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# Separation and Preconcentration of Actinides by Extraction Chromatography Using a Supported Liquid Anion Exchanger: Application to the Characterization of High-Level Nuclear Waste Solutions

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## Abstract

A novel extraction chromatographic resin comprised of a quaternary amine-based liquid anion exchanger sorbed on an inert polymeric substrate for the sorption of actinides from nitric and hydrochloric acids is described. The resin is shown to exhibit preferential retention of tetravalent actinides over a wide range of acidities. The application of this material to the separation and preconcentration of selected actinides from high level nuclear waste solutions for subsequent determination is described.

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## Introduction

The chemical pretreatment of nuclear wastes for subsequent disposal and the handling of associated effluent streams frequently require detailed knowledge of the waste composition. Typically, waste characterization involves the determination of a variety of radionuclides in a complex, multi-element solution matrix. Complicating these determinations is the fact that the waste solutions are often strongly acidic or basic and sometimes, highly radioactive (1).

Recent work in this laboratory has led to the development of a series of novel extraction chromatographic resins capable of the selective sorption of the nitrato complexes of the actinides (2,3), radiostrontium (4-6), or uranium (7) from acidic media. These materials, each comprised of a highly selective extractant originally developed for process-scale nuclear waste treatment sorbed on an inert polymeric substrate, have been shown to exhibit a number of favorable characteristics, among them flexibility in sample loading conditions, resistance to high levels of many potential interferents, and excellent stability. In previous reports (2,4,7-13), these materials have been shown to provide a simple and effective means for the separation and preconcentration of selected radionuclides from a variety of media. In this report, we describe their application to the isolation of actinides and related fission products from nuclear waste streams for subsequent determination. Because of the selectivity of the extractants employed in these chromatographic materials, no single resin is capable of the separation of all of the radionuclides of interest from a given sample. For this reason, we have examined the use of tandem column arrangements, in which the effluent from a given chromatographic column serves as the load solution for subsequent columns, and of novel single columns comprised of a series of coupled resin cartridges. In conjunction with these studies, we have developed an extraction chromatographic material incorporating a quaternary amine-based liquid anion exchanger. Its properties, along with its applications in various actinide separation schemes, are also described.

## Experimental

### Reagents

The quaternary amine employed in this study was a technical grade (85% purity) mixture of trioctyl and tridecyl methyl ammonium chlorides available commercially (Henkel Corporation) as Aliquat™•336. This material was used without further purification. 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 $^{230}$Th, $^{233}$U, $^{237}$Np, $^{239}$Np, $^{239}$Pu, $^{241}$Am, $^{85}$Sr, and $^{99}$Tc tracers. The $^{239}$Np was "milked" from $^{243}$Am in 9 M HCl using a BioRad™ AG-MP1 anion exchange column (BioRad, Richmond, CA). The Sr, TRU, and U/TEVA extraction chromatographic resins were obtained from EIChroM Industries Inc. (Darien, IL) and were appropriately preconditioned prior to use (3,5,7).

## Procedures

*Preparation of an extraction chromatographic resin incorporating a liquid anion exchanger.* The extraction chromatographic resin was prepared by impregnating Amberchrom CG-71ms with undiluted Aliquat™•336 in the manner described previously for the impregnation of this same resin with organophosphorus extractants (2,3). To ensure that the sample flow rates through a column of this new resin closely matched those obtained with equivalent columns of other resins, support material having the same particle size distribution as that used previously was typically employed (4,7).

Because of the viscosity of the quaternary amine, extra care must be taken to ensure a homogeneous distribution of the extractant on the support. Specifically, the extractant/support/methanol slurry must be thoroughly mixed during rotary evaporation of the methanol. In addition, methanol removal must not be too rapid. We have obtained satisfactory results by first evaporating the methanol from the slurry until only enough liquid remains to just cover the resin, then re-suspending the resin in a small volume of methanol, vigorously mixing the slurry, and repeating the evaporation. The resultant extraction chromatographic material, referred to hereafter as TEVA (for tetravalent actinide) resin, is now commercially available from EIChroM Industries. Table 1 summarizes the essential features of this new material.

*Determination of weight distribution ratios and column capacity factors.* The sorption of various ions by the TEVA resin from nitric and hydrochloric acid solutions was measured by equilibrating a known volume of a tracer-spiked acid solution of appropriate concentration with a known weight of resin (5). Weight distribution ratios were converted to the number of free column volumes (FCV) to peak maximum (i.e., the resin capacity factor), k', by dividing by 1.93. 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 TEVA resin. Details may be found in a previous report (5).

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.

*Kinetics experiments.* A series of thermostated screw-cap test tubes, each containing the same (within 10%) weighed amount of resin and a 2x2x10 mm magnetic bar, were used for each kinetic run. The moment when a known volume (typically 1 mL) of a thermostated solution containing tracer was introduced into the test tubes and the stirring was started was taken as $t = 0$ for the experiments. At various time intervals, one of the test tubes was quickly centrifuged at high speed, most of the aqueous phase was carefully withdrawn from the tube and filtered, and the weight distribution ratio of the metal, D, was determined as described above. In this way, a plot of the time dependence of D was obtained for which each experimental point is the result of the measurements performed on a single test tube. Kinetic experiments were also performed with the TRU and U/TEVA resins for comparison.

*Column preparation and characterization.* Columns were packed as previously described (4). All column parameters (e.g., $v_s$, $v_m$, bed density) were measured as described in Reference 5. The capacity of the TEVA resin was determined by quantitatively exchanging nitrate for chloride from a weighed quantity of the material and determining the displaced chloride by gravimetry (14).

*Elution behavior of selected elements and matrix effects.* The elution behavior of thirty-one metal cations on a TEVA column (bed volume = 1.0 mL; bed height = 5.1 cm) was evaluated using procedures described in a previous report (5). Two molar nitric acid was employed for column rinsing and 4 M hydrochloric acid for column stripping. Gravity flow rates (1-2 mL $cm^{-2}$ $min^{-1}$) were employed throughout.

The effect of macro concentrations of various cations (e.g., $UO_2^{2+}$) or aqueous complexing agents (e.g., oxalic acid) upon neptunium uptake by the resin was evaluated by measuring the sorption of $^{239}Np$ from 2-5 M nitric acid containing various concentrations of the test species.

*Analysis of high-level waste solutions.* Chromatographic columns were prepared by slurrying the appropriate resin in water, then transferring aliquots of the slurry under vacuum to a column body (Whale Scientific, Inc.) or minicartridge (Applied Separations, Inc., Allentown, PA.) until the desired bed height was reached. To reduce analysis times and to enhance column performance, small particle size (20-50 µm or 50-100 µm) resins were employed, along with a vacuum extraction system (Applied Separations, Inc.).

Flow rates of 2-4 mL/min were typically employed, much faster than the 0.5 mL/min gravity flow rates observed. Fifteen mL polypropylene reservoirs (Applied Separations, Inc.) were used in the multistage single column work for the sample loading and initial rinsing steps, as well as in the stripping of the individual cartridges.

The waste samples taken for analysis were sufficiently "cold" (gamma activity from $^{137}Cs \leq 10^9$ dpm/mL) to permit work at a radiobench, rather than in a shielded hot cell.

### Apparatus

For resin characterization studies, gamma counting was performed in either a Beckman Biogamma counter or a Packard Cobra Autogamma counter. Alpha and ß-counting of single tracers were performed via liquid scintillation on a Packard Model 2000CA counter. For $^{90}$Sr, a Beckman 6000S counter was also employed. Standard radiometric assay and counting procedures were employed throughout. In sequential elution experiments, proportional counting with argon-methane 2 $\pi$ counters and alpha pulse analyses using surface-barrier silicon detectors were also carried out.

The determination of uranium was performed by laser kinetic phosphorimetry using a Model KPA-10 Kinetic Phosphorescence Analyzer (Chem Chek Instruments, Richland, WA) or by mass spectrometry using a Finnigan TIMS system. Thorium and inactive europium and strontium were determined using a Beckman SpectraSpan V DCP.

## Results and Discussion

In an earlier report (3), a chromatographic resin comprised of a tri-n-butyl phosphate (TBP) solution of the bifunctional organophosphorus extractant octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) sorbed on an inert polymeric substrate (TRU resin) was shown to permit the rapid and selective sorption of actinides from nitric acid-containing media and, through careful choice of conditions, their sequential elution. In preliminary experiments designed to evaluate the utility of this material in waste characterization, however, it became apparent that the complexity of the elution sequence and the number of manipulations required to isolate the individual actinides precluded the its use on a stand-alone basis in routine analyses. Earlier work by one of the authors (15) had shown that the anionic complexes of tetravalent actinides are more readily extracted from nitrate media than are those of the trivalent or hexavalent actinides by the liquid anion exchanger Aliquat™•336. This suggested that a multi-column actinide separation scheme in which the sample solution is first passed through a bed of an Aliquat™•336-based extraction chromatographic material to remove tetravalent actinides might facilitate the isolation of the individual actinides.

Although a number of reports have appeared describing separations employing Aliquat™•336, both in liquid-liquid extraction (16-18) and in various chromatographic modes (19-21), there has been no systematic evaluation of the properties of an extraction chromatographic material employing this reagent as the stationary phase. For this reason, the TEVA resin was first 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. The results are reported in Figure 1. Similar data obtained with the TRU and U/TEVA resins are shown for comparison. As expected, at nitric acid concentrations ≥ 0.5 M, the sorption of each of the tetravalent actinide ions greatly exceeds that of the tri-, penta-, or hexavalents. In fact, k' for even the most poorly retained of the tetravalents, thorium, is an order of magnitude or more greater than U(VI), Np(V), or Am(III). (It is important to point out that attempts to compare the relative extractabilities of the actinides in chromatographic and liquid-liquid systems must take into account the differences in Aliquat™ concentrations in the two systems and the relationship between k' and D, the distribution ratio ($k' = D\, v_s/v_m$.)) The maximum in k' observed for each of the actinide ions is likely the result of a reduction in available Aliquat arising from its extraction of nitric acid at high acid activities (15). The strong preference of the TEVA resin for tetravalent actinides contrasts with the actinide sorption behavior exhibited by the two organophosphorus extractant-based chromatographic materials, TRU and U/TEVA, described previously (3,7). As can be seen from Figure 1, the retention behavior of uranium (VI) and neptunium (IV) on the U/TEVA resin is nearly indistinguishable over a range of acidities. Moreover, uranium (VI) retention is actually stronger than that of thorium (IV) at all but the lowest acidities. For the TRU resin, the k' value for a given ion is typically 100-1000 times greater than on U/TEVA. In fact, unlike TEVA resin, the TRU resin retains all but the pentavalent actinides strongly over a wide range of nitric acid concentrations (0.5 to 8 M). It is this strong retention of U(VI), Np(IV), and Pu(IV), even at low acidities, which complicates the elution of individual actinides from the TRU resin (3).

