment was added to the procedure when it was discovered that AlF_3 follows uranium on the U/TEVA•Spec column. In the absence of fluoride, however, Al is easily and completely separated from uranium.) The residue from the final boric acid treatment was dissolved in 3 mL of 2 M nitric acid.

The sample solution was introduced to the U/TEVA•Spec column in a single portion. This was followed by a column wash with eight or nine 3-mL aliquots of 2-3 M nitric acid. This washing yields essentially quantitative removal of most matix constituents while allowing complete uranium recovery. (See below.) Sorbed uranium was then stripped with 9 mL of dilute (0.01 M) nitric acid and collected in a new precleaned 10 mL pyrex beaker. The solution was evaporated to dryness in this beaker and the sample submitted for analysis. When this analysis was to involve thermal ionization mass spectrometry for determination of the isotopic composition of the sample, it was essential that the evaporated solution leave no visible residue. Occasionally, however, such a residue was observed in the beaker. When this occurred, the sample was taken through the separation process a second time, usually starting with the boric acid treatments. Nearly always, the second treatment gave a clean uranium product, indicating that the residue was AlF_3 arising from incomplete fluoride removal.

Apparatus.

Gamma counting was performed in either a Beckman Biogamma counter or a Packard Cobra Autogamma counter. Alpha and β-counting were performed via liquid scintillation on a Packard

Model 2000CA counter. Standard radiometric assay and counting procedures were employed throughout.

The total uranium content of selected environmental samples was determined by laser kinetic phosphorimetry [28] using a Model KPA-10 Kinetic Phosphorescence Analyzer (Chem Chek Instruments, Inc., Richland, WA) equipped with a 56-position autosampler and flow through phosphorescence cell.

Isotopic analyses were performed with a VG Isomass 54R thermal ionization mass spectrometer system equipped with a Daly scintillation detector system.

RESULTS AND DISCUSSION

Selection of support material. A wide variety of supports, both inorganic and organic, have been employed for extraction chromatography [12]. In a comparison of the absorption capacities of several types of support materials (e.g., porous glass, polyethylene, styrene-DVB copolymers), Warshawsky and Patchornik [29] demonstrated that polymeric sorbents of the Amberlite XAD series have excellent capacities for various extractants. Amberlite XAD-7, for example, was found to hold more than three times the amount of Alamine 336 (a mixture of C_8-C_{10} trialkyl amines) as porous glass. In a separate study [30], extractant-impregnated XAD resins were also found to give acceptable metal ion uptake rates. Best results, as determined by the kinetics of copper uptake by the liquid ion-exchanger Kelex 100, were obtained with Amberlite XAD-7. Finally, our own work with supported bifunctional organophosphorus extractants [23] has shown that Amberlite XAD-7 yields a more stable (to acid washing) impregnated resin than does either Porasil or any of the other XAD series materials tested. Thus, Amberlite XAD-7 appears to combine several features essential to a support in extraction chromatography: good capacity for extractant, acceptable kinetics, and some resistance to extractant loss. For this reason, it (along with its smaller particle size analog, Amberchrom CG-71 ms) was chosen for all of the work described here.

Selection of extractant. Previous work in this laboratory has led to the development of two new extraction chromatographic materials, called TRU•Spec™ and Sr•Spec™, capable of selectively removing tri-, tetra-, and hexavalent actinides [23] or radiostrontium [24], respectively, from nitric acid solution. Because it was deemed essential that any new extraction chromatographic material for uranium function effectively under the same loading conditions as these materials (thereby permitting the coupling of columns and the isolation of several species from a given sample solution in a single run), the extractant chosen had to provide high distribution ratios (e.g., $D > 100$) for uranium out of 1-3 M nitric acid. In addition, low distribution ratios

(D < 1) at low acidity were desirable for ease of stripping. Good selectivity over thorium under these same conditions was also considered important. Although several of the organophosphorus extractants considered met these criteria [22], the need for minimal extractant water solubility (for good column stability), simple extractant synthesis (so as to minimize the cost of the material), and good selectivity over iron (a common constituent of many environmental samples) led to the selection of diamyl amylphosphonate.

Acid dependency of the capacity factor, k'. In an earlier study of the extraction behavior of various neutral organophosphorus compounds, Mason and Griffin [22] examined the extractant dependency of the U(VI) (as UO_2^{2+}) distribution ratio between dodecane solutions of DAAP and nitric acid solutions, concluding that uranium extraction proceeds according to the following equation:

$$UO^{2+}_{2(aq)} + 2NO^{-}_{3(aq)} + 2\,E_{(org)} \rightleftharpoons UO_2\,(NO_3)_2{\cdot}E_{2(org)}$$

where E represents diamyl amylphosphonate. Further study showed that, as expected from this equation, the extent of extraction of uranium rises with increasing nitric acid concentration. Above ~4 M nitric acid, however, the uranium distribution ratio began to decline, probably as a result of activity effects, the formation of uranium nitrato complexes in the aqueous phase, and a reduction in the free extractant concentration in the organic phase following nitric acid extraction [22].

