Analytica Chimica Acta 281 (1993) 361-372

Separation and Preconcentration of Actinides from Acidic Media by Extraction Chromatography[a]

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ABSTRACT

A systematic examination of the effect of nitric and hydrochloric acid concentrations and of macro levels of selected elements on the sorption of actinide ions by a novel extraction chromatographic resin comprised of a solution of octyl(phenyl)-N, N-diisobutylcarbamoyl-methylphosphine oxide in tri-n-butyl phosphate supported on an inert polymeric substrate is described. Actinide sorption is demonstrated to be most efficient at high (> 1 M) nitric acid concentrations, although tetra- and hexavalent actinides are strongly retained even from dilute (e.g., 0.05 M) nitric acid solutions. Macro concentrations of several common anions (e.g., PO_4^{3-} and SO_4^{2-}) or complexing agents (e.g., oxalic acid) are shown not to adversely affect the sorption of trivalent actinides, while reducing the sorption of tetravalents. Such effects, together with oxidation state adjustments, are shown to provide a basis for the sequential elution of individual actinides and for actinide isolation from environmental and biological matrices.

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[a] A portion of this work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under contract number W-31-109-ENG-38.

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INTRODUCTION

Increased public attention to radioactive waste disposal practices and the potential public health effects of releases of radioactive materials to the environment has made accurate and reliable methods for the determination of actinides in various environmental and biological samples increasingly important. Because of the low concentrations of these elements encountered in typical samples, some method of preconcentrating the actinides and of isolating them from both the large quantities of inactive substances present and potential interferents must usually precede the determination. Numerous methods have been described for effecting this separation and preconcentration, among them procedures based on ion exchange (1-3), liquid-liquid extraction (4), precipitation (5), adsorption (6), extraction chromatography (7), and combinations thereof (8).

In an earlier report in This Journal (9), we described an extraction chromatographic resin comprised of a solution of a bifunctional organophosphorus extractant, octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (abbreviated CMPO), in tri-n-butyl phosphate (TBP) supported on an inert, polymeric substrate (Amberlite XAD-7) and its application to the separation and preconcentration of actinides from urine. Although use of this material offered definite advantages over other techniques, yielding excellent actinide recoveries and permitting the preparation of essentially massless electrodeposits for high resolution alpha-spectrometry, the resin did suffer from a significant limitation. That is, the width of the elution bands observed and the occurrence of significant tailing precluded the sequential elution of individual actinides from the resin.

Recently, resins chemically indistinguishable from Amberlite XAD-7 but with smaller average particle diameters have become available. Because it is well known that a reduction in the particle size of a chromatographic material will lead to narrower elution bands (10,11), we have examined the chromatographic properties of a CMPO/TBP mixture sorbed on one of these small particle size supports. In this report, we present a systematic evaluation of the uptake of various actinide ions by the material from nitric and hydrochloric acid solutions and of the effect of various aqueous complexants and potential interferents on this uptake. In addition, we describe the elution behavior of a wide range of other cations, particularly those commonly encountered in biological or environmental matrices. Finally, we discuss the potential application of the results obtained to the separation and preconcentration of actinides, both as a group and individually, from soil, groundwater, bioassay samples, and radioactive waste samples.

EXPERIMENTAL

Reagents

Octyl(phenyl)-N, N-diisobutylcarbamoylmethylphosphine oxide (Atochem North America, Philadelphia, PA) was purified as previously described (12). Tri-n-butyl phosphate was obtained from Eastman Chemicals and distilled (T = 143 °C; pressure = 20 mm) before use. 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. Hydroquinone-hydrochloric acid solutions were prepared daily. Ascorbic acid solutions were prepared weekly. Radiochemical experiments were performed using ^{230}Th, ^{233}U, ^{237}Np, ^{239}Np, ^{239}Pu, ^{241}Am, ^{45}Ca, ^{210}Bi, ^{210}Po, ^{59}Fe, and ^{85}Sr tracers. The ^{239}Np was "milked" from ^{243}Am in 9 M HCl using a BioRad™ AG-MP1 anion exchange column.

Procedures

Preparation of extraction chromatographic resin. The extraction chromatographic resin was prepared by impregnating Amberchrom CG-71ms with a 0.75 M solution of CMPO in TBP in the manner described previously for Amberlite XAD-7(9). Unlike XAD-7, however, the Amberchrom resin does not require water washing to remove preservatives prior to impregnation. This extraction chromatographic material, referred to hereafter as TRU•Spec™ (for transuranic specific), is now commercially available from EIChroM Industries, Inc. (Darien, IL).

Determination of weight distribution ratios and column capacity factors.

The sorption of actinide ions by the TRU•Spec resin from nitric and hydrochloric acid solutions was measured by contacting a known volume of a tracer-spiked acid solution of appropriate concentration with a known weight of resin (13). Weight distribution ratios were converted to the number of free column volumes to peak maximum (i.e., the resin capacity factor), k', by dividing by 1.85. This factor takes into account the density of the extractant solution and the typical value of v_s/v_m (the ratio of the volumes of the stationary and mobile phase) for a column containing TRU•Spec. Details may be found in a previous report (13).

To ensure that any Np(V) present was reduced to Np(IV), neptunium load solutions were made ~ 0.01 M in Fe(II) and 0.11 M in hydroxylammonium nitrate. The ferrous nitrate stock solution (0.2 M) was prepared using ferric nitrate and a large excess of hydroxylammonium nitrate (2.2 M). Plutonium was maintained in the tetravalent oxidation state by making all acid solutions 0.05 M in sodium nitrite.

Column preparation and characterization. Columns were packed as previously described (14). All column parameters (e.g., v_s, v_m, bed density) were measured as described in Reference 13. The resin capacity was determined as described earlier (13) except that a solution of 0.05 M neodymium nitrate in 2 M nitric acid was employed for all measurements.

Elution profiles for americium. The elution profile of americium with 2 M nitric acid as the eluent was measured with the same calibrated column employed for v_m and v_s measurements using procedures described previously (13).

Elution behavior of selected elements/matrix effects. The elution behavior of approximately thirty metal cations on a TRU•Spec column (bed volume = 1.0 mL; bed height = 5.0 cm) was evaluated using procedures described in a previous report (13). 2 M nitric acid was employed for column rinsing and 0.05 M nitric acid for column stripping.

The effect of macro concentrations of various commonly encountered cations (e.g., Ca^{2+}, Fe^{3+}) and anions (e.g., SO_4^{2-}) or aqueous complexing agents (e.g., oxalic acid) upon americium and neptunium uptake by the resin was evaluated by measuring the sorption of ^{241}Am and ^{239}Np from 2 M nitric acid containing various concentrations of the test species.

The influence of Fe(II) on americium uptake was examined by reducing Fe(III) in 2 M nitric acid with a freshly prepared 0.8 M solution of ascorbic acid. (Upon addition of ascorbic acid to a solution of Fe(III), a blue color forms which disappears on mixing. When the blue color no longer forms, all Fe(III) has been reduced to Fe(II). Potassium thiocyanate may also be used to indicate the presence of Fe(III). When a red color no longer remains after addition of ascorbic acid, all the Fe(III) has been reduced to Fe(II).)