Figure 2 shows the retention of the various actinides by the TEVA resin as a function of hydrochloric acid concentration and compares this retention to that observed with the TRU and U/TEVA resins. As was the case in nitric acid, the k' values observed with the TRU resin are typically substantially larger than the corresponding values on either the TEVA or U/TEVA resins. The close correspondence of the acid dependencies for the various tetra- and hexavalent actinides on the TRU resin further complicates attempts to resolve individual actinides using this resin. Noteworthy for TEVA resin is that the retention of thorium(IV) is much poorer than that of tetravalent plutonium and neptunium at all of the hydrochloric acid concentrations examined, suggesting a simple means by which a separation of thorium from other tetravalents could be effected.

Technetium-99, a fission product, is also a constituent of certain high-level liquid wastes (HLLW) and its separation from the actinides is therefore important in the analysis of HLLW. As can be seen from Figure 1, technetium(VII) retention on TEVA resin from nitric acid is greater than that of any of the actinides examined at acid concentrations less than about 0.25 M. At 0.1 M, in fact, technetium retention exceeds that of Pu(IV), the next most strongly retained species, by nearly two orders of magnitude. The strong retention of Tc(VII) by the TEVA resin at low acidity is due to the high selectivity of quaternary ammonium salts for the pertechnetate anion, $TcO_4^-$, over the anion of the acid. The differences in retention between the actinides and technetium are even more pronounced from hydrochloric acid. As shown in Figure 2, the retention of all of the actinides on TEVA resin declines precipitously as the acid concentration is reduced, while that of technetium rises. Thus, at sufficiently low acidities, $k'_{Tc}$ exceeds that of both the tetra- and hexavalent actinides by nearly five orders of magnitude. Clearly then, separation of technetium from any of the actinides can easily be effected simply by rinsing the TEVA column with 0.1 M $HNO_3$ or HCl.

*Kinetics of uptake.* The kinetics of sorption of Th(IV) by TEVA resin, of Am(III) by TRU resin and of U(VI) by U/TEVA resin at 24 °C and 50 °C are reported in Figure 3. In all cases, the metal uptake proceeds rapidly, ten minutes or less being sufficient for the attainment of a constant weight distribution ratio. Because these experiments were performed at tracer metal concentration, the rate of metal uptake is likely to be controlled by the diffusion of the metal species through the aqueous diffusion layer adjacent to the resin particles (22) and no significant differences would be expected for the kinetic behavior of the three resins.

Regarding the temperature dependence of the equilibrium D values, it is noteworthy that the metal distribution is least affected by an increase in temperature for the TEVA resin. This is consistent with Aliquat™•336 behaving predominantly as a liquid ion exchanger. That is, ion exchange is not a chemical reaction and thus occurs, as a rule, with very small enthalpy changes (22).

*Elution behavior of selected cations.* The elution behavior of thirty-one different elements (Li, Na, Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Mo, Ag, Cd, Cs, Ba, La-Eu, Hg, Th, and U)), among them a variety of alkali and alkaline earths, transition metals, and assorted fission products, was determined on a 1.0 $cm^3$ bed volume column packed with 50-100 µm TEVA resin. Two molar $HNO_3$ was used for column loading (0.60 mL) and for the first 30 free column volumes (1 FCV = 0.66 mL) of rinsing, while 4 M HCl was used to remove sorbed thorium from the column (31-40 FCV). (Tetravalent thorium was selected for this study because, as shown in Figure 1, it is typically the least strongly retained of the actinides in this oxidation state on the TEVA resin.) All of the test elements except mercury and thorium were found to elute from the column in the first 10 FCV. Mercury elution was complete in 20 FCV. No trace of thorium was observed in the first 30 FCV of rinse solution. As expected from Figure 2, however, it was readily removed from the column with a small volume of hydrochloric acid.

*Separation of hexavalent and tetravalent actinides on the TEVA resin.* The results presented in Figures 1 and 2 and those obtained in the elution study suggest that the separation of the actinides from a variety of matrices on the TEVA resin should be highly efficient. Moreover, they suggest conditions that may be employed to separate tri-, tetra-, and hexavalent actinides from each other and from various other metal ions. Figure 4a, for example, depicts a simple scheme by which uranium and thorium can be separated from neptunium and plutonium. Following loading of the sample solution, the column is rinsed with 2 M nitric acid. Because uranium sorption is far poorer than that of the tetravalent actinides at this acidity (Figure 1), it is quickly eluted. If the mobile phase is then changed to 3 M HCl, thorium (which is essentially unretained from hydrochloric acid) immediately elutes. A change to 0.5 M HCl lowers $k'_{Np}$ and $k'_{Pu}$ sufficiently (Figure 2) to permit their elution. Separation of neptunium and plutonium may be effected as shown in Figure 4b. Following sample loading and column rinsing with 9 M HCl, the plutonium (IV) is reduced by addition of hydroquinone. Because the sorption of trivalents on TEVA resin is poor, Pu (III) elution proceeds rapidly. Once plutonium elution is complete, 0.5 M HCl is used to remove Np (IV).

*Actinide / Lanthanide Separations on the TEVA resin.* Because of their chemical similarity, lanthanides and trivalent actinides are frequently recovered together in the initial stages of treatment and analysis of HLLW (23, 24). Macro levels of lanthanides, however, interfere with the formation of the very thin samples required for α-pulse analysis of the actinides. As a result, accurate actinide determinations frequently require removal of the lanthanides. Among the earliest applications described for quaternary amine extractants such as Aliquat™•336 was in fact, the separation of trivalent actinides (e.g., $^{241}Am$) from lanthanide fission products (16, 25, 26). It has been reported (25) that a satisfactory separation can be achieved from mineral acid solutions (e.g., $HNO_3$, HCl, $H_2SO_4$) to which ammonium thiocyanate has been added, with americium markedly more well extracted than trivalent lanthanides, using a 30% (w/v) solution of Aliquat™ in xylene. Recently, this separation has also been investigated from solutions containing ammonium thiocyanate and formic acid (27). Figure 5 demonstrates that an actinide/lanthanide separation can also be effected using the undiluted extractant supported on Amberchrom. Following sample loading (in 2 M ammonium thiocyanate - 0.1 M formic acid), the column is rinsed with 1 M $NH_4SCN$ - 0.1 M HCOOH to remove sorbed lanthanides. The eluent is then changed to 0.25-2 M HCl, leading (as expected from Figure 2) to the rapid elution of americium.

*Effect of matrix constituents.* The acid dependency data presented in Figures 1 and 2 and the elution behavior data are important not only because they suggest conditions that may be used to separate the actinides from each other and from various other metal ions, but also because they indicate which elements may cause a significant diminution in actinide sorption if present at sufficiently high concentrations. Uranium and thorium are major constituents in many nuclear waste samples. Therefore, the effect of increasing concentrations of uranyl and thorium nitrates on $k'_{Np}$ in 5 M $HNO_3$ was measured (Figure 6). The data show clearly that even modest concentrations of thorium ($\leq$ 0.01 M) significantly reduce neptunium sorption on TEVA resin. Although the effect of uranium is not as pronounced, at sufficiently high concentrations ($\geq$ 0.1 M), it too will appreciably reduce neptunium sorption. That a lesser concentration of thorium is required to produce a given decrease in $k'_{Np}$ is consistent with its stronger sorption on the TEVA resin (Figure 1).

The influence of various concentrations of oxalic, phosphoric, and sulfuric acids on $k'_{Np}$ from nitric acid is shown in Figure 7a. As expected, at the lowest nitric acid concentration (1.9 M), the presence of even small quantities of oxalic acid reduces neptunium sorption considerably. Only 0.01 M, for example, decreases $k'_{Np}$ by nearly an order of magnitude. Phosphoric acid and sulfuric acid have a much lower effect on $k'_{Np}$, because the anions of the respective acids are weaker complexing agents of Np(IV). Nevertheless, a considerable reduction of $k'_{Np}$ takes place as their concentrations approach 0.1 M. The decrease in neptunium sorption on the TEVA resin caused by oxalic acid can be reduced, but not entirely eliminated, either by adding macroquantities of Al(III) or, as shown in Figure 7b, increasing the nitric acid concentration. Addition of aluminum ion effectively complexes the oxalate anion, reducing its concentration, while raising the acidity effectively reduces the concentration of the complexing anion by protonation. Because $k'_{Np}$ is boosted by high nitric acid concentrations (to a maximum at 3-4 M), the latter approach is often preferred.

*Application of TEVA resin to the analysis of high-level liquid waste solutions. Tandem Column Approaches.* The measurement of trace radionuclides in high-level nuclear wastes presents a considerable challenge to the analyst and places a number of demands upon the method employed for their separation and preconcentration. For example, the method must be able to remove high levels of gamma activity (such as that arising from $^{137}Cs$) and to eliminate a variety of alpha and beta-emitting interferents. In addition, despite the difficult sample matrix, the method must allow for simple, rapid, flexible, and cost-effective separations. Finally, it must generate a minimal volume of mixed (i.e., radioactive and organic) wastes. The results presented above suggest that the TEVA resin would be well-suited to many of these demands. As expected, however, they also suggest that its use on a stand-alone basis for total actinide determinations would not be practical. Rather, a multiple column approach would be best suited to the requirements of waste analyses.

