NOVEL EXTRACTION CHROMATOGRAPHIC RESINS BASED ON TETRAALKYLDIGLYCOLAMIDES: CHARACTERIZATION AND POTENTIAL APPLICATIONS

E. P. Horwitz*, D. R. McAlister, A. H. Bond, and R. E. Barrans, Jr.

PG Research Foundation, Inc., 8205 S. Cass Ave., Suite 106, Darien, IL 60561

ABSTRACT

Two new extraction chromatographic resins containing the diglycolamide class of molecules have been prepared, characterized and potential applications identified. The new resins consist of 40 weight percent *N,N,N'N'* tetraoctyldiglycolamide (TODGA) and *N,N,N'N'* tetrakis-2-ethylhexyldiglycolamide (TEHDGA) sorbed onto 50-100 μm particle size Amberchrom® CG-71. The new resins have capacities for Eu of approximately 0.086 mmol/mL of bed and are quite stable to extractant leaching. The resins were characterized by measuring the batch uptake of actinides, lanthanides and yttrium, alkaline earths and thirteen selected transition and post-transition elements from HNO_3 and HCl. Based on the uptake data, a number of very efficient separations were achieved using 0.5 to 2mL bed volume columns and room temperature operation.

Key words: Diglycolamide, Extraction Chromatography, Actinide and Lanthanide Selectivities and Separations, Alkaline Earth Separations

INTRODUCTION

The extraction of trivalent actinides, particularly Am, from acidic nitrate media has been the focus of many studies during the last 15 to 20 years. These studies have been motivated by the need to develop processes for the treatment of high-level radioactive waste (HLW) for disposal. A summary of solvent extraction processes developed up to 1999-2000 for the treatment of HLW is described in detail in (1) and references therein.

---

* author for correspondence

Recently, a number of studies by Sasaki et al, (2-6) have described a class of extractants, based on tetraalkyldiglycolamides, that show unusually effective extraction of trivalent actinides and lanthanides from nitric acid. The tetra-n-octyl derivative (TODGA) appears to have the most favorable combination of properties (7) and has been the focus of further study (8-10).

Recently, two studies have appeared that utilize TODGA as the stationary phase in extraction chromatographic (EXC) systems (11, 12). These references are directed at the recovery of actinides and lanthanides from simulated low-level waste (LLW) and simulated HLW, respectively. We also reported in 2004 on two new EXC resins containing diglycolamides that confirmed the high uptake of Am and lanthanides from HNO_3 as well as HCl (13).

Our objective in this paper is to further evaluate the properties of EXC resins employing TODGA and the tetra-(2-ethyl-1-hexyl)-DGA derivative (TEHDGA) as the stationary phase. We selected for study not only Am, lanthanides, and yttrium, but also Th(IV), U(VI), Pu(IV), alkaline earths and selected transition and post transition element cations. Our purpose in this study was to primarily identify applications for these resins other than in nuclear waste treatment.

EXPERIMENTAL

Synthesis

The tetraalkyldiglycolamides were synthesized by reaction of diglycolyl chloride with dialkylamines and triethylamine in tetrahydrofuran (THF). All chemicals were purchased from Aldrich and used as received, except for the triethylamine that was freshly distilled from calcium hydride before use. All water was deionized using a commercial purification system. All glassware was oven-dried prior to use and the reaction was carried out at ~23°C. A positive pressure inert atmosphere of nitrogen was maintained with a latex balloon and the reaction mixture was stirred magnetically. Reactions on a larger scale required mechanical stirring because of the large amount of triethylammonium chloride precipitate that formed. A 500-mL single-neck round bottom flask was charged with anhydrous (THF) (120 mL) and diglycolyl chloride (15.0 mL, 126 mmol) and partially immersed in a water bath to dissipate the small amount of heat produced by the reaction. A dropping funnel was charged with dioctylamine, bis(2-ethyl-1-hexyl)amine or didecylamine (235–250 mmol) and triethylamine (37.2 mL, 265 mmol) in anhydrous THF (60 mL). The amine solution was added dropwise to the diglycolyl/THF mixture over a period of about 1.5 h. A white precipitate of triethylammonium chloride immediately formed upon combining the solutions. After addition of the amine solution was complete, the dropping funnel was rinsed with an additional 10 mL THF, which was added to the reaction mixture. The mixture was stirred for an additional 1 h, after which 10 mL H_2O was added. The THF was subsequently removed by rotary evaporation, leaving a yellow residue.

To the yellow residue was added 100 mL of H_2O, creating a viscous orange upper phase and a colorless, cloudy lower phase. The phases were disengaged in a separatory funnel and the lower phase was extracted twice with 10 mL petroleum ether. The petroleum ether washes were added to the initial upper phase and extracted with 15 mL H_2O, 2 x 15 mL 1 M HCl, 15 mL H_2O, and 6 x 20 mL 5% (w/w) $NaHCO_3$. The lower phases from the $NaHCO_3$ extractions appeared to be emulsions and were discarded. The upper phase was extracted with 10 mL 1 M HCl, 2 x 10 mL H_2O, and 25 mL saturated NaCl, dried over anhydrous $MgSO_4$, filtered gravitationally through fluted paper, and concentrated by rotary evaporation.

The purified final products were characterized by ^1H NMR and high performance liquid chromatography-mass spectrometry (LC-MS). The ^1H NMR characterization was performed on a Varian Inova 500 MHz NMR spectrometer. Chemical shift values are reported relative to an internal trimethylsilane (TMS) standard. LC-MS characterization was performed on an API 150EX LC-MS instrument with a single quadrupole mass spectrometer using a 100 mm x 4.6 mm 5 μm particle size Luna C18(2) column (Phenomenex) and a mobile phase of 80:20 (v:v) $CH_3CN : H_2O$.

N,N,N'N'-tetra-(1-octyl)-3-oxapentane-1,5-diamide, TODGA, F.W.: 580.98. This compound was obtained as an orange oil in 94% yield. ^{1}H NMR ($CDCl_3$, δ relative to TMS): 4.307 (s, 4 H); 3.291 (t, 4 H, J = 8.0 Hz); 3.177 (t, 4 H, J = 8.0 Hz); 1.519 (m, 8 H); 1.272 (br, 40 H); 0.885 (t, 6 H, J = 6.0 Hz); 0.876 (t, 6 H, J = 6.0 Hz). LC-MS: 3.6 min (2%, m/z 358.2, calcd. for $O[CH_2C(O)N(C_8H_{17})(H)]_2$, $C_{20}H_{40}N_2O_3 \cdot H^+$: 357.52); 4.1 min (1%, m/z 469.3, calcd. for $(H)(C_8H_{17})NC(O)CH_2OCH_2C(O)N(C_8H_{17})_2$, $C_{28}H_{56}N_2O_3 \cdot H^+$: 469.73); 4.5 min (96%, m/z 581.4, calcd for $O[CH_2C(O)N(C_8H_{17})_2]_2$, $C_{36}H_{72}N_2O_3 \cdot H^+$: 581.99).

N,N,N'N'-tetrakis-(2-ethyl-1-hexyl)-3-oxapentane-1,5-diamide, TEHDGA, F.W.: 580.93. This compound was obtained as a light yellow oil in 94% yield. ^{1}H NMR ($CDCl_3$, δ relative to TMS): 4.330 (s, 4 H); 3.370 (m, 4 H); 3.043 (d, 4 H, J = 7.0 Hz); 1.669 (m, 3 H); 1.560 (m, 3 H); 1.250 (m, 30 H); 0.880 (m, 24 H). LC-MS: 3.6 min (1%, m/z 413.1, calcd for $(C_2H_5)_2NC(O)CH_2OCH_2C(O)N(C_8H_{17})_2$, $C_{24}H_{48}N_2O_3 \cdot H^+$: 413.62; 4.5 min (91%, m/z 581.4, calcd. for $O[CH_2C(O)N(C_8H_{17})_2]_2$, $C_{36}H_{72}N_2O_3 \cdot H^+$: 581.99); 5.5 min (8%, m/z 920.4, calcd. for $(HO)C(O)CH_2OCH_2C(O)N(C_8H_{17})_2$ + $O[CH_2C(O)N(C_8H_{17})_2]_2$, $C_{56}H_{111}N_3O_6 \cdot H^+$: 923.43).