Sequential separation of actinides. The sequential separation of actinides was studied using a 2.84 mm i.d. column packed to a bed height of 9.8 cm (0.62 cm^3 bed volume, 0.422 cm^3 free column volume). A tracer stock solution containing ^{241}Am, ^{239}Pu, ^{237}Np, ^{233}U, and ^{230}Th in 2 M HNO_3 was utilized for the load. The solution was made 0.01 M in Fe by addition of ferric nitrate. The iron was reduced by addition of ascorbic acid as described above. The flow rate was maintained between 0.5 and 1.0 mL/cm^2/min throughout the column run except for the elution of thorium, during which it was necessary to elute at one-half this flow rate. Alpha pulse-height analysis was used to analyze the individual fractions. For ^{237}Np, the characteristic L X-ray addition peak was also used.

Resin Stability. The resistance of the TRU•Spec resin to extractant loss induced by the flow of aqueous phase was evaluated by determining the effect of extensive column rinsing upon the elution profile of ^{241}Am. Specifically, a small (1μL) aliquot of an ^{241}Am stock solution was introduced atop the bed of a newly prepared TRU•Spec column and eluted with 0.3 M nitric acid. The effluent was sampled at intervals and gamma -counted. The column was then washed with ca. 250 FCV of deionized water and, after preconditioning with 0.3 M nitric acid (10 FCV), an aliquot

of ^{241}Am was again eluted in the same manner. This process was repeated at ca. 250 FCV intervals until a total of 1000 FCV of rinsing had been carried out. Changes in peak position (k') and width were taken as indicators of a change in the condition of the resin arising from loss of stationary phase or a change in stationary phase configuration. Vm, the mobile phase or interstitial volume, was determined for the column by measuring the volume of effluent preceding ^{137}Cs breakthrough, both prior to any rinsing and after 1000 FCV.

Apparatus

Gamma counting was performed in either a Beckman Biogamma counter or a Packard Cobra Autogamma counter. Alpha and beta-counting were performed via liquid scintillation on a Packard Model 2000CA counter. In sequential elution experiments, proportional counting with argon-methane 2 π counters and alpha pulse analyses using surface-barrier silicon detectors were also carried out.

RESULTS AND DISCUSSION

Column characteristics. As already noted, our principal objective in this work was to prepare an extraction chromatographic resin capable of retaining tri-, tetra-, and hexavalent actinides, which exhibits minimal band spreading and tailing, thereby providing an opportunity for sequential separation of the actinides. In addition, good overall actinide recoveries and satisfactory decontamination from inert constitutents and potential interferents were deemed essential. For convenience, the ability to operate under gravity flow and room temperature was also desired. To meet these specifications, we selected the same substrate and particle size utilized for our strontium-specific and uranium/tetravalent actinide-specific extraction chromatographic resins, described in previous reports (14,15). Table 1 summarizes the characteristics of the bulk material and packed beds.

Nitric acid dependency of capacity factor, k'. The TRU•Spec chromatographic material was characterized by measuring k' (the number of free column volumes to peak maximum) as a function of nitric acid concentration for tri-, tetra-, penta- and hexavalent actinides and for selected non-actinide ions. Figure 1 depicts the nitric acid dependency of the resin capacity factor, k', for the various actinide ions. As can be seen, the sorption of most of the ions rises steadily with increasing acid concentration, as anticipated from results in the analogous liquid-liquid system (16,17). (It is important to point out that attempts to compare the relative extractabilities of the actinides in the chromatographic and liquid-liquid systems must take into account the different CMPO concentrations in the two systems and the relationship between k' and D, the distribution

ratio, $k' = D\ v_s/v_m$.) It is interesting to note that the k' value for a given ion is typically 100-1000 times greater on TRU•Spec than on U/TEVA•Spec, a recently developed extraction chromatographic material containing the monofunctional extractant diamyl amylphosphonate (15). This is significant because k'_{Am} on U/TEVA•Spec is too low to yield satisfactory retention. In contrast, TRU•Spec retains Am(III) (and other trivalent actinides) strongly over a wide range of nitric acid concentrations (0.5 to 8 M). Even Np(V) exhibits slight retention on TRU•Spec, although its k' (ca.10) is not sufficiently high to be of any use in separating neptunium from common matrix constituents.

The extremely strong retention of U(VI), Np(IV), and Pu(IV), even at low acidities, means that the elution of these ions cannot be effected simply by lowering the aqueous nitric acid concentration. Rather, a different acid or a solution of an appropriate complexing agent (e.g., ammonium oxalate) must be employed. Americium can be eluted using only dilute (e.g., 0.025 M) nitric acid, but as is discussed in more detail below, its separation from plutonium is not complete.

Figure 2 shows the retention of selected non-actinides by TRU•Spec resin as a function of nitric acid concentration. The behavior of Fe(III) is of utmost importance because of its presence in significant concentrations in soil samples and its use as a coprecipitant for actinides. (The effect of Fe(III) on the sorption of Am(III) is discussed below in more detail below.) Calcium(II) is poorly retained at all acidities and therefore causes little interference with actinide sorption. Bismuth retention is important because of its occasional presence in fecal samples. The data in Fig. 2 show that Bi(III) retention is higher than that of Am(III) except at high (> 4 M) acidities. Polonium(IV) retention, although less than that of Am(III), is not negligible. This is important because ^{210}Po is present in urine and can interfere in alpha pulse-height analysis. Technetium is a constituent of high-level liquid waste (HLLW) and its separation from ^{241}Am is therefore important in the analysis of HLLW. Figure 2 shows that Tc(VII) retention is less than that of Am(III) at nitric acid concentrations greater than about 0.25 M. Therefore, its separation from americium can be effected simply by rinsing the TRU•Spec column with 1-10 M HNO_3.

Elution behavior of Am and selected cations. Figure 3 shows the concentration profile for the elution of Am(III) from a TRU•Spec column using 2 M HNO_3. The k'_{Am} obtained from the elution curve is 98, which is identical to that obtained in an uptake experiment. (See Fig. 1.) The height equivalent to a theoretical plate (HETP) is 0.11 cm, which is the same as that obtained in the elution of Sr(II) from a Sr•Spec column containing the same particle size substrate (13).

Table 2 shows the elution behavior of thirty different elements on a 1.0 cm^3 bed volume column packed with 50-100 μm TRU•Spec column material. (Essentially all of these elements are present in high-level radioactive waste solutions.) Two molar HNO_3 was used for column loading

and for the first 30 free column volumes (FCV) of rinsing, while 0.05 M HNO_3 was used to strip sorbed Am(III) from the column (31-40 FCV). (A trivalent actinide was selected for this study because, as shown in Figure 1, actinides in the tripositive oxidation state are generally the least strongly retained on TRU•Spec). As can be seen, all constituents except zirconium and the lanthanides elute from the column in the first 10 FCV. The lower retention of La(III), Ce(III), and Y(III) relative to Am(III) was anticipated based on comparison of light lanthanide and yttrium distribution ratios in liquid-liquid extraction systems involving solutions of CMPO-TBP (18). (D_{Am}/D_Y, D_{Am}/D_{La} and D_{Am}/D_{Ce} are ~ 5, 2.5, and 1.5, respectively, with 0.25 M CMPO-0.75 M TBP in tetrachloroethylene (18)). The strong zirconium retention is also expected from prior liquid-liquid extraction studies (18), but it can be separated from actinides by making the feed solution 0.05 M in oxalic acid or by rinsing the column with 10 FCV of 2 M HNO_3-0.05 M oxalic acid.