As shown in Figure 1, which depicts the capacity factor (i.e., the number of free column volumes to peak maximum) for the U/TEVA•Spec resin for uranium and several other actinide ions as a function of nitric acid concentration, similar behavior is observed for uranium with the supported DAAP. As can be seen, k' reaches a maximum of ~300 at ~6 M nitric acid then levels off. Most significant from the point of view of chromatographic performance is the fact that k' is substantial (~70) even at 1 M acid. Thus, the resin will efficiently sorb uranium from any of a wide range of nitric acid concentrations. The much smaller capacity factors observed for lower nitric acid concentrations indicate that sorbed uranium can be readily removed (i.e., stripped) from the resin with dilute nitric acid (e.g., 0.02 M). The ability to load a sample containing any of a range of nitric acid concentrations and to strip sorbed uranium with only dilute nitric acid, it should be noted, makes uranium separation using the U/TEVA•Spec resin considerably simpler than with many previously described methods. (Users of extraction chromatographic resins based on TOPO, another neutral organophosphorus extractant, for example, have employed 1 M HF [31], 1 M H_3PO_4 [32], or 9.1 M $HClO_4$ [33] for uranium elution.) Moreover, U/TEVA•Spec offers obvious advantages in terms of minimizing reagent consumption and waste generation.

Figure 1 also indicates that several other actinide ions show significant affinity for the U/TEVA•Spec resin. The k' values for tetravalent plutonium, for example, actually exceed those of uranium by a substantial margin over the entire range of acidities considered. The behavior of both thorium (IV) and neptunium (IV) roughly parallels that of uranium (VI), although at any given acidity, k' for thorium is typically a factor of 2-5 less than that of uranium. As shown in Figure 2, which depicts the elution behavior of uranium and thorium on U/TEVA•Spec using 2 M nitric acid as the eluent, this difference in k' is sufficient to provide a separation of the two ions, although the use of 2 M HNO_3-0.05 M oxalic acid is much simpler and more effective. (See below). Note the close correspondence of the peak maximum for each ion to the corresponding k' value from Figure 1.

Unlike U/Th separation, U/Np separation cannot be conveniently effected using only nitric acid, since at concentrations yielding adequate uranium retention, the k' values of uranium and neptunium are very similar. As shown in Figure 3, however, by the addition of an appropriate aqueous complexing agent (e.g., oxalic acid) to the eluent, neptunium (as well as thorium and plutonium) sorption can be reduced dramatically, while that of uranium is changed little. Addition of 0.05 M oxalic acid to 2 M HNO_3, for example, reduces k' for Np (IV) from ~100 to ~1, a factor of 100 reduction. That of uranium, however, is reduced only from 140 to 100 under the same conditions. Addition of either phosphoric acid or sulfuric acid has a similar effect, although the impact on neptunium retention is much less pronounced, particularly for sulfuric acid.

Figure 4 depicts the dependence of k' for uranium and several other actinides on hydrochloric acid concentration. A number of similarities between the behavior of the various ions in hydrochloric acid and that described in nitric acid are apparent. The k' value for uranium, for example, reaches a maximum at ~7 M acid. Moreover, this value is quite close to the value seen in nitric acid, ~300. Also, Am(III) (not shown in Fig. 4) is poorly retained, as was the case in nitric acid. There are, however, several important differences between the capacity factor data in the two acids. For example, k' for uranium declines more steeply from its maximum in hydrochloric acid as the acid concentration falls than it does in nitric acid. Thus, while k'_U does not fall to below 10^2 until ~1.2 M in HNO_3, it reaches this value by 4 M in HCl. As a consequence, the range of acidities suitable for sample loading is narrower in HCl (ca. 4-6 M). Both the U/Np and U/Th separation factors are somewhat better in hydrochloric acid, however. At 4 M HNO_3, for example, k'_U and k'_{Np} differ by less than a factor of 2. At 4 M HCl, however, this difference is nearly a factor of 5. Such results suggest that elution sequences involving a crossover from nitric acid to hydrochloric acid (or vice versa) may offer some potential for the isolation and sequential elution of several actinides in a single run.

Table 2 summarizes the results of a U/Th elution experiment conducted entirely in hydrochloric acid. As can be seen, when the sample is loaded in 6 M HCl and the column rinsed with the same acid, > 99% of the thorium present elutes in the first – 20 FCV, while < 1% of the uranium is removed in the same volume. Reducing the hydrochloric acid concentration to 0.025 M permits essentially complete (> 99%) elution of the uranium in only 6 FCV.