Figure 8 depicts a scheme incorporating three extraction chromatographic columns arranged in series by which actinides can be rapidly isolated from the same sample solution for subsequent determination. In this scheme, the sample solution, originally strongly alkaline (1-13 M NaOH), is acidified to 2-3 M nitric acid by addition of the concentrated reagent. Next, the sample is made up to 0.1 M in ferrous sulfamate (FS) to eliminate the nitrite present and to convert the plutonium and neptunium present to Pu (III) and Np (IV), respectively. Finally, the total nitrate concentration in the sample is raised to ~ 4 M by addition of aluminum nitrate. (This additional nitrate enhances the retention of actinides, particularly thorium, on the initial (TEVA) column. In addition, the aluminum complexes any fluorides, phosphates, sulfates, or oxalates which may be present and which could diminish actinide sorption (Figure 7a). Aluminum nitrate addition also allows the nitric acid concentration to be kept low enough to allow ferrous ions to maintain plutonium in the trivalent state.) Following sample loading onto the TEVA column, the column is rinsed to remove americium, plutonium, and uranium. Thorium is then stripped from the column with 6 M HCl for determination by DCP or alpha spectrometry. Finally, neptunium is eluted with a nitric-hydrofluoric acid mixture and determined by alpha spectrometry.

The rinsings from the TEVA column (containing Am, Pu, and U) are then passed through a U/TEVA column, where uranium is sorbed and americium and plutonium (still in the trivalent state) are washed through with a small volume of 3 M nitric acid-0.05 M ferrous sulfamate. After elution with dilute nitric acid, uranium is determined by laser kinetic phosphorimetry or mass spectrometry, as appropriate. Ascorbic acid is then added to the rinsings from the U/TEVA column (containing Am and Pu) to reduce any iron (III) to the divalent state, preventing its sorption on the final (TRU) column (3). Following loading of this ascorbic acid-treated solution, the TRU column is rinsed with a small volume of 3 M nitric acid-0.1 M sodium nitrite (to ensure that plutonium will be in the tetravalent state) and fission products are removed by a 3 M nitric acid rinse. Americium and plutonium are then eluted separately using 4 M HCl and 0.1 M ammonium bioxalate, respectively, and determined by alpha spectrometry.

This separation scheme can easily be modified to take into account the goals of the particular analysis or the absence of one or more of the actinides. For example, if the co-elution of neptunium and plutonium can be tolerated, plutonium can be retained on the initial TEVA column simply by adjusting the plutonium to the tetravalent state with ferrous ammonium sulfate and sodium nitrite. Americium and uranium removal, thorium elution, and neptunium elution are then carried out as described in Figure 9. Sample treatment on the U/TEVA and TRU columns to recover uranium and americium is similar to that described in Figure 8.

*Multi-stage single column approaches to HLLW analysis.* Although this three-column approach to the recovery of actinides for subsequent determination is highly effective, it does suffer from a significant limitation. That is, waste characterization frequently requires the determination of radiostrontium as well as actinides (28-32). The volume of rinse solution collected from the final (TRU) column, however, is too large to permit the recovery of the strontium present without a preliminary volume reduction by evaporation. Therefore, unless an evaporation step is incorporated into the procedure, some means of reducing the volumes of load and rinse solutions required throughout the procedure is needed.

Figure 10 depicts one means by which this may be accomplished. Here, a single column is assembled from a series of resin cartridges coupled by means of luer connectors. With such an arrangement, the sample is, in effect, added to four columns at once, rather than to one at a time. By careful choice of load conditions, all of the radionuclides of interest can be sorbed in a single pass of the sample. The column can then be split apart into the individual cartridges for recovery of the desired species. Obviously, for this approach to be successful, the load solution must be adjusted to a condition compatible with all four cartridges. We have obtained satisfactory results for HLLW by adjusting the samples to 1.5-3 M nitric acid and to 3.5-5 M total nitrate by addition of aluminum nitrate. Ferrous sulfamate is used to fix the valence of plutonium and neptunium (at Pu(III) and Np(IV), respectively), while ascorbic acid is used to convert any iron present to the divalent state to minimize its sorption on the TRU resin cartridge. Following sample loading, the column is rinsed with 2.5 M nitric acid-0.05 M ferrous sulfamate-0.1 M ascorbic acid to remove fission products and matrix components, then split into individual cartridges for stripping of the analytes of interest. Under the conditions described here, thorium and neptunium are removed by the TEVA cartridge, uranium by the U/TEVA cartridge, plutonium and americium by the TRU cartridge, and strontium by the Sr resin cartridge. Note that because the fission product/matrix element fraction normally contains the bulk of the gamma activity associated with the sample, its removal reduces the activity level to the point that the column can be removed from a shielded hotcell and the stripping of analytes carried out in a hood or radiobench.

Figure 11 summarizes the elution sequence employed with each of the cartridges. Although this figure indicates that $^{90}$Sr can be recovered and counted after column rinses with a nitric-oxalic acid mixture (to remove any residual tetravalent plutonium, neptunium, cerium, and ruthenium that may have passed through the other cartridges) and with 8 M nitric acid (to remove barium), the high levels of $^{137}$Cs present in many nuclear waste solutions frequently necessitate additional removal of $^{137}$Cs prior to $^{90}$Sr determination. This is accomplished by acidifying the $^{90}$Sr fraction to 4-8 M nitric acid and re-loading it onto the same (well rinsed and preconditioned) Sr resin column. Following column rinsing, the strontium is stripped as before. Since a single pass through the Sr resin column can be expected to yield a decontamination factor (DF) for $^{137}$Cs of $\sim 10^5$ (11), two passes should yield a DF approaching $10^{10}$.

*Analyte recoveries on TEVA resin and on multi-stage columns.* To evaluate actinide recoveries on the TEVA resin and the quality of the Np/Pu and Np/Th separations obtained, aliquots of a simulated waste solution were spiked with $^{237}$Np ($1 \times 10^5$ dpm), plutonium ($5 \times 10^7$ dpm), and thorium (5 μg), then subjected to the procedure summarized in Figure 8. Neptunium recovery averaged 96 ± 5% (4 trials), while the removal of both thorium and plutonium exceeded 99.9%. Essentially the same results (94% recovery) were obtained for an actual caustic waste solution which had been similarly spiked with $^{237}$Np.

Table 2 summarizes the results of actinide and radiostrontium recovery trials for the multi-stage single column arrangement using as the sample either a waste simulant or an actual high-level waste solution. As can be seen, there is no significant difference in the recoveries observed for the two samples. In both cases, the recoveries of all of the test elements are high, typically exceeding 95%, and reasonably consistent.

## Conclusions

An extraction chromatographic resin comprised of Aliquat™•336 supported on an inert polymeric substrate ("TEVA resin") provides a simple and effective method for the separation and preconcentration of tetravalent actinides from aqueous solution. Tetravalent plutonium and neptunium are efficiently sorbed from a wide range of nitric and hydrochloric acid concentrations. Similarly, thorium (IV) is strongly sorbed from nitric acid solution. Under the same conditions, many commonly encountered cations are essentially unretained by the resin, making the material well-suited to the isolation of tetravalent actinides from a variety of sample types.

The use of TEVA resin in actinide separations provides several important advantages over conventional anion exchange methods for these separations. First, the separation of plutonium and neptunium can be effected in comparatively dilute (i.e., 2-3 M) nitric acid, making control of the oxidation state of plutonium simple and reducing acid waste generation. In addition, thorium elution is not subject to the tailing sometimes observed in conventional anion resin procedures. Finally, the elution of uranium requires less nitric acid, again reducing the volume of waste acid generated.

When used in conjunction with the U/TEVA and TRU extraction chromatographic resins, TEVA resin provides a reliable and facile means for the separation of americium, thorium, neptunium, plutonium, and uranium, both from one another and a variety of matrix components . As applied to the analysis of nuclear waste solutions, this three-column approach possesses a number of favorable features, among them excellent actinide recoveries, improved separation efficiency (vs. single-column methods), flexibility, and speed. Through the use of small particle size resins and a vacuum system, separations can be performed very rapidly, up to a factor of five times faster than with gravity flow column methods. The use of these same resins in a multi-cartridge single column configuration provides additional benefits, including a further reduction in separation time and waste generation, improved sample throughput, and the ability to isolate radiostrontium from the sample for subsequent determination. Although we have limited our description of the application of these separation schemes to the analysis of nuclear waste solutions, they are obviously applicable to biological, geological, and environmental samples as well, after appropriate sample pretreatment. Their application is, in fact, limited only by the need to convert the sample to a form suitable for introduction to the columns.

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Table 1. Characteristics of the TEVA Extraction Chromatographic Material and Packed Columns

| | |
|---|---|
| Bulk Material | |
| Stationary Phase | Undiluted Aliquat™•336 |
| Support | Amberchrom ™ CG-71 |
| Particle diameter | 20-50 or 50-100 micron |
| Extractant loading | 40% (w/w) |
| Density of Extractant-Loaded Beads | 1.09 g/mL [a] |
| Packed Columns | |
| $V_s$, mL./mL of bed | 0.158 |
| Bed density (g/mL.) | 0.35 |
| $V_m$, mL/mL of bed (also FCV) | 0.68 |
| $V_s / V_m$ | 0.233 |
| Capacity | |
| calculated, mmol $Cl^-$ / mL of bed | 0.268 [b] |
| experimental, mmol $Cl^-$ / mL of bed | 0.223 |

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[a] Picnometric density and flotation density values were 1.064 and 1.11 g/mL, respectively, using the 50-100 μm particle size resin. The calculated density is 1.094 g/mL, assuming 100% pore filling and no swelling.

[b] Assumes that the Aliquat™•336 is comprised of a 2:1 mixture of the trioctyl and tridecyl methyl ammonium chlorides and has an overall purity of 85%. The lower measured capacity suggests either a lower reagent purity or inaccessability of some fraction of the sorbed extractant.

Table 2. Recovery of Actinides and Radiostrontium from Waste Solutions Using the Multi-stage Single Column Procedure

| Test Element[a] | Recovery (%)[b] | |
|---|---|---|
| | Simulated Waste | HLLW |
| Np | 97±5 | 100±6 |
| Pu | 97±5 | 106±6 |
| U | 101±4 | 98±4 |
| Th | 106±5 | 104±6 |
| Am | 96±6 | 94±6 |
| Sr | 103±7 | 97±12 |

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[a] These trials employed 2.5 E+4 dpm $^{90}$Sr, 4.0 E+4 dpm $^{241}$Am, 2.0 E+7 dpm $^{239}$Pu, and 8 E+5 $^{237}$Np, along with 4 µg uranium, 50 µg thorium, and 5 and 50 µg of inactive strontium and europium, respectively.

[b] Mean ± 1 standard deviation

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# Figure Captions

Figure 1. Nitric acid dependencies of k' for selected elements with the TEVA, TRU, and U/TEVA extraction chromatographic resins (T = 23-25 °C; 50-100 µm particle size resins).