Effect of matrix constituents. The nitric acid dependency data presented in Figs. 1 and 2 and the elution data in Table 2 are important not only because they show conditions that may be used to separate tri-, tetra-, and hexavalent actinides from various metal ions, but also because they indicate which elements may cause a significant diminution in actinide sorption if present at sufficiently high concentrations (i.e., those that represent more than 20% of the column capacity). Sodium, potassium, calcium, iron, and aluminum are major constituents of many environmental and geological samples (e.g., soils, minerals, and groundwaters). The effect of increasing concentrations of several of these matrix constituents on k'_{Am} was therefore measured. Figure 4 shows the effect of Ca(II), Al(III) and Fe(III) in 2 M HNO_3 on k'_{Am}. (The quantities of iron selected for the study were based on the application of $Fe(OH)_3$ to coprecipitate actinides from groundwater. Sodium and potassium were not included in the study because their retention on TRU•Spec is less than that of Ca.) The data show clearly that only Fe(III) has a significant negative impact on Am sorption, as expected from the acid dependency of its capacity factor (Fig. 2.). Al(III) actually enhances k'_{Am} through its salting-out effect. The effect of Fe(III) on k'_{Am}, even at low concentrations, is sufficiently pronounced that its presence must be considered in developing schemes involving TRU•Spec resin for the separation and preconcentration of actinides. Fortunately, when Fe(III) is reduced to Fe(II) with ascorbic acid, its effect on k'_{Am}, like that of Ca(II), is practically negligible. The effect of Fe(III) and Fe(II) on the uptake of Am on TRU•Spec is also tabulated in Table 3.

The influence of phosphoric, sulfuric, and oxalic acids in 2 M HNO_3 on k'_{Am} is also shown in Fig. 4. None of the acids has a significant effect on k'_{Am} below 0.2 M. All three acids, as expected, are much more influential on the sorption of tetravalent actinides, as represented by Np(IV) (Fig. 5). The influence of these acids (and presumably HF) on both Am(III) and Np(IV)

sorption on TRU•Spec resin can be largely eliminated either by adding macroquantities of Al(III) or by increasing the nitric acid concentration to 4 M. Addition of aluminum ion effectively complexes the anions, reducing their concentrations, while raising the acidity effectively reduces the concentration of the complexing anion by protonation. Because k'_{Am} is only slightly influenced by nitric acid concentration above 0.5 M and because k'_{Np} is increased by high nitric acid concentrations, the latter approach is normally preferred. Note, however, that Fe(III) retention increases dramatically above 1 M HNO_3 (Figure 2).

Sequential separations of actinides. Although the results presented in Figures 1 and 2 and Tables 2 and 3 suggest that the separation of the actinides from a variety of matrices should be highly efficient, the sequential separation of individual actinides on the basis of the differences in their retention on TRU•Spec does not appear possible in nitric acid media, despite the improved chromatographic performance of the small particle size material. In fact, except for Am(III), none of the actinides can be readily eluted from a TRU•Spec column using only nitric acid. Moreover, when americium is eluted with dilute (e.g., 0.025M) nitric acid, 1 to 5% of the Pu is always found in the americium fraction. (Most likely, this is due to hydrolysis of Pu(IV).)

Earlier studies on the liquid-liquid extraction of tri-, tetra-, and hexavalent actinides from chloride media (19) suggest that the situation may be improved through the use of hydrochloric acid as a stripping agent. In hydrochloric acid media, large separation factors between individual oxidation states can be achieved. In addition, the distribution ratios of tri- and tetravalent actinides are low in 1 to 2 M hydrochloric acid. Figure 6 shows the capacity factors, k', for tri-, tetra-, and hexavalent actinides as a function of hydrochloric acid concentration. Comparison of these results to those shown in Figure 1 indicates that while the order of extractability of the various actinides from hydrochloric acid is essentially the same as that found in nitric acid, there are important differences between the two systems. Most notable is the extremely steep decline observed in k' for the tetravalent actinides as the hydrochloric acid concentration is lowered from 7-8 M. In the case of thorium(IV), for example, k' decreases from $>10^4$ to ~1 as the hydrochloric acid concentration is reduced from ~8 M to 1 M. In nitric acid, however, a comparable reduction in acid concentration produces only a one order of magnitude drop in k'_{Th}, from 10^5 to 10^4. As a result, while it is not feasible to strip sorbed tetravalent actinides from a TRU•Spec column using dilute nitric acid, it is feasible with dilute hydrochloric acid. K'_U does not exhibit this same steep decline from its maximum at 4-5 M hydrochloric acid. In fact, k'_U exceeds 100 even at 0.7 M acid. Since k' values for neptunium, plutonium, and thorium are 10 or less at this acidity, the separation of uranium from tetravalents should pose little or no difficulty in an HCl medium. The behavior of americium in this system also merits comment. As Figure 6 shows, k'_{Am} never exceeds 30, even at high (e.g., 8 M) hydrochloric acid concentrations. Thus, a column rinse with,

for example, 4 M hydrochloric acid will easily remove sorbed americium, while leaving U(VI) and tetravalents essentially untouched.

Taken together, these observations can serve as the basis of an elution scheme for the isolation of individual actinides using the TRU•Spec resin. Figure 7 summarizes one possible scheme which incorporates both nitric and hydrochloric acid rinse steps and various complex formation or oxidation state adjustment steps to effect the separation of actinides from both matrix constituents and one another. The sample load solution and column rinse are performed in nitric acid to take advantage of the high selectivity of the TRU•Spec for actinides over most matrix constituents in nitrate media (Table 2). Any iron present in the sample is reduced to Fe(II) to prevent interference with Am(III) retention (Table 3) and to ensure reduction of Np(V) to Np(IV). Two FCV of 9 M HCl are then used to convert the column to the chloride system. This reagent is used sparingly because Am is poorly retained in 9 M HCl. After the crossover to chloride, Am is eluted with 4 M HCl. The first 5 FCV contained > 99% of the Am and no detectable Pu. The third 5 FCV portion, however, contained 2.7% of the Pu activity. Next, plutonium is eluted with 4 M HCl - 0.1M hydroquinone. Approximately 91% of the Pu was found in the first 10 FCV. No detectable Am was found in the Pu fraction. Thorium and Np(IV) are eluted sequentially using 1.5 M HCl and 1.0 M HCl - 0.03 M oxalic acid, respectively. Approximately 94% of the Th and 2% of the Pu was in the first 5 FCV of 1.5 M HCl. The third 5 FCV portion of 1.5 M HCl contained only 1% of the Th, 1.4% of the Pu, and 1.5% of the Np activities. Virtually all of the Np was eluted in the first 5 FCV of 1.0 M HCl - 0.03 M oxalic acid and no other activity was discernible by alpha pulse-height analysis of this fraction. Finally, ~95% of the U is eluted with 5 FCV of 0.1 M ammonium bioxalate. No other activity was evident in the U fraction by alpha pulse-height analysis. The second 5 FCV portion contained only 2.4% of the U, but also contained ^{233}Pa (introduced from ^{237}Np).