N,N,N'N'-tetra-(1-decyl)-3-oxapentane-1,5-diamide, TDDGA, F.W.: 693.19. This compound was obtained as a white waxy solid in 72% yield. ^{1}H NMR ($CDCl_3$, δ relative to TMS): 4.300 (s, 4 H); 3.289 (t, 4 H, J = 7.7 Hz); 3.171 (t, 4 H, J = 7.7 Hz); 1.517 (m, 8 H); 1.260 (br, 56 H); 0.883 (t, 6 H, J = 7.0 Hz); 0.878 (t, 6 H, J = 7.0 Hz). LC-MS: 3.3 min (2%, m/z every 44 amu from 532.2 to 796.2); 4.6 min (2%, m/z 581.4, calcd. for $(C_2H_5)(C_{10}H_{21})NC(O)CH_2OCH_2C(O)N(C_{10}H_{21})_2$, $C_{36}H_{72}N_2O_3 \cdot H^+$: 581.93); 5.4 min (95%, m/z 693.5, calcd. for $O[CH_2C(O)N(C_{10}H_{21})_2]_2$, $C_{44}H_{88}N_2O_3 \cdot H^+$: 694.20).

Preparation of Extraction Chromatographic Materials

The extraction chromatographic materials containing *N,N,N'N'*-tetra-(1-octyl)-3-oxapentane-1,5-diamide (TODGA) or *N,N,N'N'*-tetrakis-(2-ethyl-1-hexyl)-3-oxapentane-

1,5-diamide (TEHDGA) were prepared using a general procedure described previously (14, 15). A portion of TODGA or TEHDGA (4.0 g) was dissolved in about 30 mL of CH_3OH and combined with a slurry of 50-100 μm Amberchrom®-CG71 (6.0 g) (Eichrom Technologies, Inc.) in about 20 mL of CH_3OH. The mixture was swirled to mix, and the methanol was removed by rotary evaporation at reduced pressure at 50 ^oC. After condensate ceased to collect and no further bubbling was observed from the free-flowing solid, the resin was rotated under full vacuum at 40-50 ^oC for another 30 min to remove residual CH_3OH. The resulting solid corresponds to 40% (w/w) loading of extractant on 50-100 μm Amberchrom-CG71 (40 weight percent loading assumes 100% purity of extractant). The resins are now commercially available from Eichrom Technologies, Inc. as DGA Resin, normal (TODGA) and DGA Resin, branched (TEHDGA).

Analytical Reagents

Nitric and hydrochloric acid solutions were prepared from Trace Metal Grade acids (Fisher Scientific) and deionized water obtained from a Milli-Q2 water purification system. The radionuclides ^{85}Sr, ^{90}Sr, ^{133}Ba, ^{139}Ce, ^{147}Pm, ^{152}Eu, ^{207}Bi, ^{226}Ra, ^{230}Th, ^{239}Pu and ^{241}Am were obtained from Isotope Product Laboratories. ^{225}Ac was provided by MedActinium, Inc. and was separated from ^{229}Th stocks at Oak Ridge National Laboratory. ^{212}Pb was milked from ^{228}Th adsorbed onto a column of TRU Resin (Eichrom Technologies, Inc.) with 4 M HNO_3. Residual ^{224}Ra was removed using Sr Resin (Eichrom Technologies, Inc.) to selectively retain the ^{212}Pb. The ^{212}Pb was stripped from the Sr Resin using 0.1 M ammonium oxalate, evaporated to dryness on a hotplate at ~300^oC (to destroy the ammonium oxalate) and dissolved in 0.5 M HNO_3. ^{90}Y was milked from ^{90}Sr adsorbed onto a column of Sr Resin using 4 M HNO_3. A secondary column of Sr Resin was used to scavenge any ^{90}Sr that may have channeled through the first Sr Resin column. The ^{90}Y was evaporated to dryness and dissolved in 0.5 M HNO_3 prior to use in batch uptake or column elution experiments. Metal ion solutions for ICP-AES experiments were prepared from 1000-10,000 ppm standard solutions in nitric acid (Al, Ba, Ca, Ce, Co, Cu, Dy, Er, Eu, Fe, Gd, Ho, La, Lu, Mg, Nd, Ni, Pr, Sm, Sr, Tb, Th, Tm, U, Y, Yb, Zn, Zr), hydrochloric acid (Cu, Ti, V) or water (Be, Cr, Nb) (Fisher Scientific).

Batch Uptake of Metal Ions

The uptake of metal ions by the DGA resins from acidic solutions was measured by contacting a known volume of solution (1.0 mL for radiotracer experiments and 5.0-7.5 mL for ICP-AES experiments) with a known weight of resin (10-20 mg for radiotracer experiments and 100-300 mg for ICP-AES experiments) in a borosilicate glass culture tube. All experiments were performed at 22(1)°C using 50-100 μm particle size resin. The exact ratio of resin to aqueous phase was varied to produce a measurable difference in the initial and final activities (concentrations) of metal ion in the aqueous phase and to ensure that the molar ratio of extractant to metal ion was at least 50:1. The mixing of resin and the aqueous phase was performed by intermittent agitation on a vortex mixer and by using a small magnetic stir bar rotated at a speed sufficient to keep the resin beads suspended in the aqueous phase. Following equilibration with the resin, the aqueous phase was filtered through a 0.45 μm PTFE syringe filter to remove any resin particles.

A model E5003 Packard Cobra Autogamma counter, was used to assay for ^{85}Sr, ^{133}Ba, ^{139}Ce, ^{152}Eu, ^{212}Pb, ^{225}Ac(^{221}Fr) and ^{241}Am. The radiotracers ^{90}Y, ^{147}Pm, ^{207}Bi, ^{226}Ra, ^{230}Th and ^{239}Pu were measured on a Packard TriCarb 2550 TR/AB liquid scintillation counter using Ultima Gold scintillation cocktail. Metal ion concentrations for all other elements were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Varian Liberty Series II sequential inductively coupled plasma atomic emission spectrometer using the parameters listed in Table 1. The uptake of the entire series of lanthanides (excluding Pm) and Y were determined from three stock solutions: 1) Eu, Er, Pr, Sm, Tm and Y; 2) Eu, Ce, Gd, Lu, Tb and Yb; 3) Eu, Dy, Ho, La and Nd, as outlined in (16). Europium was employed as a common standard in each lanthanide stock solution. The free column volume to peak maximum (k′) values for Eu determined using each stock solution agreed within 5%, except for the highest acid concentrations, where the aqueous phase was nearly completely depleted of metal ions following equilibration with the DGA resin and error between measurements was substantially higher. The k' for macroscopic quantities of Eu measured by ICP-AES also agreed within 5% of the k' value obtained using a ^{152}Eu tracer. However, k′ values obtained at tracer scale (radiometric) and using macroquantities of metal ions (ICP-AES) can differ by as much as ±20% due to the consumption of resin capacity when macroquantities of metal ion are present. All comparisons of the uptake of different metal ions were therefore made between k′ values obtained at the same scale, tracer or macro, when possible. Preliminary experiments showed that the uptake of ^{152}Eu approached equilibrium after 10 minutes. An equilibration time of one hour was used in all determinations of weight distribution ratios.

Weight distribution ratios (D_w) were calculated using the following equation:

$$D_w = [(A_o - A_s)/w]/(A_s/V) \qquad (1)$$

where A_o and A_s are the aqueous phase metal ion concentrations (parts per million) or activity (counts per minute) before and after equilibration, w is the weight of the resin in grams and V is the volume of aqueous phase in milliliters. Duplicate experiments showed that the reproducibility of the D_w measurements was generally within 10%, although the uncertainty was somewhat higher for the D_w values $>10^3$. The D_w values were converted to the number of free column volumes to peak maximum, k′ (the resin capacity factor), by first calculating the volume distribution ratio (D_v, a value calculated from equation 1 in which the weight of the resin, w, is replaced by the volume of extractant) using the following equation:

$$D_v = D_w \text{ x } d_{extr}/0.4 \qquad (2)$$

where d_{extr} is the density of the extractant and 0.4 is the extractant loading in grams of extractant per gram of resin. The D_v values were then converted to k′ by using the following equation:

$$k' = D_v \text{ x } (v_s/v_m) \qquad (3)$$

where v_s and v_m are the volumes of stationary phase (extractant) and mobile phase, respectively, for a slurry packed column of DGA Resin. The physical constants necessary to convert D_w to k′ for slurry packed columns of 50-100 μm particle size DGA Resin in 0.1 M HNO_3 are listed in Table 2. The bed density for dry packed columns is somewhat higher than for slurry packed columns, so k′ values for dry packed columns are ≈ 5% higher than corresponding values for slurry packed columns. By combining equations (2) and (3) and using the values reported in Table 2 for d_{extr} and v_s/v_m, one obtains:

$$k' = D_w \times 0.57 \qquad (4)$$

Thus, for each weight distribution ratio measured on DGA Resin, the corresponding k′ value can be obtained by multiplying the D_w value by 0.57.