Figure 2. Hydrochloric acid dependencies of k' for selected elements with the TEVA, TRU, and U/TEVA extraction chromatographic resins (T = 23-25 °C; 50-100 µm particle size resins).

Figure 3. Kinetics of uptake of Th(IV) (TEVA resin), Am(III) (TRU resin), and U(VI) (U/TEVA resin) from 2 M $HNO_3$ at 24 °C and 50 °C (mass of resin = 10 ± 1 mg; solution volume = 1.00 mL; stirring speed = 200 rpm; 50-100 µm particle size resin).

Figure 4a. Separation of U(VI), Th(IV), and Np(IV) / Pu(IV) on the TEVA resin ($V_{column}$ = 0.59 mL; bed height = 10.1 cm; T = 23 °C; flow rate = ≤ 2 mL $min^{-1}cm^{-2}$; 50-100 µm particle size resin).

4b. Separation of Pu(IV) and Np(IV) on TEVA resin (conditions as per panel a).

Figure 5. Separation of light lanthanides (represented by $^{152}Eu$) from Am(III) using TEVA resin (conditions as per Fig. 4).

Figure 6. Effect of matrix constituents on neptunium retention on TEVA resin from 5 M nitric acid (mass of resin = 3±0.5 mg; solution volume = 1.00 mL; T = 23-25 °C; 50-100 µm particle size resin).

Figure 7a. Effect of oxalic, phosphoric and sulfuric acids concentration on $k'_{Np(IV)}$ on TEVA resin at 1.9 M $HNO_3$ (mass of resin = 4 ± 1 mg; solution volume = 1.00 mL; T = 23-25 °C, 50-100 µm particle size resin).

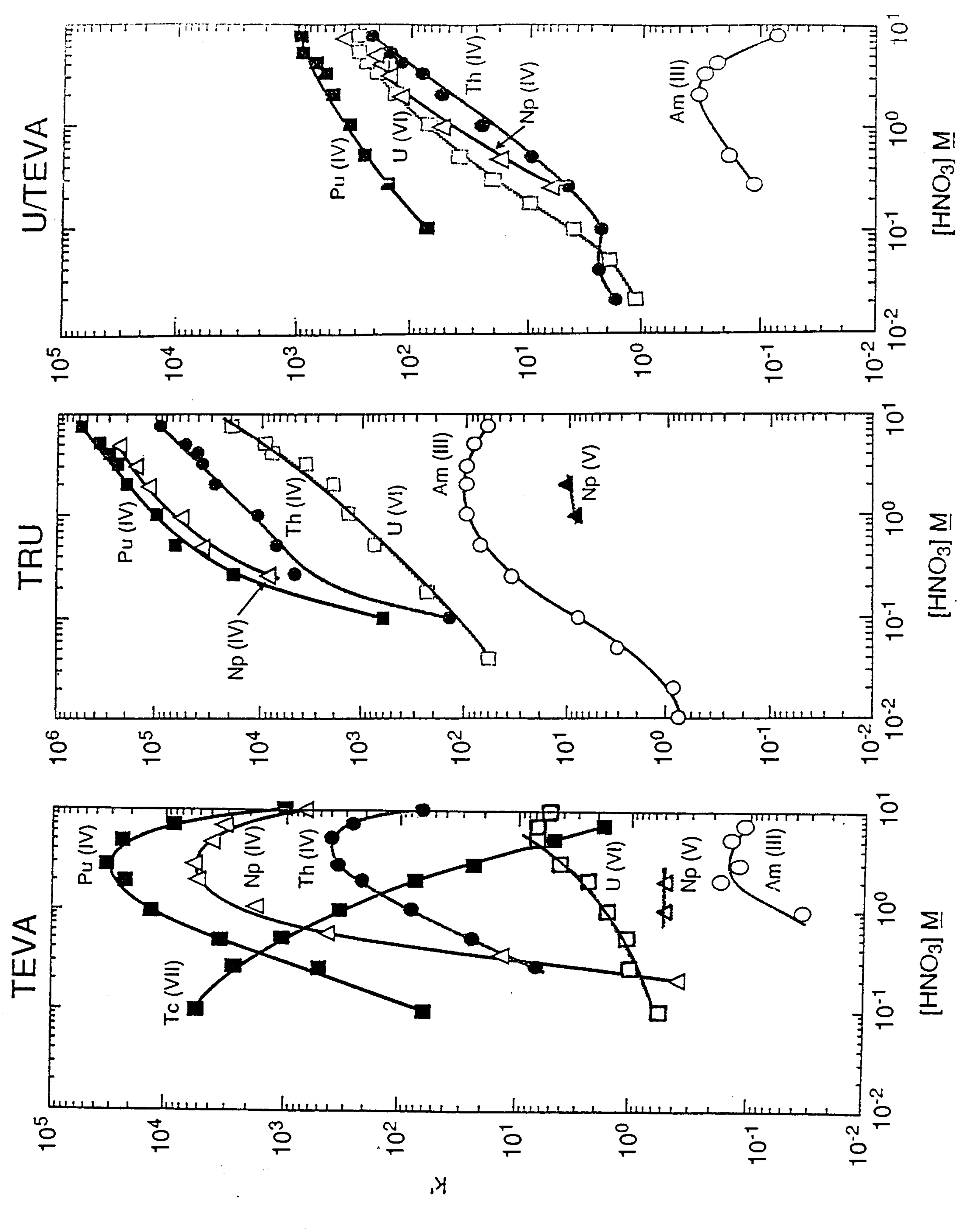
7b. Effect of oxalic acid concentration on $k'_{Np(IV)}$ on TEVA resin at various nitric acid concentrations (conditions as per panel a).

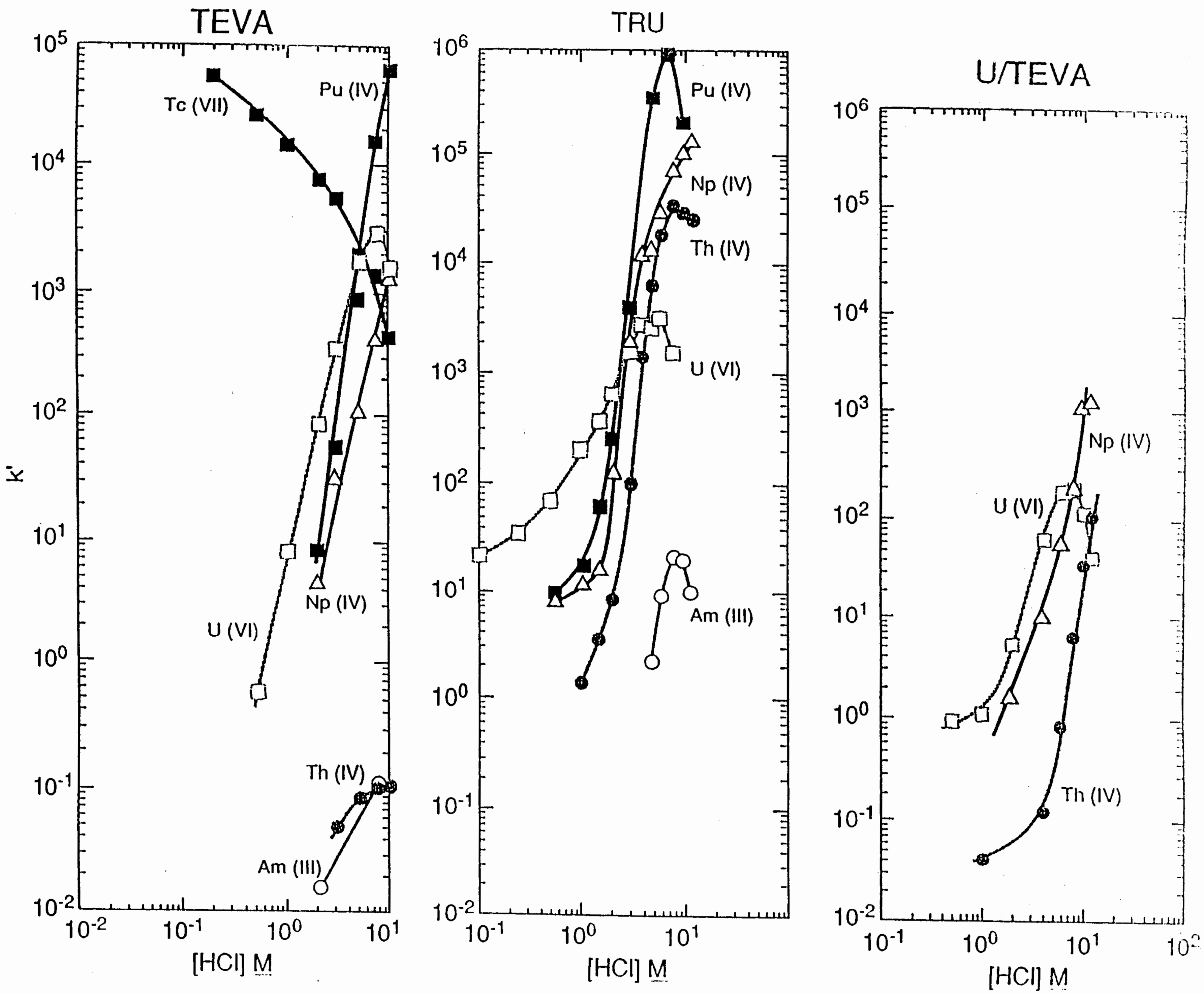
Figure 8. Tandem column scheme for the separation of actinides.