Supplementary experiments have shown that Th must be eluted slowly when using hydrochloric acid to achieve good reproducibility. Tetravalent Np also shows slow kinetics when eluted with HCl alone, but not when elution is carried out with HCl and oxalic acid.

Alternative sequential separation schemes of actinides. Although the procedure depicted in Figure 7 provides a reasonably good separation of the five actinides from each other, it is probably too tedious for routine analytical use. However, variations on this sequential elution scheme are possible in which TRU•Spec is used in conjunction with anion exchange columns to achieve an efficient separation with fewer manipulations. For example, tetravalent actinides (Th, Np, and Pu) may be selectively separated from trivalent and hexavalent actinides (Am, U) and all matrix constituents by using a strong-base anion exchange resin (preferably macroporous) loaded in and rinsed with 7 to 8 M HNO_3. (Separation of Th(IV) from Np(IV) and Pu(IV) or separation of all

three elements from each other is carried out in the conventional manner.) The load and rinse solution from the anion exchange column may be treated in one of two ways. First, if the sample contains large quantities of matrix constituents (e.g., Fe and Ti), which is frequently the case with soils, a coprecipitation of the Am (and under certain conditions, U) on calcium oxalate gives a convenient feed material for dissolution and subsequent loading onto a TRU•Spec column. (The calcium oxalate is easily dissolved in 2 to 3 M HNO_3, but ascorbic acid should still be added before loading to ensure the absence of trivalent iron.) After loading and rinsing the TRU•Spec column with 2 -3 M nitric acid, an abbreviated sequential separation is carried out in which Am is stripped with 4 M HCl, residual Pu (that was not retained by the anion exchange column) is stripped with 4 M HCl - 0.1 M hydroquinone, residual Th and Np (also that was not retained by the anion exchange column) are stripped with 1.0 M HCl - 0.05 M oxalic acid, and U is stripped with $NH_4HC_2O_4$. This procedure has several advantages. First, dissolved soil and ashed fecal or waste samples are much easier to keep in solution in strong nitric acids. Second, the anion exchange - coprecipitation - TRU•Spec scheme is robust and applicable to a wide range of sample types. Third, macroquantities of the Th and U are separated from the TRUs and thus do not interfere with alpha pulse-height analysis. Finally, the Am fraction is highly decontaminated from all other actinides. If the procedure is applied to soil samples, sufficient concentrations of lanthanides are usually present in the Am fraction to form a visible deposit that may interfere with alpha-pulse height analysis. In such cases, the Am is separated from the lanthanides.

A second method of treating the load and rinse solution from the anion exchange column involves eliminating the coprecipitation step and loading directly onto a TRU•Spec column. This procedure should only be used if macro quantities of Fe, Zr, and Bi are not present. A 2 M HNO_3 - 0.05 M oxalic acid rinse should be used prior to the HCl crossover step to remove traces of transition and post-transition elements. The balance of the procedure is as described above.

It is important to note that both of the alternate sequential separation schemes involve a Pu strip step using HCL - hydroquinone even though Pu(IV), like Th and Np(IV), can be eluted with HCL - oxalic acid. If this Pu strip step is eliminated, a significant fraction of the Np is found in the uranium fraction, presumably due to the presence of Np(VI). However, if one does not wish to recover U, then the TRU•Spec column can be stripped with 0.1 M $NH_4HC_2O_4$ following the stripping of Am with 4 M HCL.

Resin Stability. Column stability studies carried out with the TRU•Spec resin show that the americium elution band peaks at approximately 25 ml (~ 41 FCV) on a freshly prepared column when 0.3M nitric acid is employed as the eluent. The first and second column rinses (ca. 250 FCV and 500 FCV of rinse, respectively) produce a shift in this peak to higher volumes, ~32 mL and and 35 mL, respectively. Additional rinsing, however, produces a shift to smaller elution volumes

until at 1000 FCV, the volume at peak maximum is only ~ 10% greater than that observed before any column rinsing. The initial increase in elution volume is consistent with the preferential dissolution of the more soluble TBP, the solvent for CMPO in TRU•Spec resin. The effect of such dissolution would be to increase the concentration of CMPO in the stationary phase and thus, the retention volume of sorbed ions. More extensive washing apparently removes CMPO as well, effectively stripping the stationary phase from the most readily accessible resin pores and leaving behind a material whose stationary phase composition more closely approximates that of the unwashed resin. Additional evidence of stationary phase loss is found in the fact that v_m, which was 0.60 mL initially, rises to 0.78 mL after 1000 FCV of washing, suggesting the presence of empty pores. Interestingly, estimates of theoretical plate numbers appear to indicate that in the early stages of column rinsing (500 FCV), column efficiency decreases, while additional rinsing yields a gradual improvement in efficiency. The reason for this behavior is unclear at present. What is clear is that the performance of TRU•Spec after ~1000 FCV of water washing does not differ substantially from that of pristine material. From the standpoint of 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. Second, it indicates that a given column could be used more than one time, provided of course, that care is taken to ensure that all traces of sorbed ions are removed prior to reuse.

CONCLUSIONS

An extraction chromatographic resin comprised of a CMPO-TBP solution supported on an inert polymeric substrate provides an effective method for the separation and preconcentration of actinides from aqueous solution. The tri-, tetra-, and hexavalent actinides are efficiently sorbed by the resin from solutions containing a wide range of nitric acid concentrations. Under these same conditions, most other commonly encountered cations (e.g., Ca, Na) are only poorly retained, making the material potentially well-suited to the isolation of actinides from various environmental or biological samples. By exploiting differences in the retention of actinides in various oxidation states in hydrochloric acid in the presence and absence of oxalic acid, individual actinides can be separated from one another. This versatility too should make the resin applicable in a wide variety of analytical schemes for actinide separation and quantitation.

ACKNOWLEDGMENT

The authors wish to thank Dr. Claudia Felinto for assistance in the measurement of TRU•Spec resin stability.

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Table 1. Characteristics of the TRU•Spec extraction chromatographic material and packed columns.

Bulk Material	
Stationary Phase	0.75 M CMPO in TBP (ρ= 0.971 g/ml)
Support	Amberchrom™ CG-71
Particle Diameter	50-100 µm
Extractant Loading	40%
Average Density of Extractant-Loaded Beads[a]	1.12 g/mL
Packed Columns	
v_s	0.152 mL/mL of bed
Bed Density	0.370 g/mL
v_m (also FCV)	0.68 mL/mL of bed
v_s/v_m	0.223
Calculated Capacity	5.49 mg Nd or 9.18 mg ^{241}Am/mL of bed
Expe•rimentally Measured Capacity	4.1 mg Nd or 6.8 mg ^{241}Am/mL of bed

[a] Picnometric density and flotation density were 1.081 (in water) and 1.158 (in 4.9 M HNO_3) g/mL, respectively. The calculated density is 1.094 g/ml assuming 100% pore filling and no swelling.