Elution behavior of selected cations. The large values of k' obtained for uranium in the range of 1-6 M nitric acid suggest that it should easily be possible to elute off many of the commonly encountered constituents of various samples (e.g., transition metals, alkali and alkaline earth elements) from the U/TEVA•Spec column prior to uranium breakthrough. Table 3 shows the elution behavior of nearly three dozen elements. As can be seen, nearly all of the test elements can be removed with only 10 FCV of 2 M nitric acid. (Zr and Ru each require ~15 FCV.) As expected from Figures 1 and 2, no trace of uranium is observed even after 30 FCV of the 2 M acid. Once the eluent is changed to dilute (here, 0.02 M) nitric acid, however, the removal of uranium is essentially complete in only 10 FCV. (In a similar experiment using XAD-7 supported TBP, uranium recovery in the dilute HNO_3 fraction was only 17%, even when the acidity of the load and rinse solutions was raised to 3 M to enhance sorption.)

Application of U/TEVA•Spec to the determination of uranium in environmental samples. The isolation and purification of uranium from environmental samples provides an especially stringent test of the capabilities of the U/TEVA•Spec resin because, often, a relatively large amount of sample (1 or more grams) contains only microgram quantities of uranium. Moreover, the composition of such samples is variable and often quite complex. Thus, an acceptable separation method must give excellent decontamination from the macro constituents of a typical environmental sample (e.g., sodium, calcium, and iron) and must do so despite variations in sample composition. In situations in which the determination performed includes mass spectrometric measurement of the isotopic composition of the uranium recovered, as is often the case in this laboratory, the need for effective removal of major sample constituents may be even more pressing, since ideal samples for certain types of mass spectrometry (e.g., thermal ionization MS) are nearly weightless (µg-mg range).

To evaluate the performance of the resin, aliquots of solutions prepared from several typical environmental samples, water, sediment, soil, and glassblasting residue, were spiked with an appropriate isotope dilution standard prior to column treatment. A second portion of each solution was similarly spiked after column treatment. Mass spectrometric analysis of the solutions permitted calculation of the uranium recovery for each sample. The results of these analyses, summarized in Table 4, show that the recovery of uranium is both high (averaging 95%) and

remarkably consistent, despite the different matrix compositions and the high weight of certain samples required. (Note particularly the 3 g limestone gravel/sediment sample.)

As a further test of the resin, its application to the separation and preconcentration of uranium from high silica soils was investigated. Such soils present a great challenge because quantitative recovery of the uranium requires complete dissolution of siliceous mineral phases. (The sample selected, NBS-SRM 4353 - "Rocky Flats Soil No. 1", contains 55-60 wt. % quartz, 25-30% clays, 5-10% alkali feldspars, and 5% plagioclase. Its total silicon content corresponds to more than 73 weight percent SiO_2.) Following sample dissolution and elimination of fluoride by treatment with boric acid (see Experimental section), sample solutions were passed through a U/TEVA•Spec column. Following a rinse with ~20 FCV of 2 M nitric acid, the uranium was stripped from the column with 7 FCV of 0.01 M nitric acid and aliquots of the strip solution were subjected to TIMS isotopic analysis. Table 5 summarizes the results of these analyses. (Note that the total uranium content of the soil sample was sufficiently high that its determination in the solution resulting from the initial dissolution of the sample did not require column preconcentration.) As can be seen, the measured isotopic abundances for ^{234}U and ^{238}U are in good agreement with the certificate values. The experimental value of the ^{235}U abundance, however, differs by ~6% relative from the uncertified value listed by the National Bureau of Standards. Furthermore, the standard deviation (0.018 wt. %) of the measured ^{235}U abundance is well above the usual TIMS measurement variability. (A standard deviation of 0.0007 wt. % is expected.) This suggests to us that the ^{235}U is not uniformly distributed in the SRM and that much of the observed variation in the ^{235}U abundance arises from the use of small (0.25 g) portions of the material for analysis.

Column stability. Because extraction chromatography involves the contact of a small volume of a highly dispersed organic extractant (having some finite water solubility) with a much larger volume of aqueous phase, the possibility of extractant (stationary phase) loss and a concomitant decrease in column capacity is of particular concern with any new resin. For this reason, a portion of the U/TEVA•Spec resin was subjected to washing with nearly 1000 FCV of 2 M nitric acid solution and portions of the effluent subjected to analysis for phosphorus. Not surprisingly, the loss of extractant was found to be most pronounced in the early stages of the run, when extractant is still in the outermost regions of the support. In the first 100 FCV, for example, 5.8% of the extractant was removed. An additional 900 FCV, however, removed only 6% more. Because the working capacity of the resin (i.e., the recommended degree of loading) is usually only 20% of the total capacity of the material, this loss of extractant should have essentially no impact upon the performance of the resin in an ordinary run, where the total volume of load, rinse, and strip solutions is, at most, 100 FCV. In addition, these results indicate that the column material is

sufficiently stable for reuse. Note, however, that reuse requires that the resin be carefully washed between runs to eliminate any possibility of cross contamination.