Column Elution of Metal Ions

Column chromatographic experiments were performed with slurry-packed columns of the DGA resins. The resin was slurried by gently swirling or vortexing the resin in 0.1 M HNO_3. However, the DGA resins frequently floated on top of the HNO_3 solution and did not appear to wet readily. Since wetting of the EXC material is critical to optimal chromatographic performance, methods to better wet the DGA resins were explored. Placing the resin into a sealed container and equilibrating with 0.1 M HNO_3 over an extended period of time (2-3 h or even overnight) was found to effectively wet the resin. Sonication and occasional swirling of the resin/HNO_3 mixture and increasing the concentration to 1-2 M HNO_3 helped to speed the wetting of the resin. Additionally, the application of weak vacuum pressure helped to remove air bubbles and facilitate the wetting of the resin. Even after the above measures were taken, a small portion of the DGA resin did not appear to wet and floated on top of the nitric acid solution. This portion of the resin was not used to pack the chromatographic columns. The slurried, wetted resin was packed into polypropylene or glass chromatographic columns (BioRad) with 10 mm inner diameters. Medium porosity polyethylene frit material (Fisher Scientific) was used for the bottom and top bed supports.

The slurry-packed columns of DGA resin were then preconditioned with 5 bed volumes of the desired load solution free of metal ions, and solutions of metal ions were subsequently eluted through the column at a flow rate of 1-2 mL/min (1.3-2.5 mL/cm^2/min). Flow rates were either gravity or adjusted by over-pressure applied by syringe. Aliquots of the eluate were collected into tared polypropylene gamma counting tubes, 7 mL liquid scintillation vials or 15 mL polypropylene centrifuge tubes and analyzed for metal ions as described above.

Metal Ion Capacity

The capacity of the TODGA and TEHDGA resins were determined by loading a 0.5 mL slurry packed column of the resin with a solution of 0.0274 M Eu in 4.0 M HNO_3 spiked with ^{152}Eu. Loading was continued until the concentration of Eu in the effluent was the same as the concentration of Eu in the load. The column was then rinsed with 5 bed volumes of 4.0 M HNO_3, stripped with 0.1 M HCl and aliquots of the eluate collected into tared polypropylene gamma counting tubes. The resin capacity was determined from the ^{152}Eu activity depleted from the load fractions and from the ^{152}Eu activity recovered in the strip fractions. The two capacity determinations agreed within 5%.

Resin Leaching

The leaching of the TODGA and TEHDGA extractants from the extraction chromatographic materials was studied by passing large volumes of 6 M HNO_3, 0.1 M HNO_3 and 0.1 M HCl through 12 mL bed volume columns of the DGA resin (1.0 cm internal diameter, 15.3 cm bed height) at 25°C and 50°C to simulate typical load, rinse and strip conditions. The resin was slurry packed into a jacketed 30 mL column (Ace Glass) and medium porosity polyethylene frit material was used for the bottom and top bed supports. The temperature of the column was maintained using a circulating water/ethylene glycol bath. A peristaltic pump was used to achieve a flow rate of 11 mL/min (14 mL/cm^2/min) and aliquots of the eluate were collected into glass round bottom flasks. The eluate was extracted with 3 x 2 mL of CH_2Cl_2. The CH_2Cl_2 extracts were then washed with 5 mL of H_2O, and the H_2O washes later extracted with 2 x 2 mL of CH_2Cl_2. The combined CH_2Cl_2 extracts were then dried over anhydrous $MgSO_4$ and evaporated to dryness on a rotary evaporator. The leachate residue was submitted for LC-MS analysis as described in the synthesis section above. *N,N,N',N'*-tetra-(1-decyl)-3-oxapentane-1,5-diamide was used as an internal standard for the quantitation of DGA in the leachates by LC-MS.

RESULTS AND DISCUSSION

Kinetics of Uptake of Eu on TODGA

Figure 1 depicts the kinetics of uptake of tracer-level Eu(III) from 3 M HNO_3 at room temperature by TODGA resin. It can be seen that equilibrium is essentially reached within 10 minutes, which is consistent with kinetics data reported for a similar TODGA-EXC resin (11) and generally consistent with prior kinetic data reported for other EXC resins studied by Horwitz et al (14). (The variation in k' after 25 minutes is within experimental error.)

Nitric and Hydrochloric Acid Dependencies of Capacity Factor, k'

Comparison with TRU-EXC resin

Figures 2 and 3 compare the uptake, as measured by k', of selected actinides as a function of nitric and hydrochloric acid for TRU-, TODGA-, and TEHDGA-EXC resins. TRU Resin contains 40 weight percent of a solution of 0.75 M CMPO in undiluted TBP sorbed onto Amberchrom® GT-71. The data for the TRU Resin is from (15). The difference in the DGA and TRU Resins is striking. For TRU Resin, the order of uptake is typical of a neutral hard donor extractant containing a phosphoryl oxygen; that is, tetra- >

hexa- > tri-valent. In comparison to TRU Resin, the uptake of U(VI) is significantly suppressed and the uptake of Am(III) significantly enhanced relative to each other and to Th(IV) and Pu(IV) for both DGA resins. The k'_{Am} values for the DGA resins are orders of magnitude higher than those of TRU Resin above one molar acid concentrations. A comparison of the uptake of Am with that of Th and Pu is also noteworthy. With TRU Resin, the k' values for Th and Pu are orders of magnitude greater than the k' of Am, but in the case of the DGA resins, the k's of tri- and tetra-valent actinides above 0.5 M acid are much closer. This is especially the case at high nitric acid concentrations. In general, our data are consistent with data reported for similar EXC resins in (11,12) where valid comparisons can be made.

The differences between the TRU and DGA resins lay in the number of donor oxygens and the configuration of the extractant. As described in (17, 18), the carbamoylmethylphosphoryl group acts as a monodentate ligand with metal ions at the tracer-scale level. The DGA group has been shown to be tridentate in configuration (2-6), complexing trivalent metal ions through two carbonyl oxygen donors and an ether oxygen donor forming two stable five-membered chelate rings. Although the carbonyl oxygen is less electronegative than a phosphoryl oxygen, the coordination of DGA to a tri-positive actinide probably involves less liquid strain and/or rearrangement, which may compensate for the lower electron density of the donor groups in DGA. The higher extraction constants of the DGA class of extractants compared to the corresponding bifunctional malonamide extractants (7) is also noteworthy and supports the importance of the tridentate coordination of the DGA. Based on the data in Figures 2 and 3, the coordination of a tridentate DGA to uranyl ion appears significantly less favorable than coordination to a trivalent or tetravalent actinide.

An interesting feature of the data for DGA-EXC resins shown in Figure 2 is the lack of the so-called hyperstoichiometry (sixth power HNO_3 dependency) observed for trivalent f-element cations when extracted by TODGA in a liquid-liquid extraction system (19). Nitric and hydrochloric acid dependencies are closer to second and third power for the EXC system; however, comparisons between EXC and conventional liquid-liquid extraction frequently show such significant differences. This is not surprising when one takes into consideration that the thickness of an extractant sorbed onto a porous solid support having a surface area of 400-500 m^2/g (e.g. Amberchrom® CG-71m) containing 40 weight percent of an extractant with a density of 0.8-0.9 g/mL, is only about 1-2 x 10^{-3} µm. Furthermore, the stationary phase in EXC systems is frequently a neat extractant. Thus, the physical and chemical properties, such as aggregation and metal ion/extractant stoichiometry, in EXC systems may deviate from those of the corresponding liquid-liquid extraction systems.

The data in Figures 2 and 3 also show that the EXC resin using the sterically hindered TEHDGA extractant has lower uptake of actinides in both HNO_3 and HCl, except at the highest acid concentrations, where the differences are minimal. Uptake of cations by TODGA and TEHDGA are lower from HCl than from HNO_3, which is consistent with the behavior of neutral extractants, i.e., nitrato complexes are usually (but not always) more extractable than chloro complexes (15). A clear comparison of TODGA and TEHDGA for Am(III) in both HNO_3 and HCl is depicted in Figure 4.

In general, the TODGA resin gives higher uptakes and is more selective than TEHDGA, as will be shown below for other metal ion systems. The data in Figures 2-4 suggest the conditions for a number of novel and practical chromatographic separations of actinides. These separations will be shown and discussed in a later section of this manuscript.

Comparison of lanthanides, yttrium and americium

Figures 5 and 6 compare the HNO_3 and HCl dependencies of Ce, Eu and Y with americium for both TODGA and TEHDGA resins. The HNO_3 data are consistent with the results reported for TODGA in (6,11,12). As expected, the uptake of Am is similar to the lanthanides and close to the uptake of Eu. The data in Figures 5 and 6 again demonstrate that one obtains higher k's and higher selectivity with TODGA and higher k's and selectivity for both TODGA and TEHDGA from HNO_3 versus HCl.