Table 2. Elution behavior of selected elements on a TRU•Spec column.[a]

	←2 M HNO_3→					←0.05 M HNO_3→	
	Number of free column volumes						
Element	1-5	6-10	11-15	16-20	21-25	26-30	31-40
Li	98.4	< 19	—	—	—	—	—
Na	92.8	< 1.2	—	—	—	—	—
Mg	100	—	—	—	—	—	—
Al	99.8	< 2.9	—	—	—	—	—
K	81.8	40.9	—	—	—	—	—
Ca	100	—	—	—	—	—	—
Cr	100	—	—	—	—	—	—
Mn	100	—	—	—	—	—	—
Fe	102	< 12.3	—	—	—	—	—
Co	100	—	—	—	—	—	—
Ni	100	—	—	—	—	—	—
Cu	100	—	—	—	—	—	—
Zn	100	—	—	—	—	—	—
Sr	100	—	—	—	—	—	—
Y	23.4	76.8	3.5	—	—	—	—
Zr	—	—	—	—	—	—	75.0
Ru	82.6	<19.2	—	—	—	—	—
Rh	100	—	—	—	—	—	—
Ag	100	—	—	—	—	—	—
Cd	100	—	—	—	—	—	—
Ba	100	—	—	—	—	—	—
La	—	—	—	—	—	30.0	72.0
Ce	—	—	—	—	—	<25.0	75.0
Pr	—	—	—	—	—	—	100
Nd	—	—	—	—	—	—	96.0
Sm	—	—	—	—	—	—	100
Eu	—	—	—	—	—	—	>99
Hg	(100)	(60)	(19)	—	—	—	—
Pb	100	—	—	—	—	—	—
Am[b]	—	—	—		—	—	>99

Conditions:
T= 23 °C
particle size = 50-100μm diameter
1 FCV = 0.60 mL

[a] Because of uncertainties inherent in the ICP-AES method, the fractions shown for each element may not total 100%. Values in parentheses are subject to considerable uncertainty and are intended only as a rough guide.

[b] radiometric.

Table 3. Effect of Fe on Am uptake by TRU•Spec[a]

mg of Fe/10 mL	M of Ascorbic Acid	k'Am
25	—	28
50	—	17
100	—	9.1
25	0.3	88
50	0.3	72
100	0.3	65

[a] Reference k'Am at 2 M HNO_3 and 23 ° C = 98.

FIGURE CAPTIONS

Figure 1. Nitric acid dependencies of k' for selected actinide ions with TRU•Spec resin (T = 23-25 °C ; 50-100 μm particle size resin).

Figure 2. Nitric acid dependencies of k' for selected non-actinide ions on TRU•Spec resin (T = 23-25 °C ; 50-100 μm particle size resin).

Figure 3. Elution curve for Am(III) using TRU•Spec resin (Eluent = 2.0 M HNO_3 ; T = 23 °C ; Flow rate = 1 to 2 mL/cm^2 min. ; 50-100 μm particle size resin ; bed volume = 0.59 mL ; bed length = 10.1 cm.)

Figure 4. Effect of matrix constituents and acidic complexing agents on Am retention. TRU•Spec resin/2 M HNO_3.

Figure 5. Effect of acidic complexing agents on Np retention on TRU•Spec resin from 2 M HNO_3.

Figure 6. Hydrochloric acid dependencies of k' for selected actinide ions on TRU•Spec (T = 23-25 °C ; 50-100 μm particle size resin.)

Figure 7. Sequential elution of five actinides from a TRU•Spec column. (Column dimensions: bed diameter = 2.84 mm; bed length = 9.8 cm. Flow rate: 0.5-1.0 ml/ cm^2/min.) 2 FCV of 9M HCL follow the 2M HNO_3 scrub.

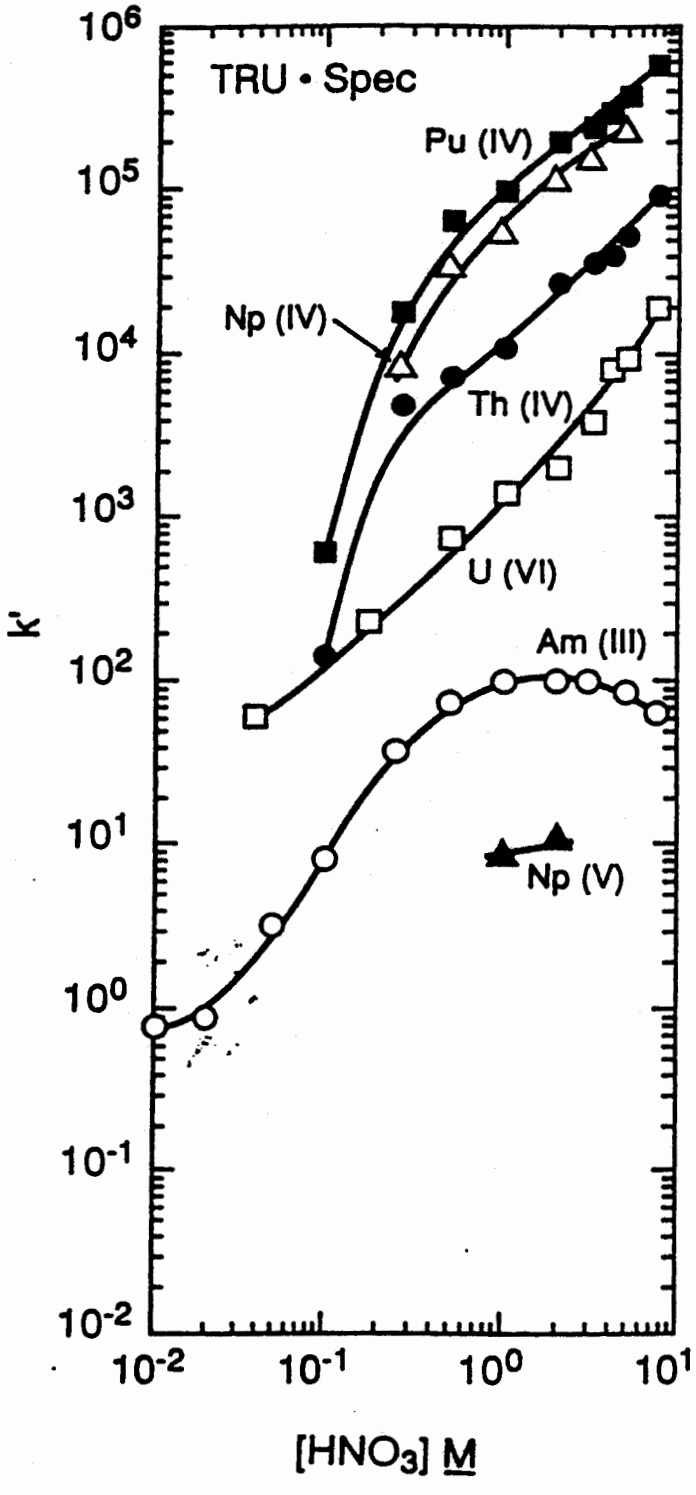
TRU • Spec
Pu (IV)
Np (IV)
Th (IV)
U (VI)
Am (III)
Np (V)
k'
10^6
10^5
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-2}
10^{-1}
10^0
10^1
[HNO_3] M

Fig. 1.