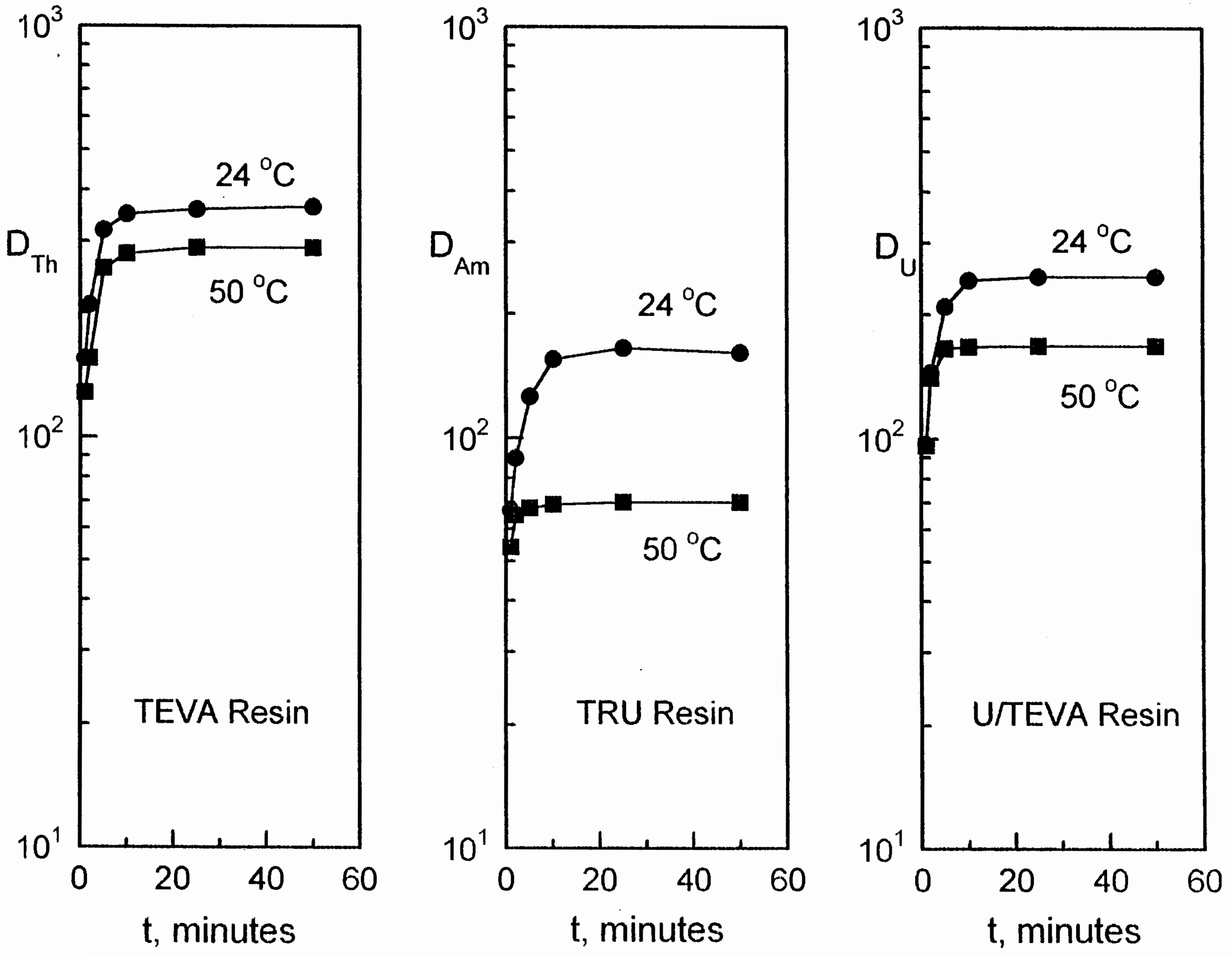
Figure 9. Alternative tandem column scheme for the separation of actinides.

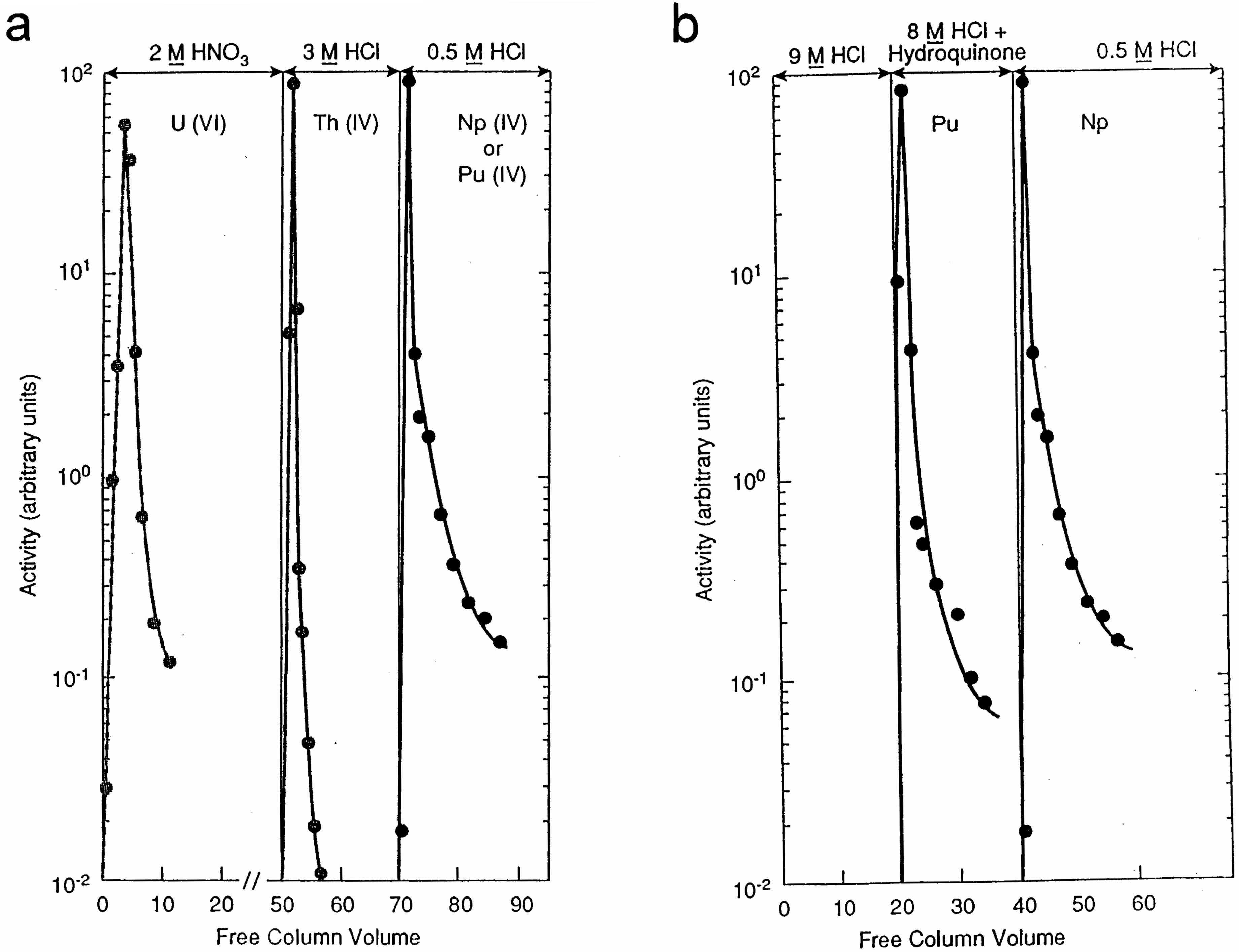
Figure 10. Multi-stage single column method for the isolation of actinides and radiostrontium - column loading and initial rinse step.

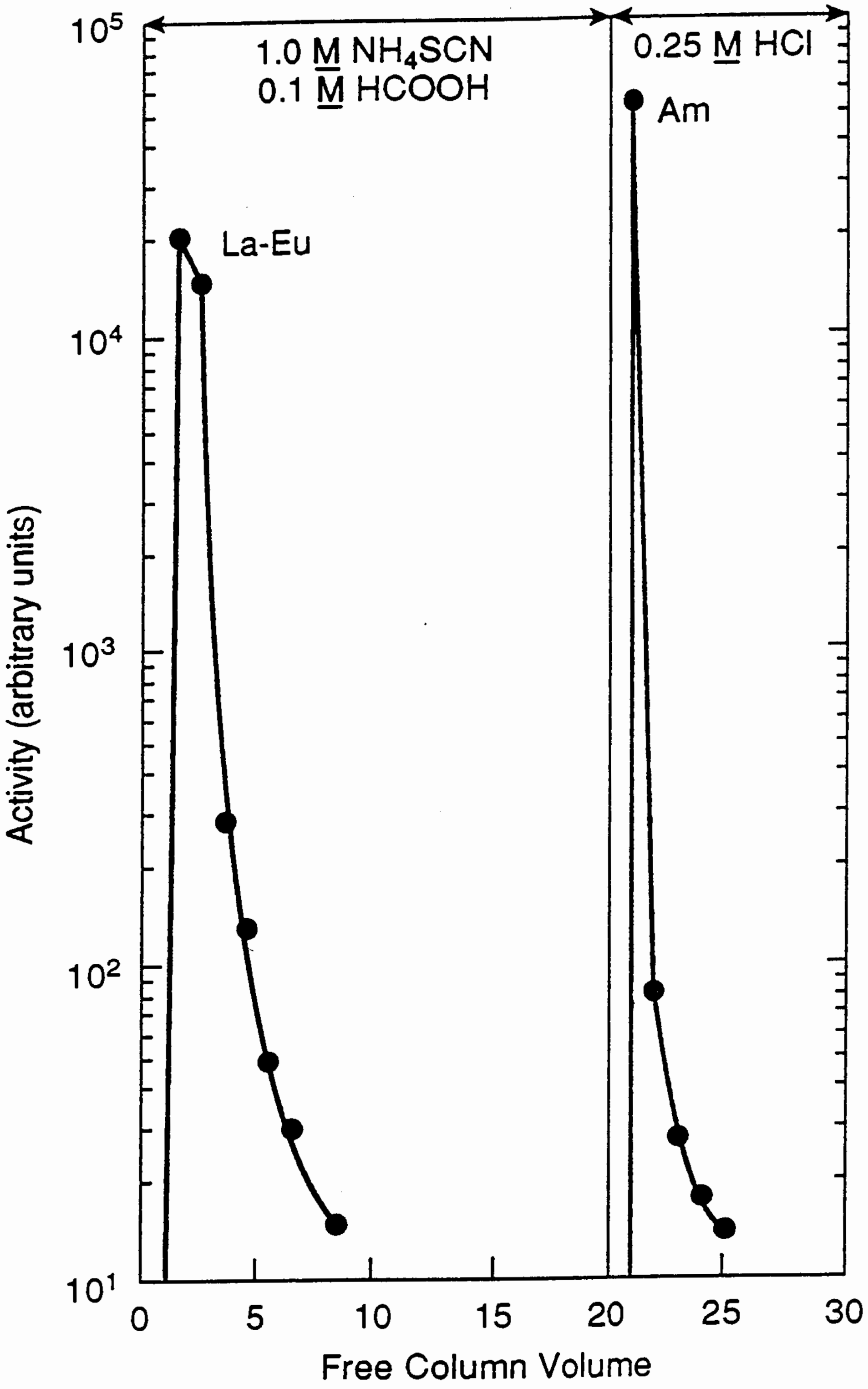
Figure 11. Multi-stage single column method for the isolation of actinides and radiostrontium - cartridge rinses and actinide elution.