Figure 7 shows k's obtained for the entire lanthanide series and yttrium by TODGA resin from 0.5 M and 0.05 M and by TEHDGA resins from 1.0 M. The data in Figure 7 for the TODGA resin approximately parallels the liquid-liquid extraction data for the TODGA-dodecane system reported in (6) where selectivity changes very little among the heavy lanthanides. However, the selectivity obtained with the TODGA resin for La through Gd from 0.05 M HNO_3 is noteworthy and actually slightly higher than the selectivity obtained for the same lanthanides using an extraction chromatographic material containing bis(2-ethyl-1-hexyl)phosphoric acid (HDEHP) (20). The trend in k's may be explained by a combination of electrostatic and steric effects. From atomic numbers 57 to 66 electrostatic effects appears to dominate whereas above $Z = 66$, the decreasing ionic radii of the lanthanide cation introduces a steric issue that levels the k' values.

Alkaline earths, strontium and yttrium

Figure 8 shows the HNO_3 and HCl dependencies for the entire series of alkaline earth cations, Be through Ra. Most of the alkaline earth cations show negligible uptake, especially from HCl, however, the retention of Ca and Sr from 0.5 M to 3 M HNO_3 is significant. Reference 8 reports similar behavior for the corresponding liquid-liquid extraction system. The trend in k' (Ca>Sr>Ba) may be explained by the fact that the cation with the smaller ionic radius is more readily complexed by the TODGA, as was observed with the lanthanides. The lower uptake of Be and Mg is likely a continuation of steric effects and the inability of the donor groups in DGA to dehydrate Be^{2+} and Mg^{2+}, which have much higher hydration energies than Ca^{2+}, Sr^{2+}, and Ba^{2+}. Although the uptake of Ca and Sr is not particularly strong relative to the lanthanides, the k' values are sufficiently high to enable one to achieve some novel separations. An example of such a separation will be shown in a later section.

The separation of Y from Sr is a frequently performed separation because of the production of ^{90}Y from ^{90}Sr for application in nuclear medicine. Figure 9 depicts the conditions in which TODGA resin could be utilized to carry out this separation.

Selected transition and post transition elements

Figure 10 shows the nitric and hydrochloric acid dependencies of selected transition and post transition elements with TODGA resin. The elements selected for this study are those that most likely could be present in matrices of environmental or nuclear waste samples. The behavior of Al and Fe in nitric acid is particularly noteworthy because of their frequent presence in soil samples. The low uptake of both Al and Fe by TODGA can be exploited in a number of actinide separations. An example will be described below.

Column Studies

Column capacity

The calculated capacity of a slurry-packed column (packing density 0.38g/mL) containing 40 weight percent of 94% pure TODGA or TEHDGA is 0.246 mmol of extractant per mL of bed. The measured capacity for a trivalent actinide, using Eu(III) as a stand-in for Am(III), was 0.077 and 0.095 mmol of Eu/mL of bed for TODGA and TEHDGA, respectively. These Eu capacities represent approximately a 3 to 1 stoichiometry. Solvent loading studies reported by Tachimori et al (9) using Nd in 3 M HNO_3 and the liquid-liquid extraction system TODGA-dodecane in the presence of a monoamide, *N, N*-dihexyloctanamide (to prevent third phase formation) also gave a 3 : 1 stoichiometry.

Actinide separations

Figure 11 shows an efficient separation of U, Pu and Am in the presence of 0.45 M Fe(III) using a 2.0 mL TODGA column. The conditions used for the separation were based on the uptake data in Figures 2, 3 and 10. Although the recovery of uranium was 82% in the presence of 250 mg of Fe(III), the recovery of uranium improved to over 90% when the Fe(III) concentration was $\leq$ 100 mg. The difference in the k's of Am and Pu at low acidity was exploited in performing their separation. Plutonium can also be efficiently eluted with dilute HCl or HNO_3 – HF mixtures. Another, perhaps more efficient way to use the TODGA column, is to precede the TODGA column with a TEVA resin column. The TEVA resin, which contains a quaternary amine, selectively removes all tetravalent actinides and rejects Am and U (14). TEVA resin is also insensitive to macroconcentrations of Fe(II) and Fe(III). Individual columns can be coupled together on loading and rinsing, then separated for stripping. In this manner, the TODGA is used to remove U and Am from the matrix constituents and then to separate U and Am from each other by selective elution as shown in Figure 11.

Another potential application of the DGA resins is in the recovery of ^{241}Am from large volumes of concentrated HNO_3 and HCl wastes. For example, a frequently used procedure to purify Pu is by anion exchange in 7 to 8 M HNO_3, in which small quantities of ^{241}Am are present from the decay of ^{241}Pu. The ^{241}Am is not retained by the anion-exchange resin and, therefore, passes with the HNO_3 effluent. Figure 2 shows that both TODGA and TEHDGA resins retain Am from high nitric acid concentrations. Dilute HCl must be used to efficiently strip Am from TODGA resin (see Figure 11), but dilute HNO_3 can be used to strip Am from TEHDGA resin. Figure 12 shows the concentration profiles for the elution of Am from a 0.50 mL TEHDGA column using dilute HNO_3. The Am was initially loaded from 10 mL (20 B.V.) of 7 M HNO_3. Clearly, the 0.01 M HNO_3 elutes the Am more efficiently than the 0.1 M HNO_3. The elution of Eu showed similar behavior. The broad elution curve obtained with 0.1 M HNO_3 is most likely due to slow kinetics but we have no explanation why this phenomenon occurs under these conditions. Other acids, such as formic or acetic acid can be used to efficiently strip Am from either TODGA or TEHDGA.

Radium/actinium separation

The separation of Ra from Ac is frequently performed in the analysis of ^{228}Ra and in the purification of ^{225}Ac for the preparation of ^{213}Bi generators. Although the HNO_3 and HCl dependencies of Ac(III) were not measured, the extraction of Ac follows that of La and Ce for acidic organophosphorus extractants, but is generally a factor of 2 to 3 times lower (21). Therefore, the conditions for separating Ac from Ra using either TODGA or TEHDGA resins can be ascertained from the data in Figures 5 and 8. Figure 13 shows an efficient separation of ^{226}Ra (a stand-in for ^{225}Ra) and ^{225}Ac using only a 0.5 mL bed volume column. Total separation time was 5 minutes. The load solution was the effluent from a UTEVA column (diamyl amylphosphonate on Amberchrom® CG-71) used to remove ^{229}Th parent and any trace quantities of ^{233}U.

Strontium/yttrium separation

An earlier publication by Horwitz, et al described the use of a strontium selective resin for the isolation of ^{90}Y from multicurie quantities of ^{90}Sr (22). In this process the ^{90}Y is recovered from the Sr selective resin in 5 M HNO_3 and then put through a final step using TRU Resin in which the ^{90}Y is concentrated and further purified. Figure 14 shows a particularly effective concentration and recovery of ^{90}Y from 5 M HNO_3 using TODGA resin. The ^{90}Y is recovered in dilute HCl which is the preferred medium for subsequent processing procedures. In addition to the concentration and recovery of the ^{90}Y, additional decontamination from ^{90}Sr and many other possible trace contaminants (e.g., Fe) is achieved.

The chemistry of Sr and Y on the DGA resins and the Sr selective resin is an example of selectivity inversion; that is, in the former case Y is selectively retained and in the latter case, Sr is selectively retained. By using two such columns sequentially, selectivity inversion can be exploited to achieve multiplication of decontamination factors to conveniently give very high purity analytes (23).

The TODGA and TEHDGA resins can also be used to separate ^{90}Y from macro quantities of Sr. Figure 15 shows the separation of ^{90}Y from a load solution of low specific activity ^{90}Sr. In this experiment, the quantity of Sr (250 mg) exceeded the capacity of the column for Sr by a factor of 30. The figure clearly shows that the ^{90}Y is effectively removed and decontaminated from the Sr and efficiently recovered in dilute HCl.

Calcium and strontium separation

Figure 16 depicts a most unusual separation in which Sr and Ca are separated from all other alkaline earths and then selectively eluted from each other. This separation validates the uptake data shown in Figure 8. In addition to achieving the separation depicted in Figure 16, the same column run conditions could be used to separate Sr and Ca from a host of other metals; for example, Fe, Al, Ni, Co, Cu, Zn and Pb (see Figure 10).

If one is interested only in purifying Ca, a selectivity inversion system could be used in which the TODGA resin column is preceded by a Sr resin column. Calcium is not retained by Sr Resin in 4 M HNO_3, but Sr and Pb are strongly retained. The load and rinse effluent from the Sr Resin column is loaded onto the TODGA resin column and the balance of the separation proceeds as shown in Figure 16. The selectivity inversion system would produce a Ca fraction more highly purified from Sr and Pb than would be obtained by a single TODGA column run.