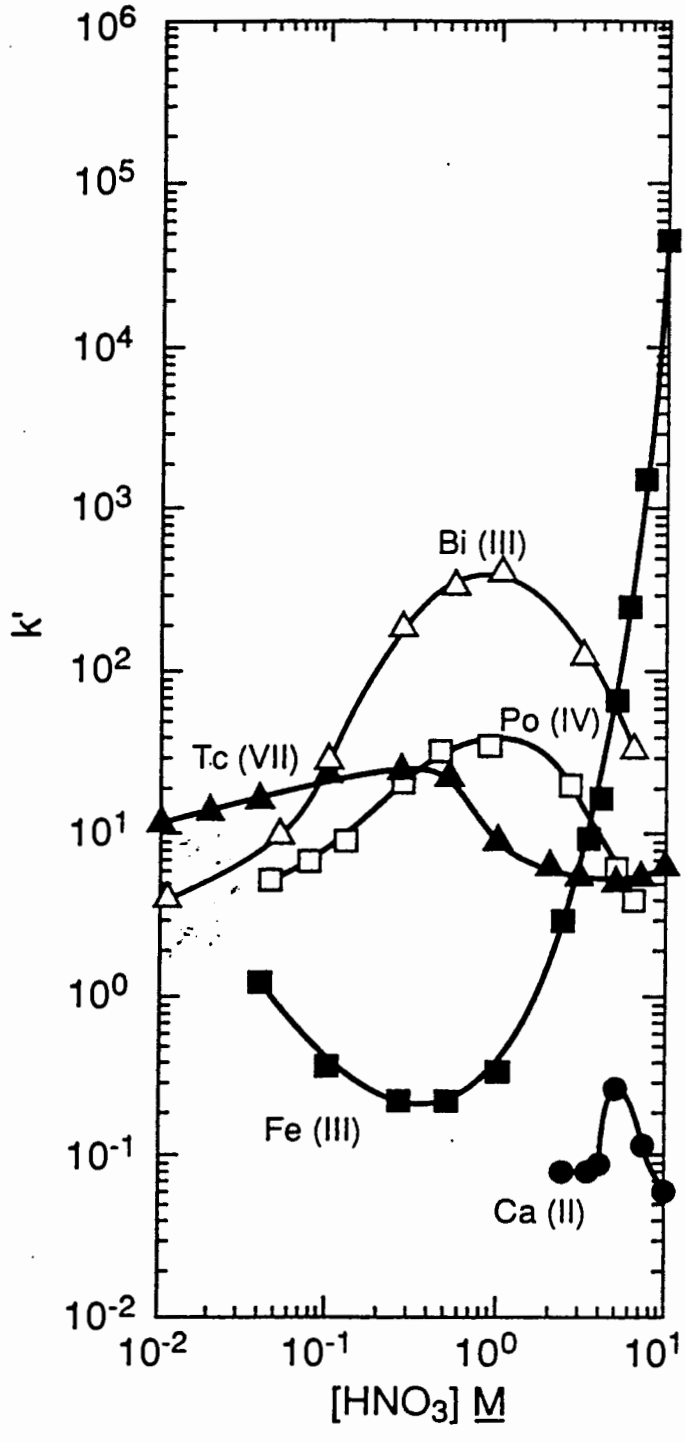
10^6
10^5
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
K'
Bi (III)
Po (IV)
Tc (VII)
Fe (III)
Ca (II)
10^{-2}
10^{-1}
10^0
10^1
[HNO_3] M

Fig. 2.