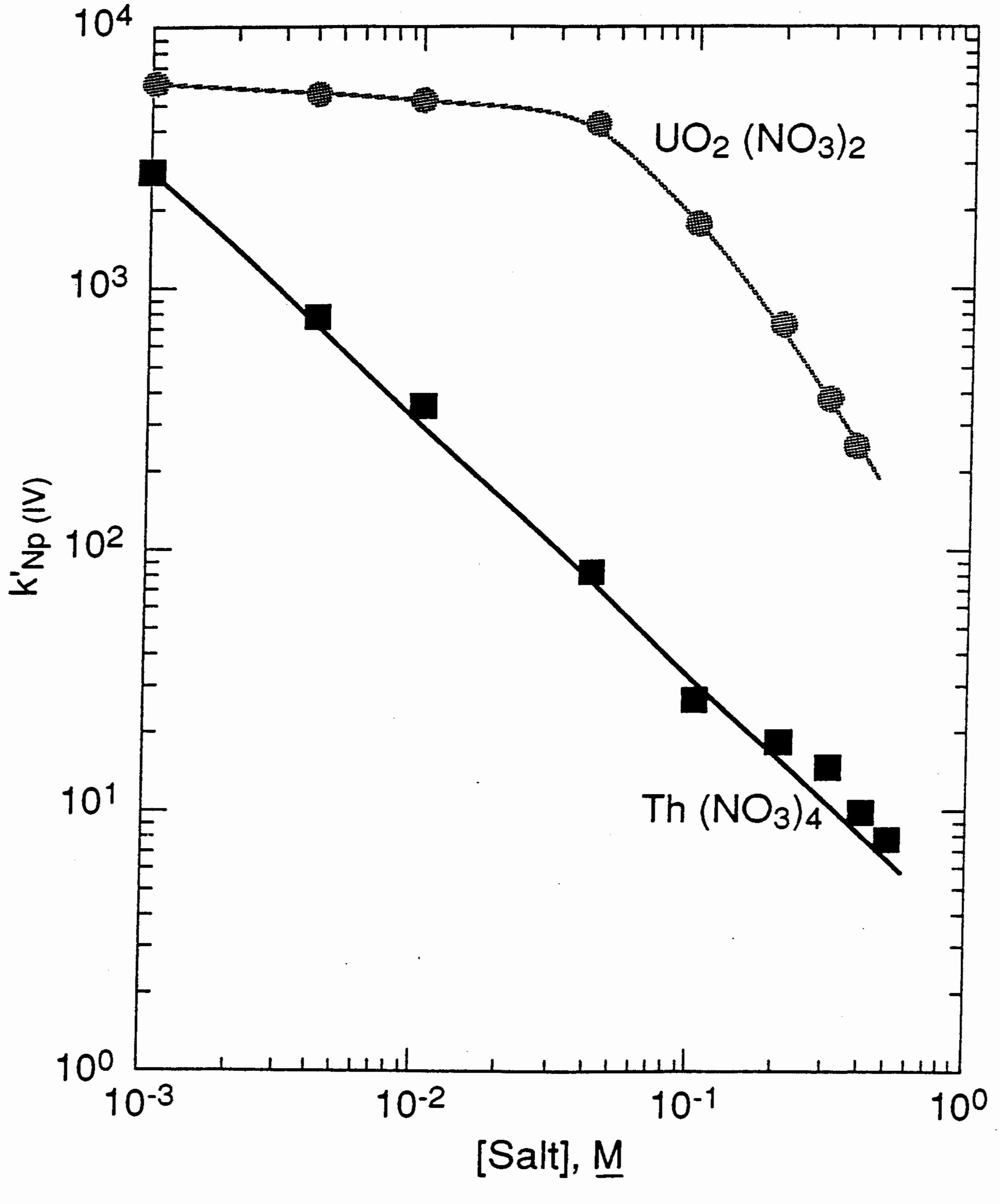

TEVA
TRU
U/TEVA
k'
[HNO3] M
[HNO3] M
[HNO3] M
$10^{5}$
$10^{4}$
$10^{3}$
$10^{2}$
$10^{1}$
$10^{0}$
$10^{-1}$
$10^{-2}$
$10^{6}$
$10^{-2}$
$10^{-1}$
$10^{0}$
$10^{1}$
Tc (VII)
Pu (IV)
Np (IV)
Th (IV)
U (VI)
Np (V)
Am (III)
Pu (IV)
Np (IV)
Th (IV)
U (VI)
Am (III)
Np (V)
Pu (IV)
U (VI)
Np (IV)
Th (IV)
Am (III)


TEVA
TRU
U/TEVA
k'
10^5
10^4
10^3
10^2
10^1
10^0
10^-1
10^-2
10^6
10^-2
10^-1
10^0
10^1
10^2
[HCl] M
Tc (VII)
Pu (IV)
Np (IV)
U (VI)
Th (IV)
Am (III)

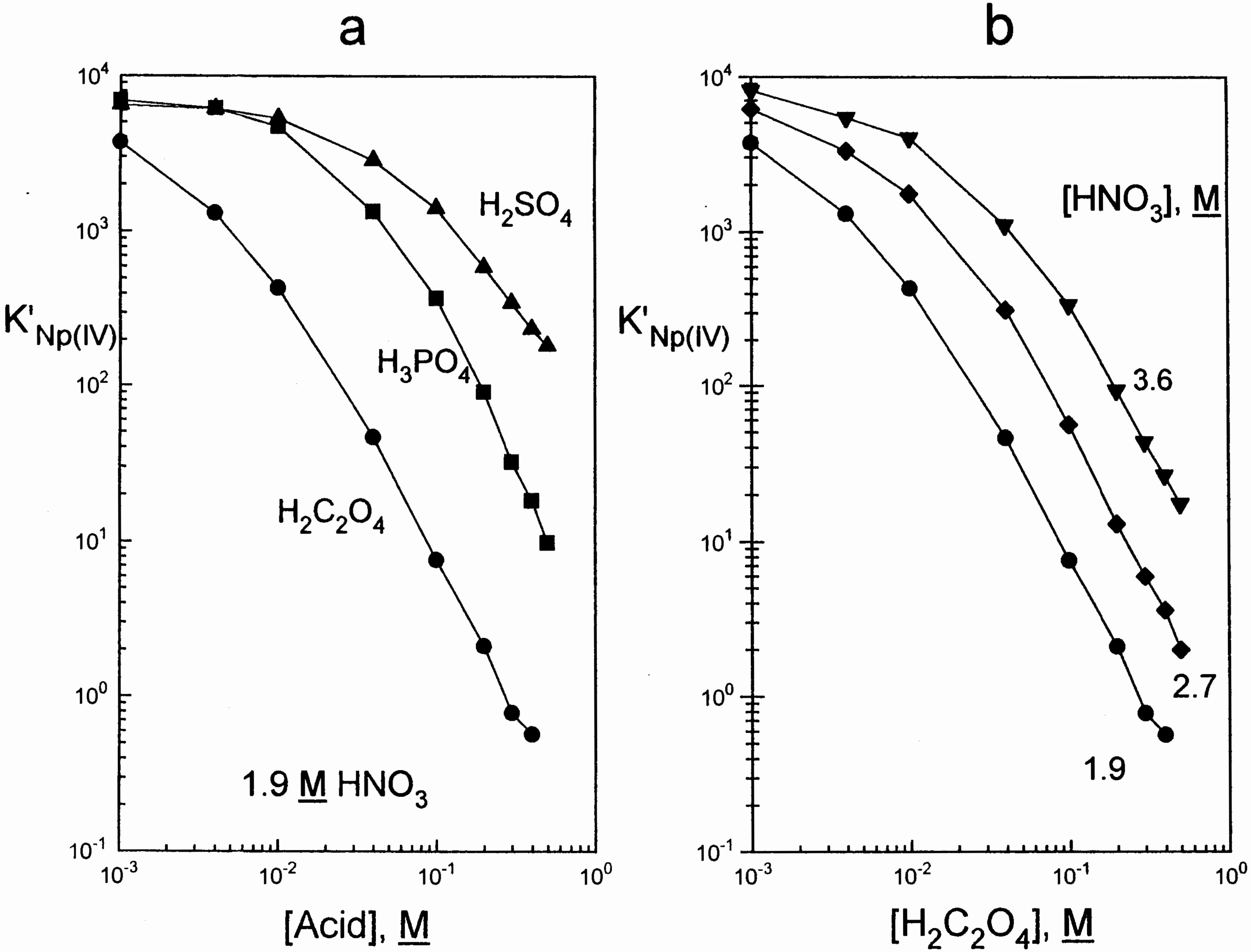

$10^3$
$D_{Th}$
$10^2$
$10^1$
24 °C
50 °C
TEVA Resin
0
20
40
60
t, minutes
$10^3$
$D_{Am}$
$10^2$
$10^1$
24 °C
50 °C
TRU Resin
0
20
40
60
t, minutes
$10^3$
$D_U$
$10^2$
$10^1$
24 °C
50 °C
U/TEVA Resin
0
20
40
60
t, minutes