CONCLUSIONS

An extraction chromatographic resin comprised of diamyl amylphosphonate supported on an inert polymeric substrate provides a simple and effective method for the separation and preconcentration of uranium from aqueous solution. Uranium is efficiently sorbed by the resin from solutions containing a wide range of either nitric or hydrochloric acid concentrations and is readily eluted with dilute acid. Although several other actinides are also sorbed by the resin to varying degrees, the differences in the resin capacity factors for the various ions, particularly in the presence of certain aqueous complexing agents, are sufficient to permit the isolation of only uranium. Many other commonly encountered cations (e.g., Ca, Fe, Na) are essentially unretained by the resin, making the material well-suited to the isolation of uranium from a variety of environmental samples. Although we have described only a limited number of applications for the U/TEVA•Spec resin, its good uranium selectivity should make it suitable for use in a variety of situations, including bioassays, uranium determination in nuclear waste and reprocessing solutions, and the elimination of uranium interference in various trace element determinations in uranium-rich samples. Work addressing some of these opportunities is currently underway in this laboratory.

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Table 1. Characteristics of the U/TEVA•Spec extraction chromatographic material and packed columns.

Bulk Material	
Stationary Phase	Diamyl amylphosphonate (ρ = 0.926 g/ml)
Support	Amberchrom™ CG-71 or Amberlite™ XAD-7
Particle Diameter	50-100 μm (Amberchrom); 80-160 μm; 100-125 μm
Extractant Loading	40 weight percent
Average Density of Extractant-Loaded Beads[a]	1.10 g/mL
Packed Columns	
v_s	0.167 mL/mL of bed
Bed Density	0.386 g/mL
v_m (also FCV)	0.65 mL/mL of bed
v_s/v_m	0.257
Calculated Capacity	37 mg U/mL of bed
Experimentally Measured Capacity	37 mg U/mL of bed

a Picnometric density and flotation density were 1.065 and 1.133, using the 50-100 μm particle size resin. The calculated density is 1.094 g/ml assuming 100% pore filling and no swelling.

Table 2. Separation of uranium and thorium on U/TEVA•Spec: hydrochloric acid eluent.[a]

Fraction	Volume (FCV)[b]	Fraction of Total Activity Observed (%)	
		U	Th
Load (6.1 M HCl)	15.4	<0.4[c]	84.9
Rinse 1 (6.1 M HCl)	5.0		14.7
Rinse 2 (6.1 M HCl)	5.0		0.18
Rinse 3 (6.1 M HCl)	10.0		0.15
Strip 1 (0.025 M HCl)	3.0	73.5	0.06
Strip 1 (0.025 M HCl)	3.0	25.5	
Strip 3 (0.025 M HCl)	3.0	0.5	

[a] Uses fine particle resin; T = 24 °C; ^{233}U and ^{230}Th tracers; bed volume = 2 mL.

[b] Here, 1 FCV = 1.3 mL.

[c] Essentially all of this activity can be attributed to the presence of impurities in the ^{233}U stock.

Table 3. Elution behavior of selected elements on a U/TEVA•Spec (fine particle) column.

	Portion eluting (%)[a]						
	← 2 M HNO_3						0.02 M HNO_3 →
	Number of free column volumes[b]						
Element	1-5	6-10	11-15	16-20	21-25	26-30	31-40
Li	99.4	—	—	—	—	—	—
Na	95.0	<1.2	—	—	—	—	—
Mg	101	—	—	—	—	—	—
Al	92.0	<5.8	—	—	—	—	—
K	<123	—	—	—	—	—	—
Ca	92.4	<13.3	—	—	—	—	—
Cr	94.7	<3.3	—	—	—	—	—
Mn	96.5	<0.7	—	—	—	—	—
Fe	94.0	<0.3	—	—	—	—	—
Co	99.1	<7.1	—	—	—	—	—
Ni	97.8	<2.0	—	—	—	—	—
Cu	98.1	<2.6	—	—	—	—	—
Zn	96.8	<1.2	—	—	—	—	—
Rb[c]	102	—	—	—	—	—	—
Sr	101	—	—	—	—	—	—
Y	97.9	<2.9	—	—	—	—	—
Zr	56.4	35.7	(1.4)	—	—	—	—
Ru	59.6	<19.2	<19.2	—	—	—	—
Rh	91.7	—	—	—	—	—	—
Ag	103	—	—	—	—	—	—
Cd	96.4	<0.7	—	—	—	—	—
Cs[d]	100	—	—	—	—	—	—
Ba	96.6	<14.4	—	—	—	—	—
La	108	—	—	—	—	—	—
Ce	96.3	<25	—	—	—	—	—
Pr	(136)	—	—	—	—	—	—
Nd	99.0	—	—	—	—	—	—
Sm	120	—	—	—	—	—	—
Eu	100	—	—	—	—	—	—
Pb	98.4	<5.8	—	—	—	—	—
U[e]	—	—	—		—	—	>99