Column stability

Table 3 summarizes the results of leaching experiments carried out with 12 mL bed volume columns packed with TODGA and TEHDGA resins. Both resins demonstrated very low levels of extractant leaching; however, duplicate runs showed fluctuations and in most cases the results shown in Table 3 represent the average of two or more determinations. In no case was extractant loss greater than $3 \times 10^{-4}\%$ per bed volume. Elevating the temperature to 50°C did not appear to have any significant effect on extractant loss. The presence of incomplete alkylation products mentioned in the experimental section were not detected in the leachates. The high stability of the DGA resins with respect to extractant loss shows that such columns could be used a number of times without a major diminution in capacity.

CONCLUSION

The liquid extractants *N,N,N'N'* tetraoctyl-1,5-diglycolamide (TODGA) and *N,N,N'N'* tetrakis-(2-ethyl-1-hexyl)-1,5-diglycolamide (TEHDGA) sorbed on Amberchrom® CG71 produces excellent extraction chromatographic resins. Forty weight percent of the extractants sorbed onto 50-100 μm particle size polyacrylate polymer beads forms EXC resins with a good capacity and an unusually high stability with regards to extractant leaching. The most noteworthy chemical property of the resins is their high uptake of trivalent actinides and lanthanides from high concentrations of HNO_3 and HCl acids. Although the uptake of tetravalent actinides is comparable to that of trivalent actinides especially at high HNO_3 concentrations, the retention of uranyl ion is marginal. The insensitivity of the uptake of actinides and lanthanides to common elements present in soil and water; for example, Fe, is an important property of the DGA resins.

We believe that the major application of the resins is primarily in analytical chemistry and in the purification of radionuclides for use in nuclear medicine. The high selectivity of TODGA resin shown for lanthanides from La through Dy could be exploited to separate adjacent lanthanides. Most likely, a smaller resin size and longer columns would be required. The versatile DGA resins can be of particular value when used in conjunction with other EXC resins to perform multiple radionuclide separations using the selectivity inversion concept. Application of the resin in the treatment of radioactive waste is also a possibility but stability to radiation and leaching over a period of time is a major issue which would need to be studied. Both resins are commercially available from Eichrom Technologies, Inc as DGA Resin, normal (TODGA) and DGA Resin, branched (TEHDGA).

References:

1. Horwitz, E.P.; Schulz, W.W. Solvent Extraction in the Treatment of Acidic High-Level Liquid Waste: Where do We Stand? in “Metal Ion Separation and Preconcentration: Progress and Opportunities,” Bond, A.H.; Dietz, M.L.; Rogers, R.D.; Editors, ACS Symposium Series 716, American Chemical Society, Washington, D.C., 1999, 20-50.

2. Sasaki, Y.; Choppin, G.R. Solvent extraction of europium, thorium, uranium, neptunium and americium with N,N′-dimethyl-N,N′-dihexyl-3-oxapentanediamide and its analogous compounds. Anal. Sci. 1996, 12, 225-230.

3. Sasaki, Y.; Choppin, G.R. Extraction behaviors of Eu, Th, U and Am with diamides + thenoyltrifluoroacetone, J. Radioanal. Nucl. Chem. 1996, 207, 383-394.

4. Sasaki, Y.; Choppin, G.R. Extraction of Np(V) by N,N′-dimethyl-N,N′-dihexyl-3-oxapentanediamide. Radiochim. Acta. 1998, 80, 85-88.

5. Sasaki, Y.; Choppin, G.R. Extraction and mutual separation of actinide(III), (IV) and (VI) ions by N,N′-dimethyl-N,N′-dihexyl-3-oxapentanediamide and thenoyltrifluoroacetone, J. Radioanal. Nucl. Chem. 2000, 246, 267-273.

6. Sasaki, Y.; Sugo, Y.; Suzuki, S.; and Tachimori, S. The novel extractants, diglycolamides, for the extraction of lanthanides and actinides in HNO_3-n-dodecane system, Solvent Extr. Ion Exch. 2001, 19, 91-103.

7. Sasaki, Y.; Tachimori, S. Extraction of actinides(III), (IV), (V), (VI) and lanthanides(III) by structurally tailored diamides, Solvent Extr. Ion Exch. 2002, 20, 21-34.

8. Tachimori, S.; Suzuki, S.; Sasaki, Y.; Apichaibukol, A. Solvent extraction of alkaline earth metal ions by diglycolic amides from nitric acid solutions, Solvent Extr. Ion Exch. 2003, 21, 707-715.

9. Tachimori, S.; Sasaki, Y.; Suzuki, S. Modification of TODGA-n-dodecane solvent with a monoamide for high loading of lanthanides(III) and actinides(III), Solvent Extr. Ion Exch., 2002, 20, 687-699.

10. Sugo, Y.; Sasaki, Y.; Tachimori, S. Studies on hydrolysis and radiolysis of N,N,N′,N′-tetraoctyl-3-oxapentane-1,5-diamide, Radiochim. Acta. 2002, 90, 161-165.

11. Van Hecke, K.; Modolo, G. Separation of actinides from low level liquid wastes(LLLW) by extraction chromatography using novel DMDOHEMA and TODGA impregnated resins, J. Radioanal. Nucl. Chem. 2004, 261, 269-275.

12. Hoshi, H.; Wei, W.-Z.; Kumagai, M.; Asakura, T.; Morita, Y. Group separations of trivalent minor actinides and lanthanides by TODGA extraction chromatography for radioactive waste management, J. Alloy Compds. 2004, 374, 451-455.

13. Horwitz, E.P.; Bond, A.H.; Barrans, Jr., R.E.; McAlister, D.R.; Jassin, L.E.; Thakkar, A.H.; Williamson, J.M. New extraction chromatographic resins for recovery of TRUs and lanthanides from acidic and nitrate and chloride wastes. 227th American Chemical Society National Meeting, Anaheim, CA, March 28-April 1, 2004, IE&C-226.

14. Horwitz, E.P.; Dietz, M.L.; Chiarizia R.; Diamond, H.; Maxwell, III, S.L.; Nelson, M.R.; Separation and preconcentration of actinides by extraction chromatography using a supported liquid anion exchanger: application to the characterization of high-level nuclear waste solutions, Anal. Chim. Acta. 1995, 310, 63-78.

15. Horwitz, E.P.; Chiarizia, R.; Dietz, M.L.; Diamond, H. Separation and preconcentration of actinides from acidic media by extraction chromatography, Anal. Chim. Acta. 1993, 28, 361-372.

16. Huff, E.A.; Horwitz, E.P. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) in support of nuclear waste management, Spectrochimica Acta. 1985, 408, 279-286.

17. Horwitz, E.P.; Muscatello, A.C.; Kalina, D.G.; Kaplan, L. The extraction of selected transplutonium(III) and lanthanide(III) ions by dihexyl-N,N-diethylcarbamoylmethylphosphonate from aqueous nitrate media, Sep. Sci. Technol. 1981, 16, 417-437.

18. Horwitz, E.P.; Kalina, D.G.; Kaplan, L.; Mason, G.W.; Diamond, H. Selected alkyl(phenyl)-N,N-dialkylcarbamoylmethylphosphine oxides as extractants for Am(III) from nitric acid media, Sep. Sci. Technol. 1982, 17, 1261-1279.

19. Yaita, T.; Herlinger, A.W.; Thiyagarajan, P.; Jensen, M.P. Influence of extractant aggregation of trivalent f-element cations by a tetraalkyldiglycolamide, Solvent Extr. Ion Exch. 2004, 22, 553-571.

20. Peppard, D.F., Bloomquist, C.A.A.; Horwitz, E.P.; Lewey, S.; Mason, G.W. Analogous actinide(III) and lanthanide(III) tetrad effects, J. Inorg. Nucl. Chem.1970, 32, 339-343.

21. Horwitz, E.P.; Bloomquist, C.A.A. Chemical separations for super-heavy searches in irradiated uranium targets, J. Inorg. Nucl. Chem. 1975, 37, 425-434.

22. Dietz, M.L.; Horwitz, E.P. Improved chemistry for the production of yttrium-90 for medical applications, Appl. Radiat. Isotopes. 1992, 43, 1093-1101.

23. Horwitz, E.P.; Bond, A.H. Purification of radionuclides for nuclear medicine: the multicolumn selectivity inversion generator concept, Czech. J. Phys. 2002, 53, A717-723.

List of Figures:

Figure 14. Separation of Y(III) and Sr(II) on TODGA resin (50-100 μm) with 5.0 M HNO_3, 0.1 M HNO_3 and 0.1 M HCl, 1.0 mL bed volume, flow rate equals 2 mL/min load/rinse, 1 mL/min strip, 22(1)^{o}C.

Figure 15. Separation of Y(III) and Sr(II) on TODGA resin (50-100 μm) with 0.1 M HNO_3 and 0.1 M HCl, 1.0 mL bed volume, flow rate equals 2 mL/min load/rinse, 1 mL/min strip, 22(1)^{o}C.