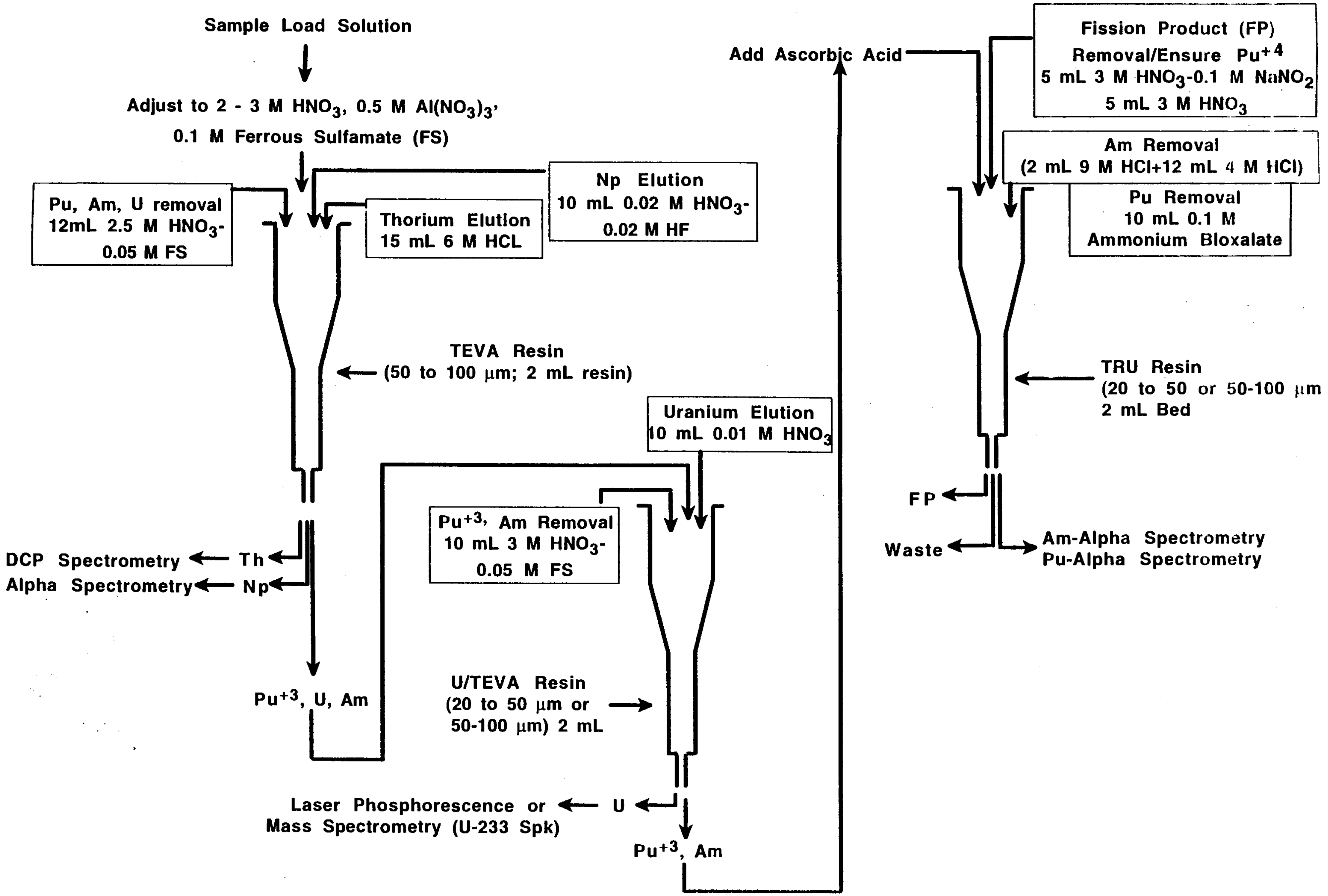

a
2 M HNO$_3$
3 M HCl
0.5 M HCl
U (VI)
Th (IV)
Np (IV) or Pu (IV)
Activity (arbitrary units)
$10^2$
$10^1$
$10^0$
$10^{-1}$
$10^{-2}$
0
10
20
//
50
60
70
80
90
Free Column Volume
b
9 M HCl
8 M HCl + Hydroquinone
0.5 M HCl
Pu
Np
Activity (arbitrary units)
$10^2$
$10^1$
$10^0$
$10^{-1}$
$10^{-2}$
0
10
20
30
40
50
60
Free Column Volume

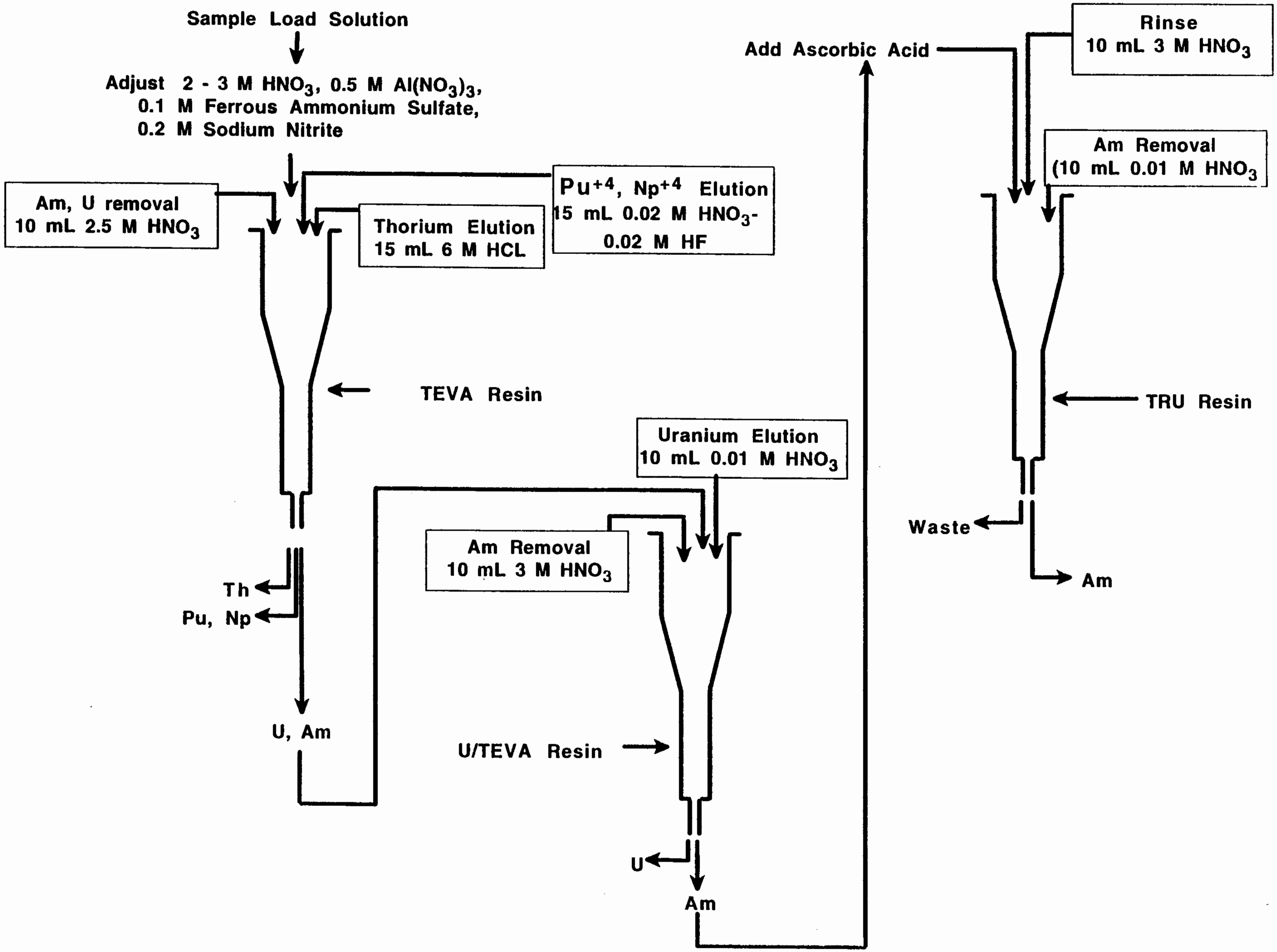

1.0 M NH$_4$SCN
0.1 M HCOOH
0.25 M HCl
Am
La-Eu
Activity (arbitrary units)
10$^5$
10$^4$
10$^3$
10$^2$
10$^1$
0
5
10
15
20
25
30
Free Column Volume