[a] Because of uncertainties inherent in the ICP-AES method used for quantitation, the fractions shown for a given element may not total 100%. Values in parentheses are subject to considerable uncertainty and are intended only as a guide. Feed solution contained ~0.02 M oxalic acid to solubilize zirconium.

[b] 1 FCV = 0.60 mL here.

[c] By flame atomic emission.

[d] By atomic absorption.

[e] Radiometric.

Table 4. Uranium recovery from actual and standard environmental samples.

Sample description	Weight or volume analyzed	Uranium present, µg		Recovery (%)
		Before column	After column	
Water-NBS 950a	5.0 mL	26.1	24.8	95.3
Limestone gravel and sediment	3.12 g	18.3	17.6	95.9
Limestone gravel and sediment	2.32 g	25.2	23.8	94.6
Surface soil	1.03 g	23.5	22.3	95.1
Glassblasting residue	1.49 g	35.1	33.8	96.2
				Mean: 95.4

Table 5. Uranium isotopic distribution in a standard soil sample (NBS-SRM 4353).

Isotope	Activity[a] (Bq/g)	Concentration[b] (μg/g)	Isotopic abundance (wt.%) Calculated	Experimental
U-234	0.0391±0.0014	0.000170±0.000006	0.0054±0.0002	0.0055±0.0003
U-235	0.0019[c]	0.024[c]	0.76[c]	0.719±0.018
U-238	0.0389±0.0020	3.13±0.16	99.23[c]	99.275±0.018

Total uranium (μg/g): 3.15±0.16 (NBS certificate)
3.04±0.15 (experimental)

[a]From NBS certificate.

[b]Calculated by converting activities to masses via specific activities.

[c]No uncertainty given on NBS certificate.

FIGURE CAPTIONS

Figure 1. Nitric acid dependency of k' for selected ions on U/TEVA•Spec resin (T = 23-25 °C; 50-100 μm particle size resin).

Figure 2. Elution profiles of U(VI) and Th(IV) on U/TEVA•Spec resin (Eluent = 2 M HNO_3; T = 23-25 °C; Flow rate = 2 mL/min cm^2; 50-100 μm particle size resin; bed volume = 0.59 mL; bed length = 10.1 cm)..

Figure 3. Effect of oxalic acid on the sorption of Np(IV) and U(VI) by U/TEVA•Spec from 2 M nitric acid.

Figure 4. Hydrochloric acid dependency of k' for selected ions on U/TEVA•Spec resin (T = 23-25 °C; 50-100 μm particle size resin).