Figure 16. Separation of alkaline earth cations on TODGA resin (50-100 μm) with 4.0 M HNO_3, 0.25 M HNO_3 and 0.1 M HCl, 2.0 mL bed volume, flow rate equals 2 mL/min load/rinse, 1 mL/min strip, 22(1)^{o}C.

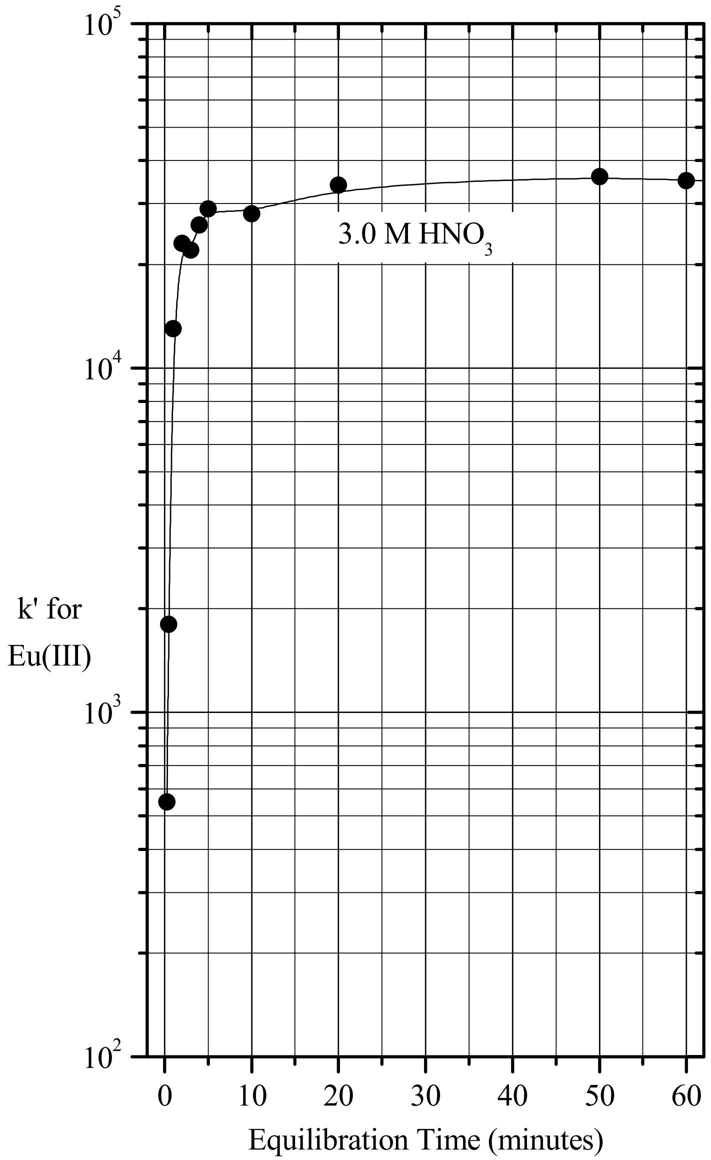

Figure 1. k′ for Eu(III) vs. time on TODGA resin (50-100 μm) from 3.0 M HNO_3, 22(1)°C.

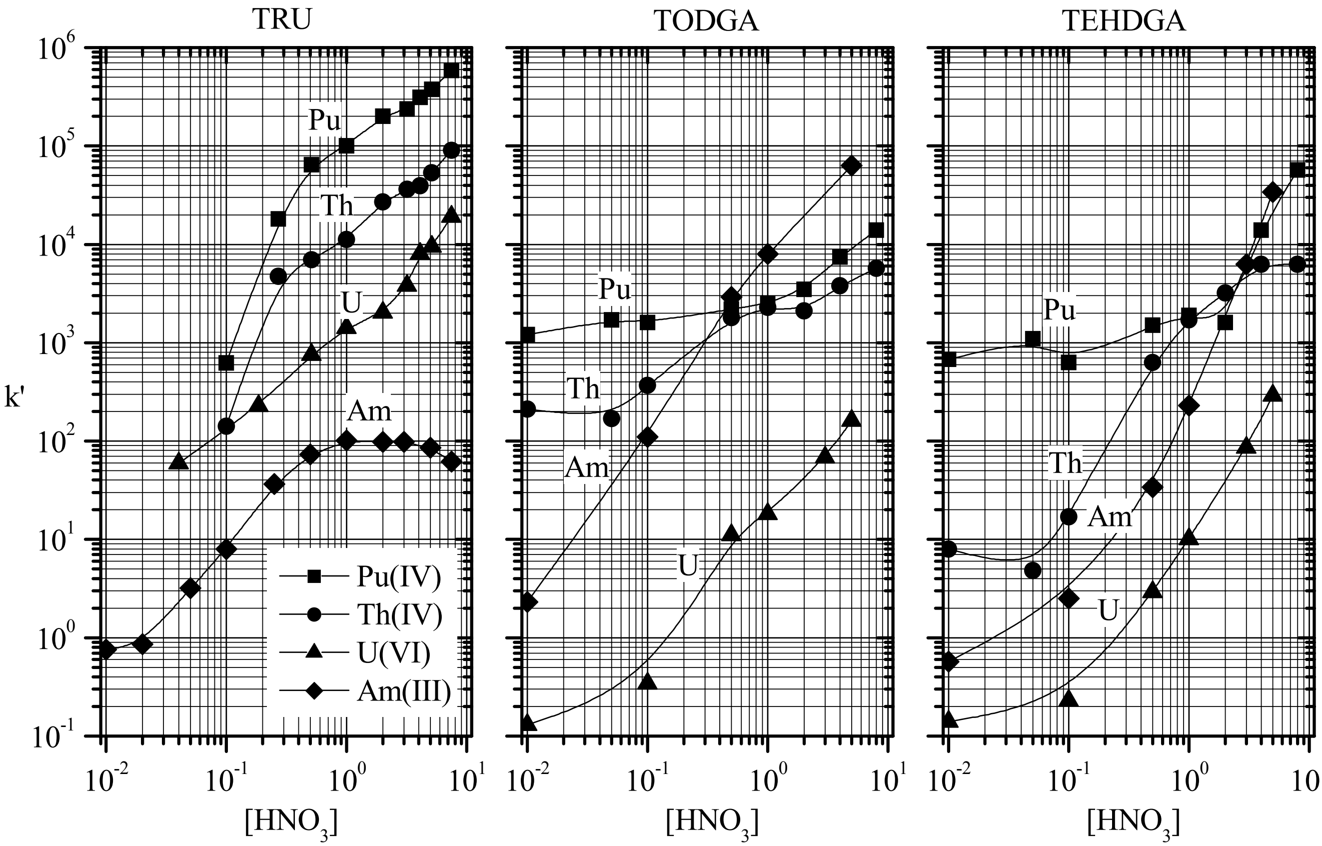

Figure 2. k′ for Th(IV), U(VI), Am(III) and Pu(IV) on TRU, TODGA and TEHDGA resins (50-100 μm) versus HNO_3, 1 hour equilibration time, 22(1)°C.