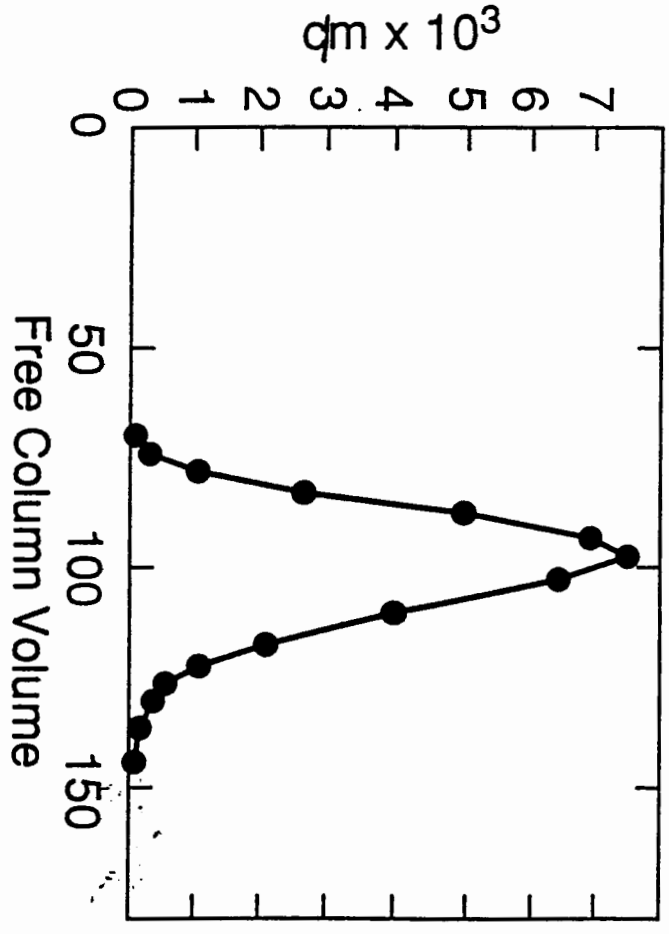

Fig. 3

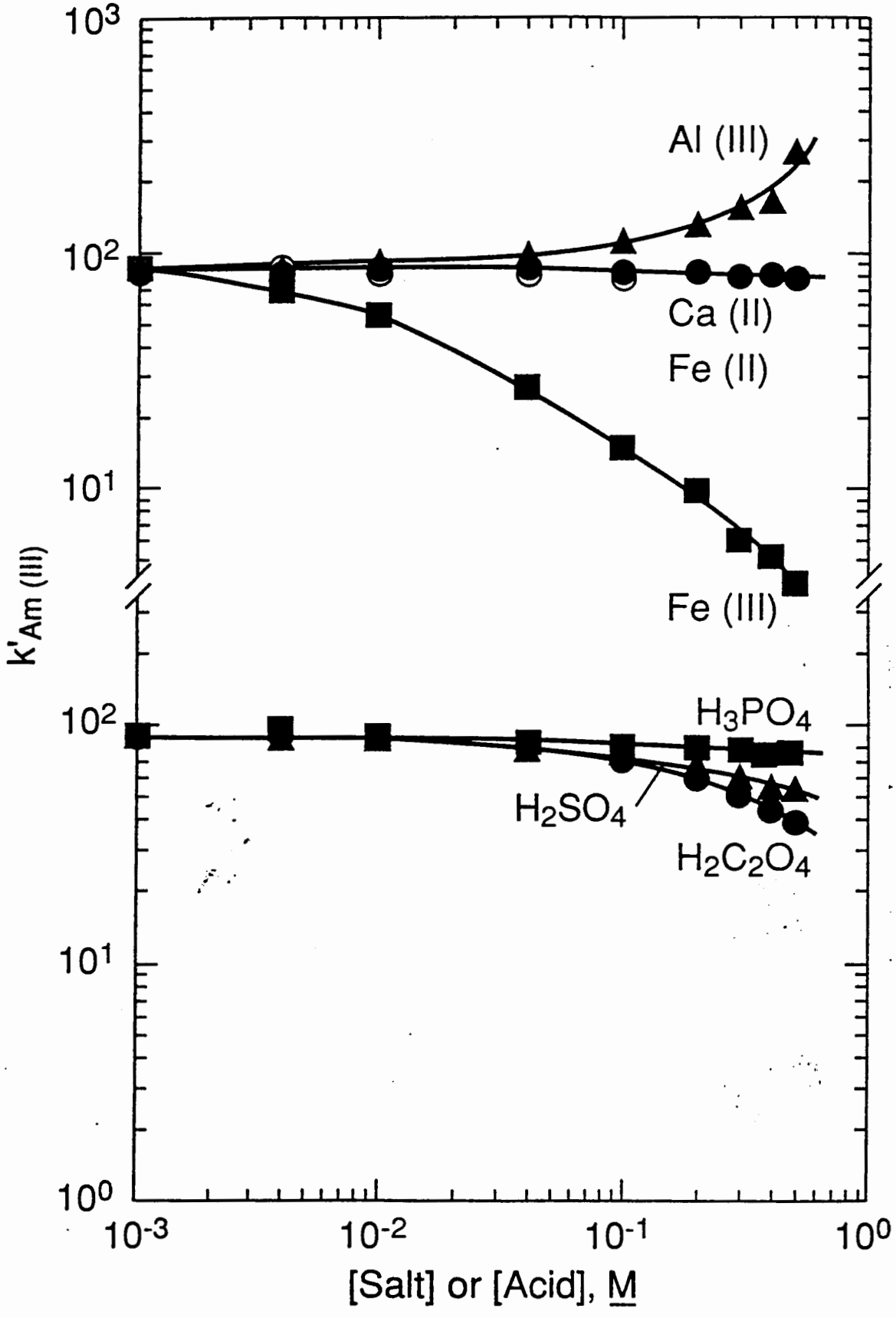
10^3
10^2
10^1
10^2
10^1
10^0
$k'_{Am\ (III)}$
Al (III)
Ca (II)
Fe (II)
Fe (III)
H_3PO_4
H_2SO_4
$H_2C_2O_4$
10^{-3}
10^{-2}
10^{-1}
10^0
[Salt] or [Acid], M

Fig. 4.

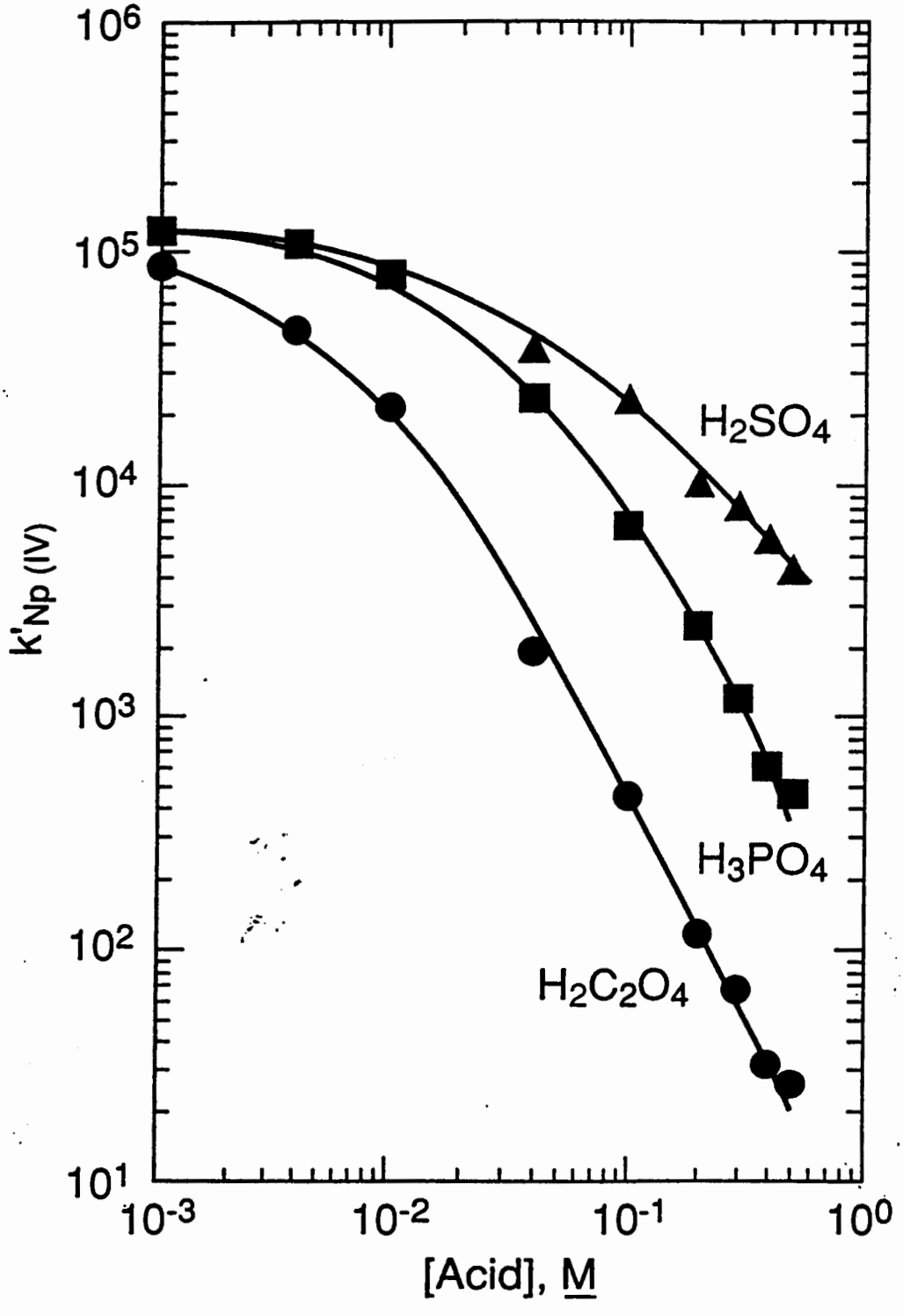
10^6
10^5
10^4
10^3
10^2
10^1
k'_{Np} (IV)
H_2SO_4
H_3PO_4
$H_2C_2O_4$
10^{-3}
10^{-2}
10^{-1}
10^0
[Acid], M

Fig. 5.