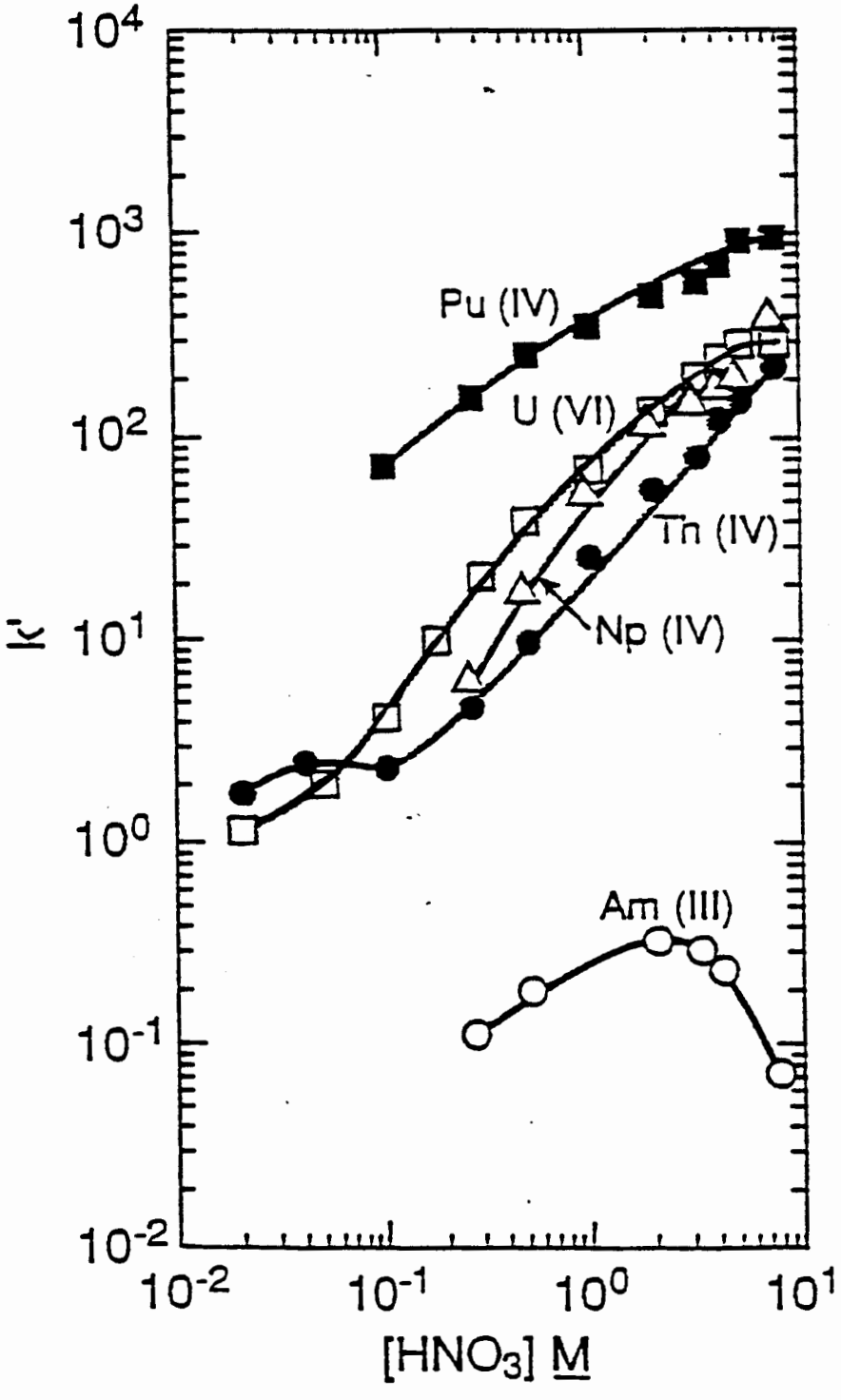
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
D
Pu (IV)
U (VI)
Th (IV)
Np (IV)
Am (III)
10^{-2}
10^{-1}
10^0
10^1
[HNO_3] M

Figure 1.