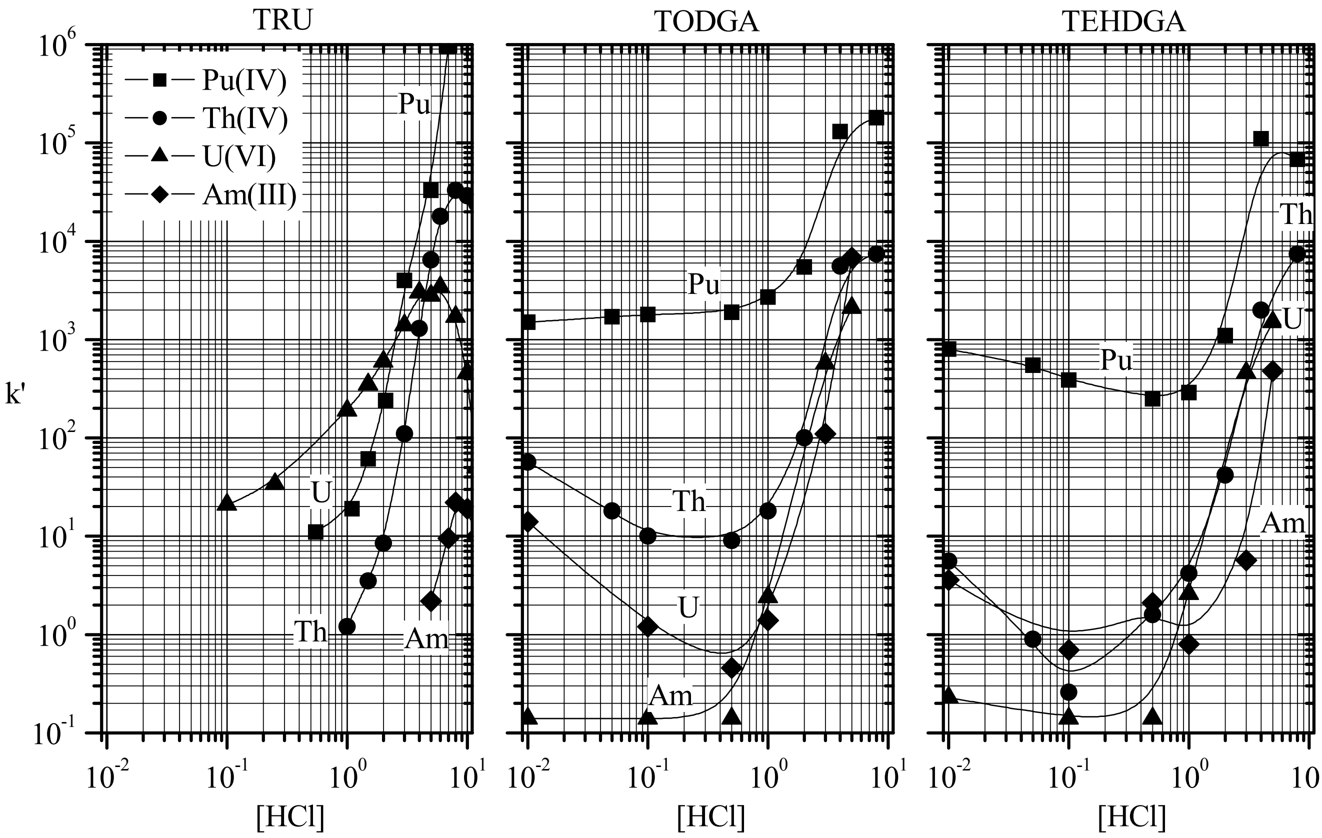

Figure 3. k′ for Th(IV), U(VI), Am(III) and Pu(IV) on TRU, TODGA and TEHDGA resins (50-100 µm) versus HCl, 1 hour equilibration time, 22(1)°C.

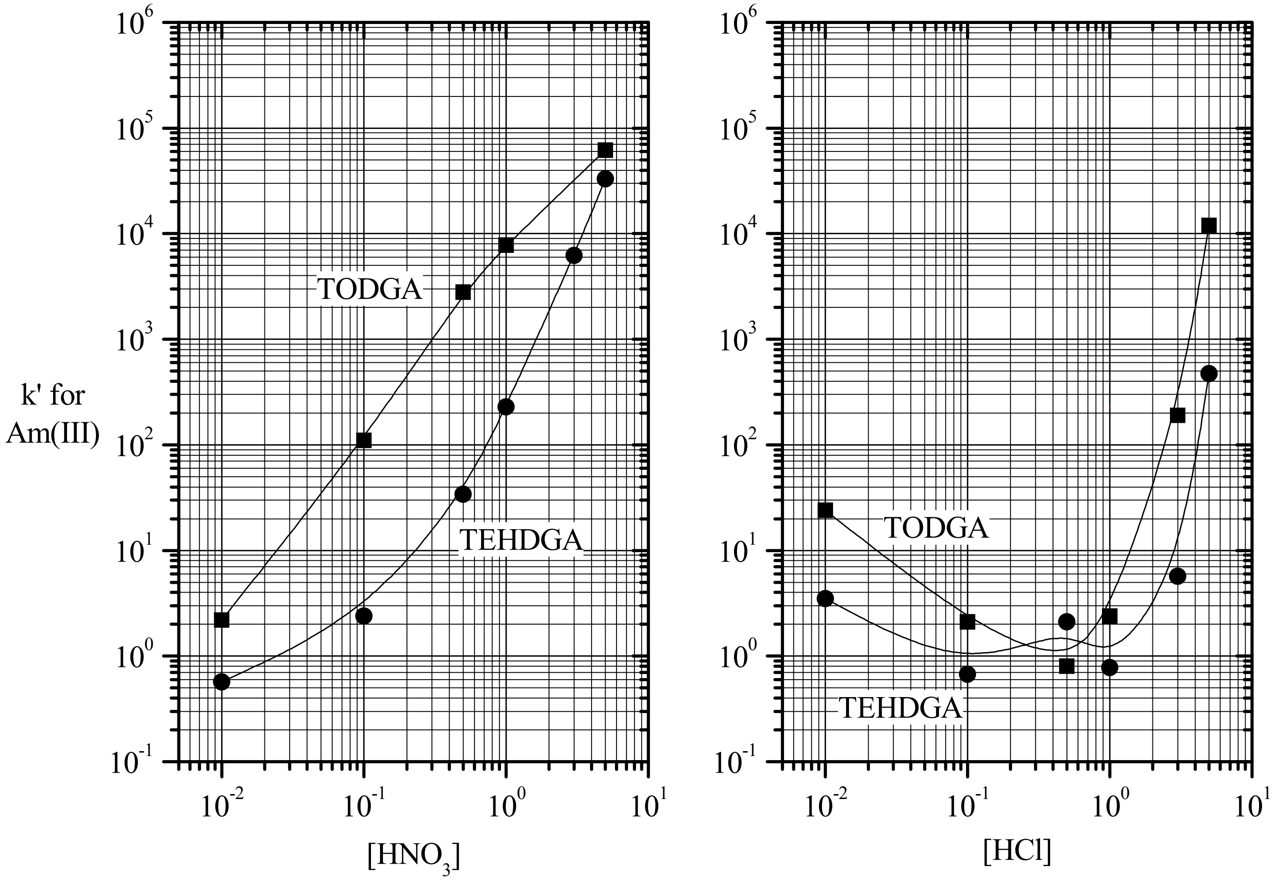

Figure 4. k′ for Am(III) on TODGA and TEHDGA resins (50-100 μm) versus HNO$_3$ and HCl, 1 hour equilibration time, 22(1)°C.

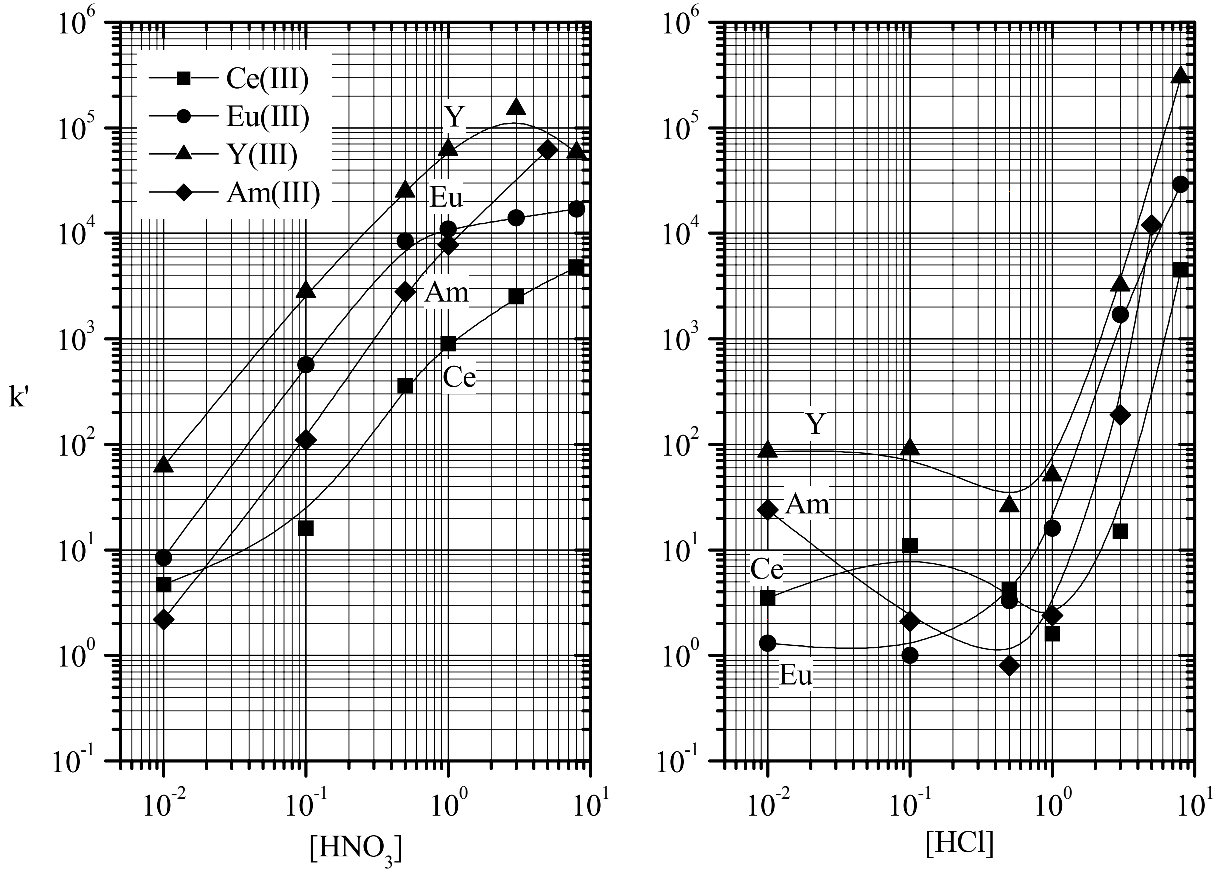

Figure 5. k′ for Y(III), Eu(III), Am(III) and Ce(III) on TODGA resin (50-100 μm) versus HNO_3 and HCl, 1 hour equilibration time, 22(1)°C.