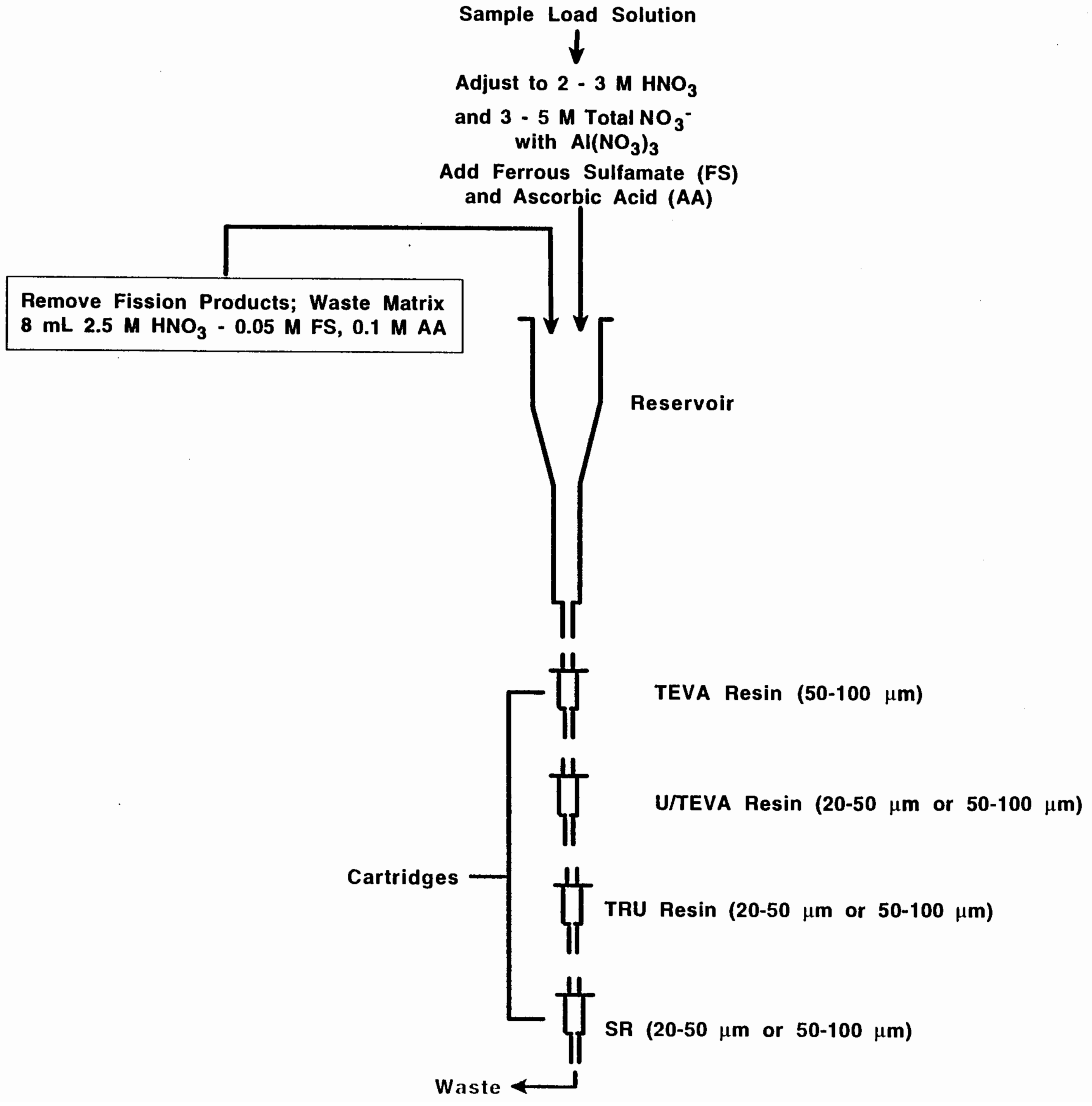


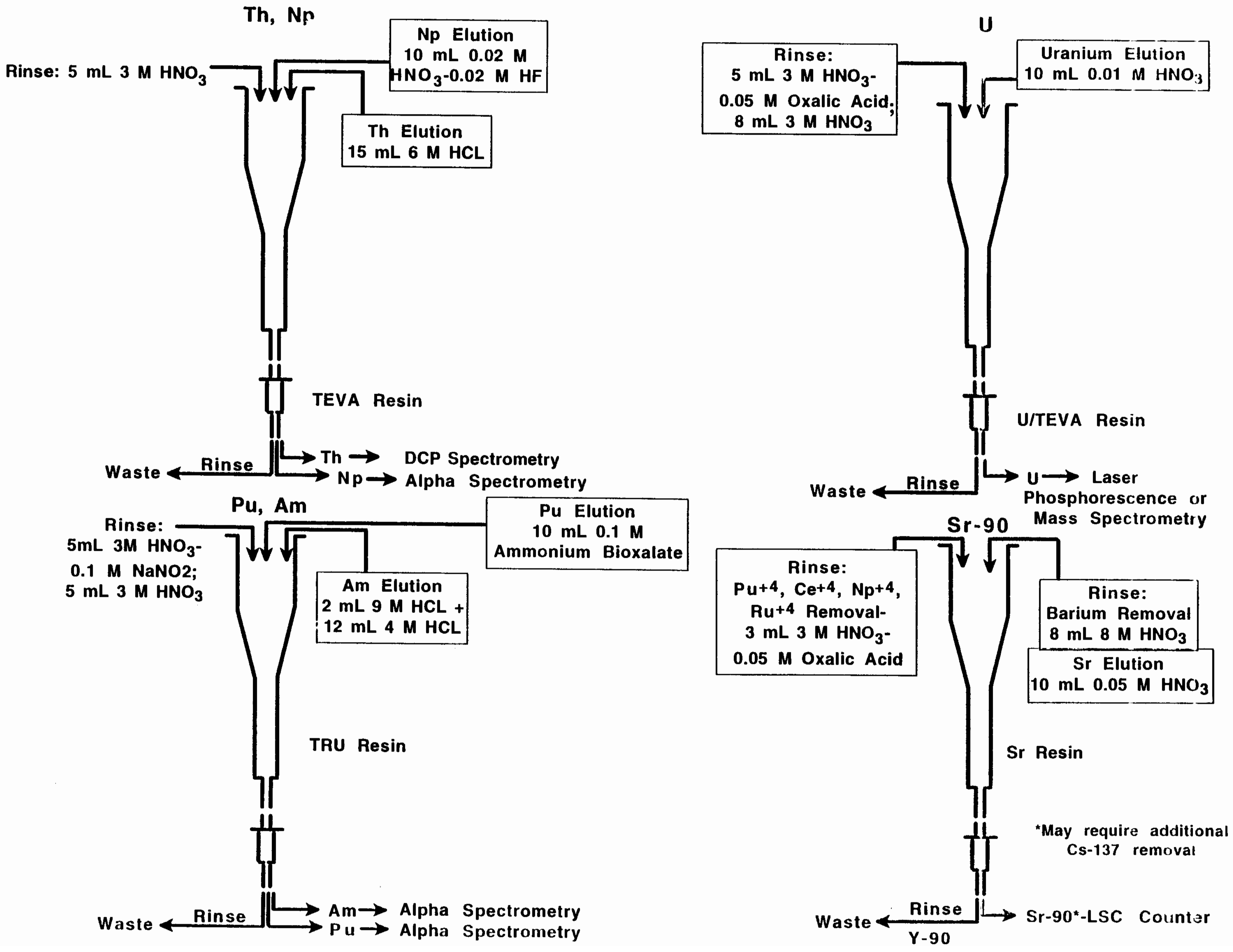
$10^4$
$10^3$
$10^2$
$10^1$
$10^0$
$k'_{Np}$ (IV)
$UO_2(NO_3)_2$
$Th(NO_3)_4$
$10^{-3}$
$10^{-2}$
$10^{-1}$
$10^0$
[Salt], M


a
b
K'$_{Np(IV)}$
$10^{-1}$
$10^{0}$
$10^{1}$
$10^{2}$
$10^{3}$
$10^{4}$
$10^{-3}$
$10^{-2}$
$10^{-1}$
$10^{0}$
$H_2SO_4$
$H_3PO_4$
$H_2C_2O_4$
1.9 M $HNO_3$
[Acid], M
$[HNO_3]$, M
3.6
2.7
1.9
$[H_2C_2O_4]$, M


Sample Load Solution
Adjust to 2 - 3 M HNO$_3$, 0.5 M Al(NO$_3$)$_3$,
0.1 M Ferrous Sulfamate (FS)
Pu, Am, U removal
12mL 2.5 M HNO$_3$-
0.05 M FS
Thorium Elution
15 mL 6 M HCL
Np Elution
10 mL 0.02 M HNO$_3$-
0.02 M HF
TEVA Resin
(50 to 100 µm; 2 mL resin)
DCP Spectrometry
Th
Alpha Spectrometry
Np
Pu$^{+3}$, U, Am
Uranium Elution
10 mL 0.01 M HNO$_3$
Pu$^{+3}$, Am Removal
10 mL 3 M HNO$_3$-
0.05 M FS
U/TEVA Resin
(20 to 50 µm or
50-100 µm) 2 mL
Laser Phosphorescence or
Mass Spectrometry (U-233 Spk)
U
Pu$^{+3}$, Am
Add Ascorbic Acid
Fission Product (FP)
Removal/Ensure Pu$^{+4}$
5 mL 3 M HNO$_3$-0.1 M NaNO$_2$
5 mL 3 M HNO$_3$
Am Removal
(2 mL 9 M HCl+12 mL 4 M HCl)
Pu Removal
10 mL 0.1 M
Ammonium Bloxalate
TRU Resin
(20 to 50 or 50-100 µm
2 mL Bed
FP
Waste
Am-Alpha Spectrometry
Pu-Alpha Spectrometry


Sample Load Solution
Adjust 2 - 3 M $HNO_3$, 0.5 M $Al(NO_3)_3$,
0.1 M Ferrous Ammonium Sulfate,
0.2 M Sodium Nitrite
Am, U removal
10 mL 2.5 M $HNO_3$
Thorium Elution
15 mL 6 M HCL
$Pu^{+4}$, $Np^{+4}$ Elution
15 mL 0.02 M $HNO_3$-
0.02 M HF
TEVA Resin
Th
Pu, Np
U, Am
Uranium Elution
10 mL 0.01 M $HNO_3$
Am Removal
10 mL 3 M $HNO_3$
U/TEVA Resin
U
Am
Add Ascorbic Acid
Rinse
10 mL 3 M $HNO_3$
Am Removal
(10 mL 0.01 M $HNO_3$
TRU Resin
Waste
Am


Sample Load Solution
Adjust to 2 - 3 M $HNO_3$
and 3 - 5 M Total $NO_3^-$
with $Al(NO_3)_3$
Add Ferrous Sulfamate (FS)
and Ascorbic Acid (AA)
Remove Fission Products; Waste Matrix
8 mL 2.5 M $HNO_3$ - 0.05 M FS, 0.1 M AA
Reservoir
TEVA Resin (50-100 μm)
U/TEVA Resin (20-50 μm or 50-100 μm)
TRU Resin (20-50 μm or 50-100 μm)
SR (20-50 μm or 50-100 μm)
Cartridges
Waste


Th, Np
Rinse: 5 mL 3 M HNO$_3$
Np Elution
10 mL 0.02 M
HNO$_3$-0.02 M HF
Th Elution
15 mL 6 M HCL
TEVA Resin
Waste
Rinse
Th → DCP Spectrometry
Np → Alpha Spectrometry
Pu, Am
Rinse:
5mL 3M HNO$_3$-
0.1 M NaNO2;
5 mL 3 M HNO$_3$
Pu Elution
10 mL 0.1 M
Ammonium Bioxalate
Am Elution
2 mL 9 M HCL +
12 mL 4 M HCL
TRU Resin
Waste
Rinse
Am → Alpha Spectrometry
Pu → Alpha Spectrometry
U
Rinse:
5 mL 3 M HNO$_3$-
0.05 M Oxalic Acid;
8 mL 3 M HNO$_3$
Uranium Elution
10 mL 0.01 M HNO$_3$
U/TEVA Resin
Waste
Rinse
U → Laser Phosphorescence or Mass Spectrometry
Sr-90
Rinse:
Pu+4, Ce+4, Np+4,
Ru+4 Removal-
3 mL 3 M HNO$_3$-
0.05 M Oxalic Acid
Rinse:
Barium Removal
8 mL 8 M HNO$_3$
Sr Elution
10 mL 0.05 M HNO$_3$
Sr Resin
*May require additional Cs-137 removal
Waste
Rinse
Y-90
Sr-90*-LSC Counter