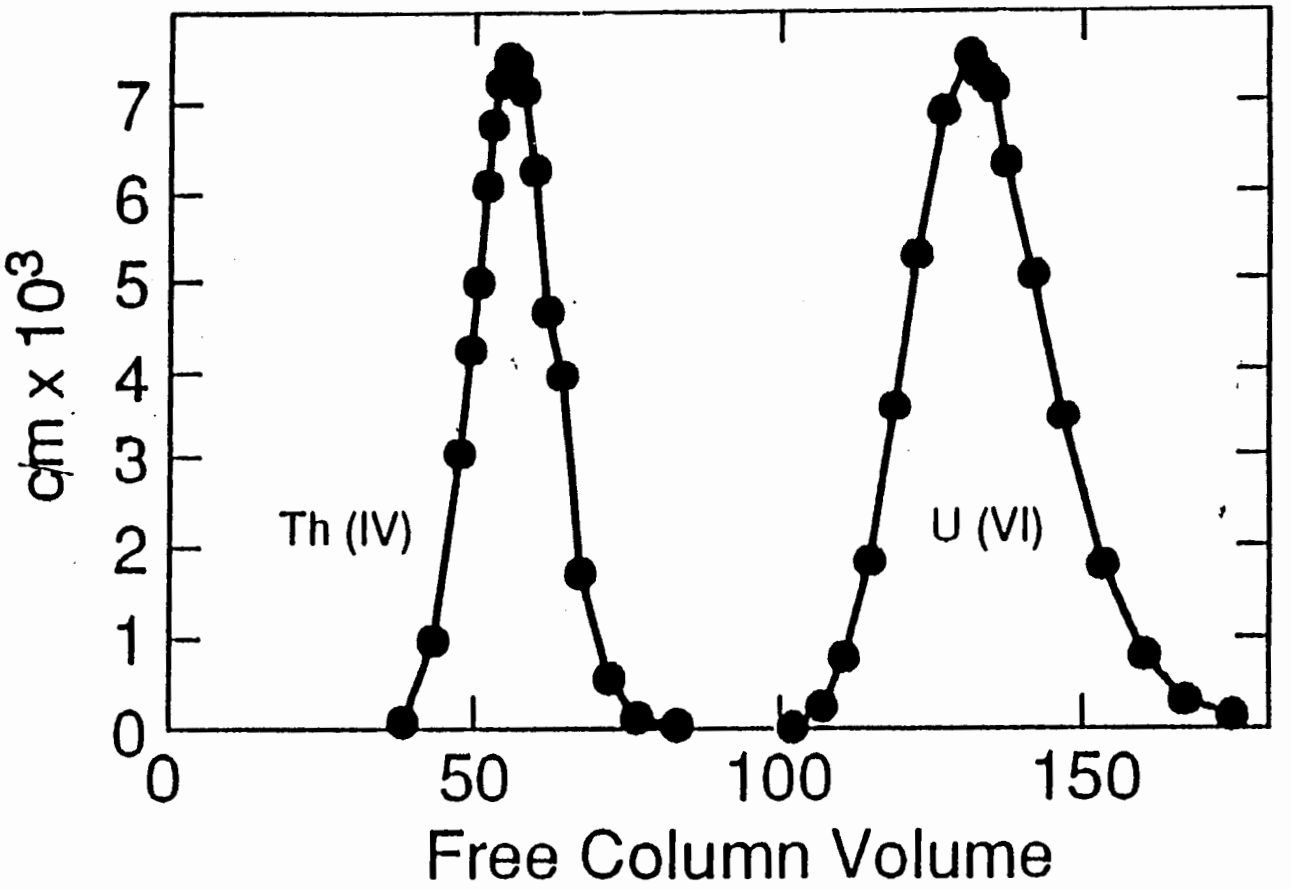

Figure 2.