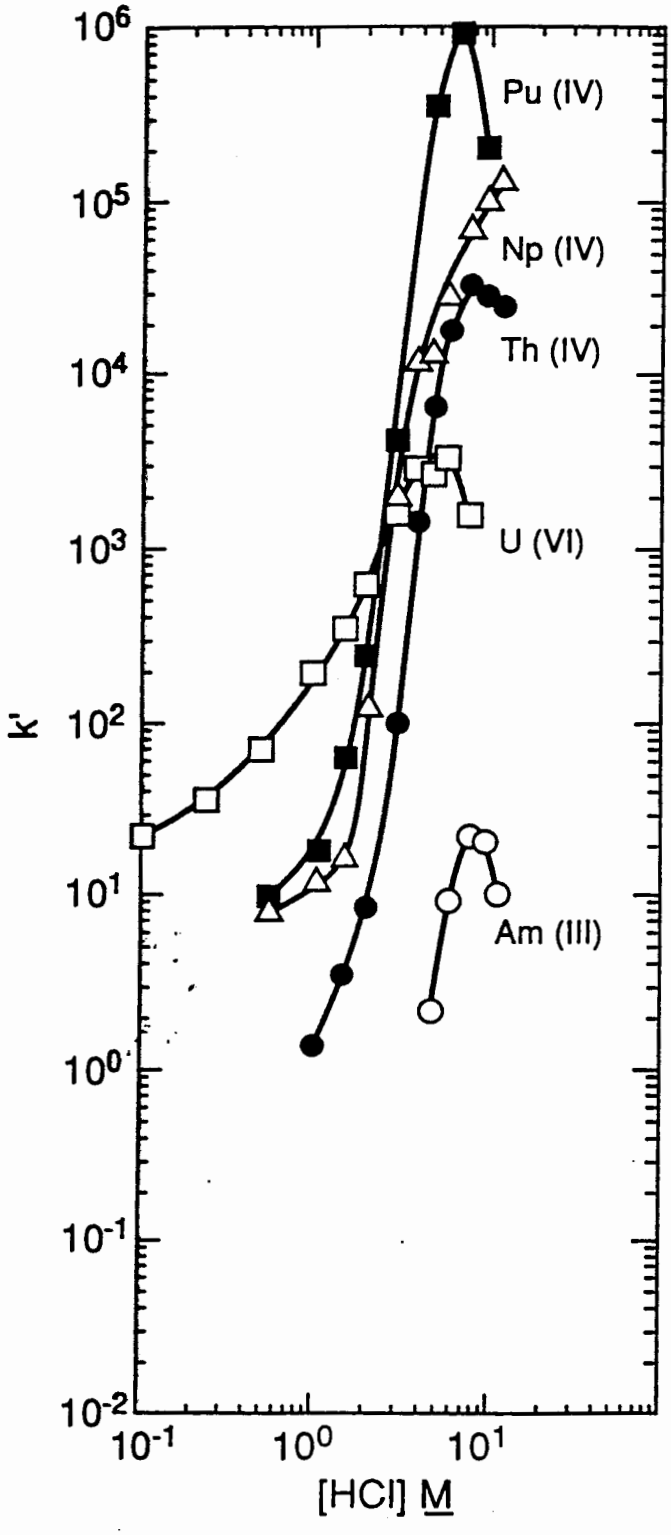

Fig. 6.

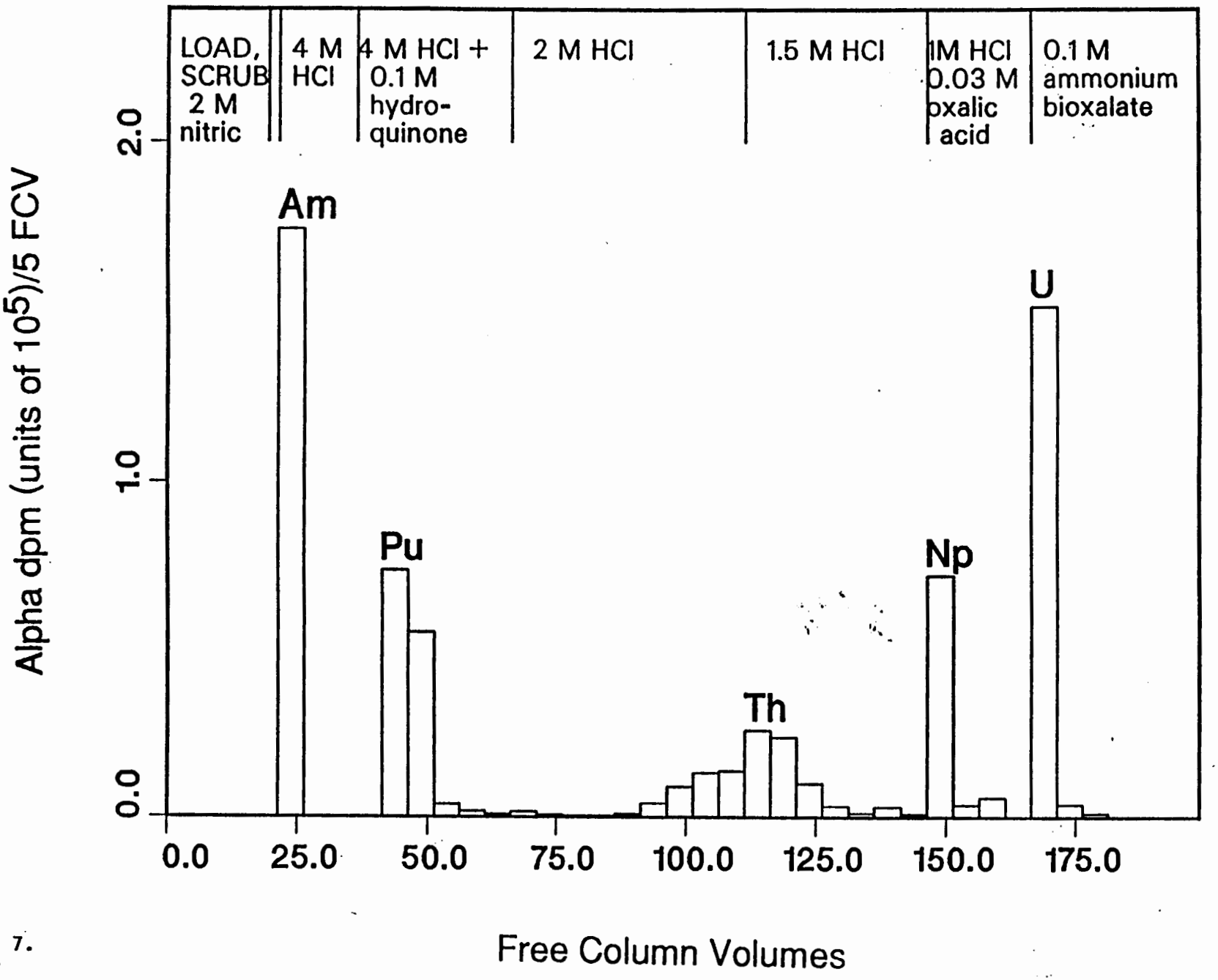
LOAD, SCRUB 2 M nitric
4 M HCl
4 M HCl + 0.1 M hydro-quinone
2 M HCl
1.5 M HCl
1M HCl 0.03 M oxalic acid
0.1 M ammonium bioxalate
Am
Pu
Th
Np
U
Alpha dpm (units of 10^5)/5 FCV
2.0
1.0
0.0
0.0
25.0
50.0
75.0
100.0
125.0
150.0
175.0
Free Column Volumes

Fig. 7.