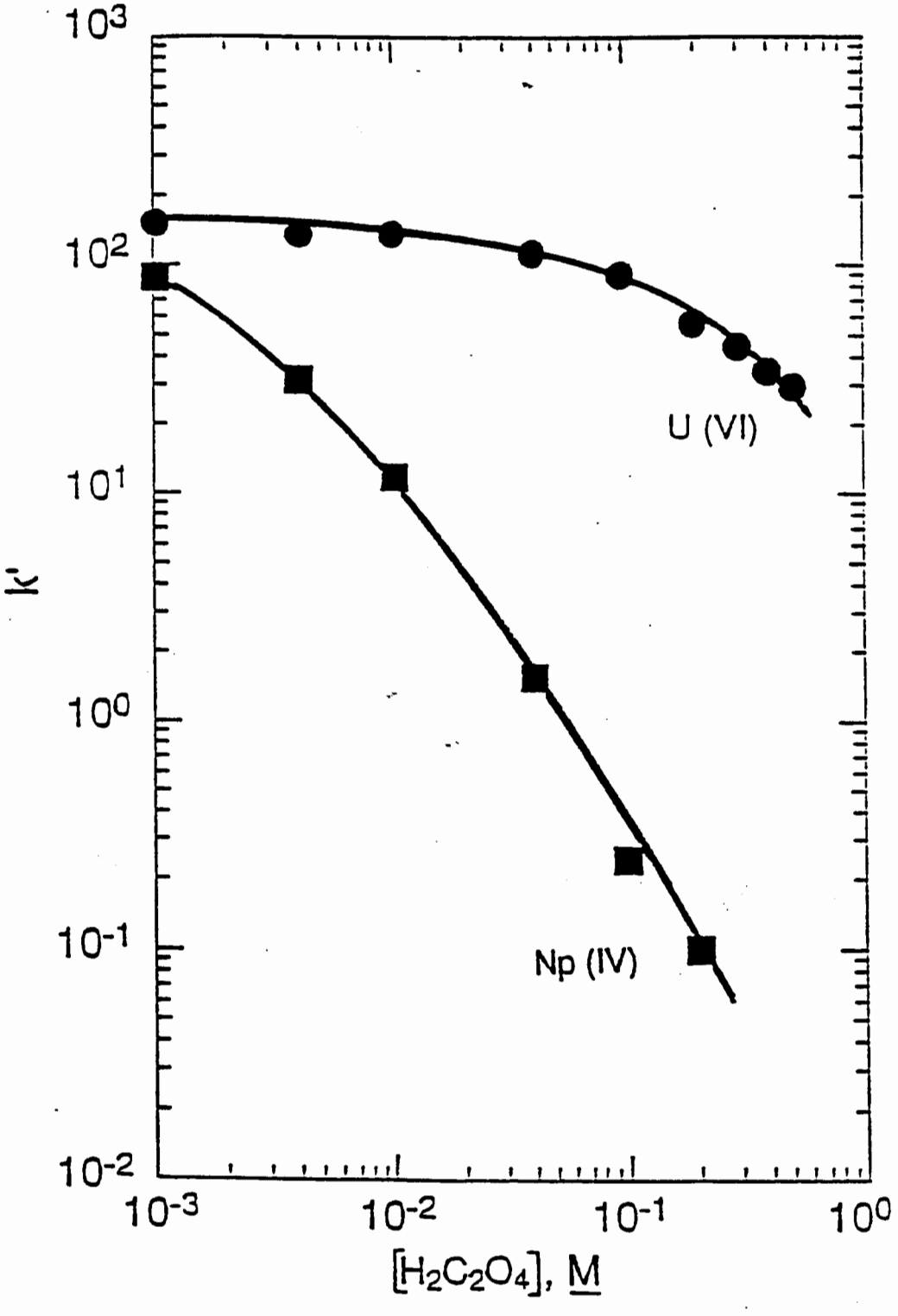

Figure 3.

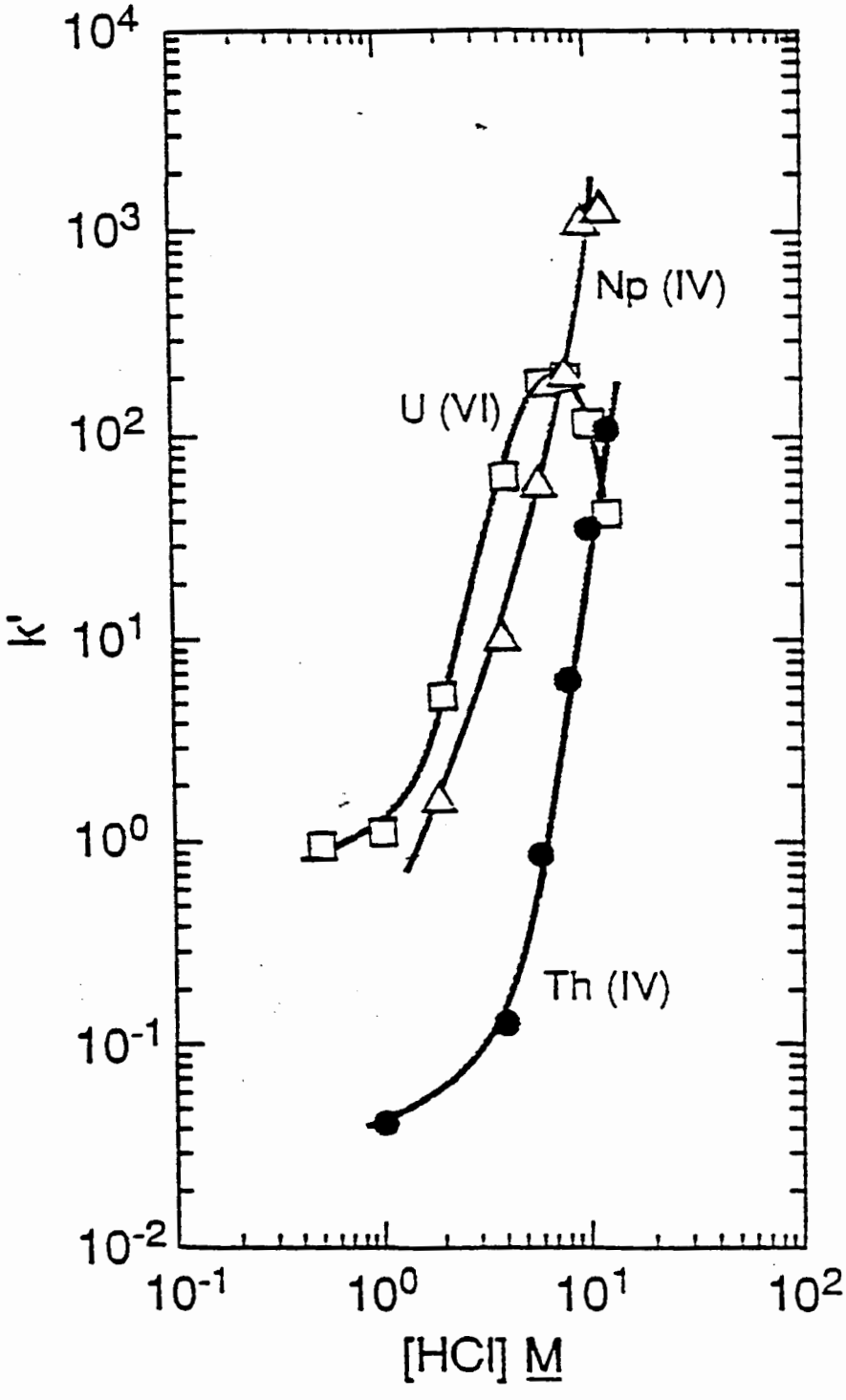

Figure 4.