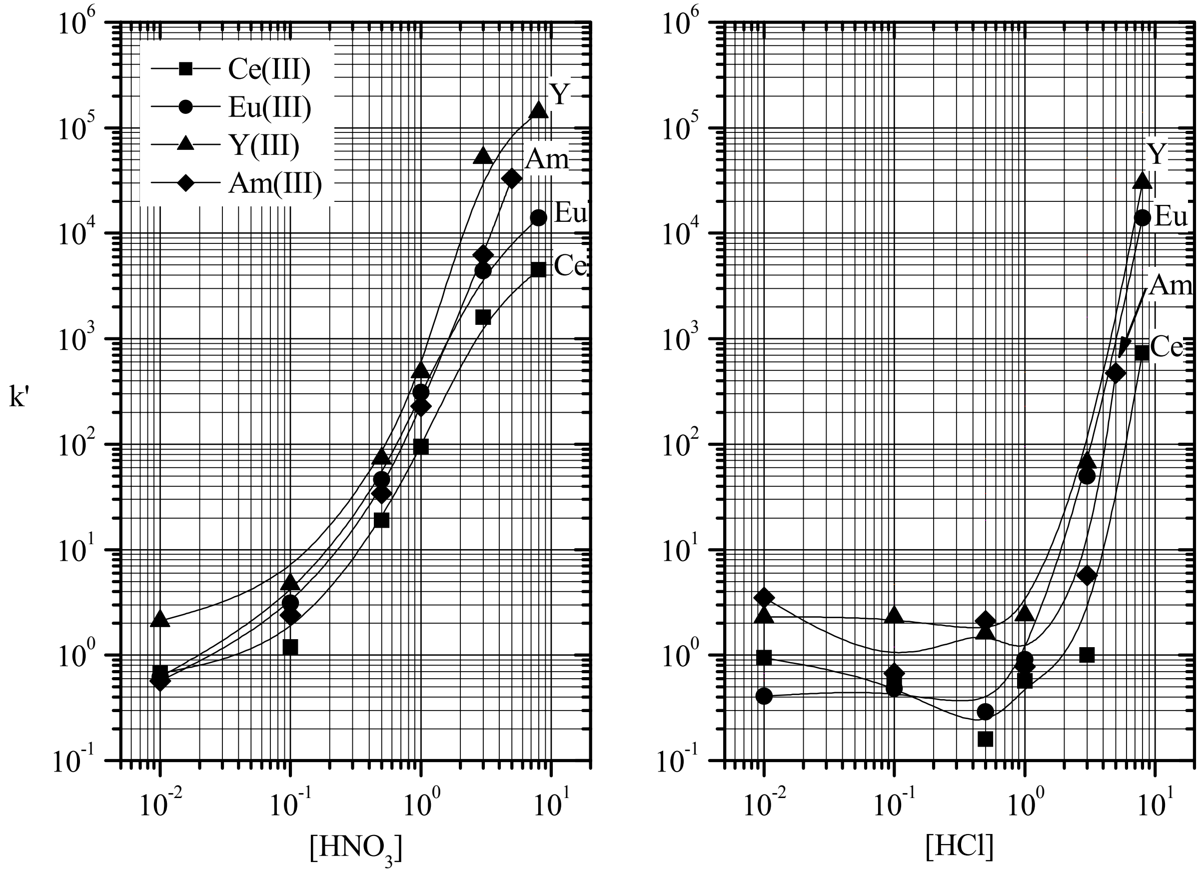

Figure 6. k′ for Y(III), Eu(III), Am(III) and Ce(III) on TEHDGA resin (50-100 μm) versus HNO_3 and HCl, 1 hour equilibration time, 22(1)°C.

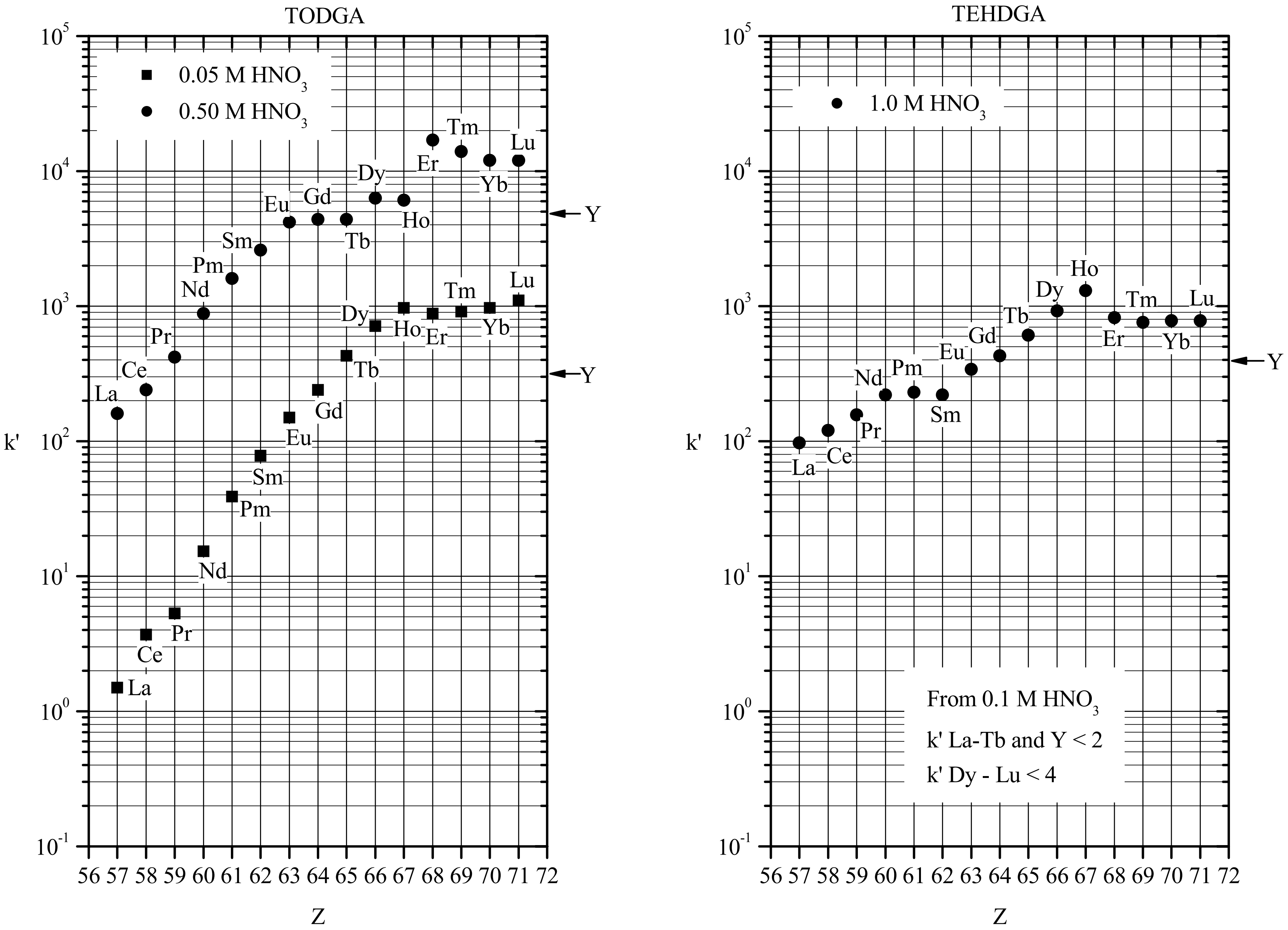

Figure 7. k′ for Ln(III) cations and Y(III) on TODGA resin (50-100 μm) from 3.0 M and 0.1 M HNO_3 and on TEHDGA from 1.0 M HNO_3 versus atomic number, 1 hour equilibration time, 22(1)°.

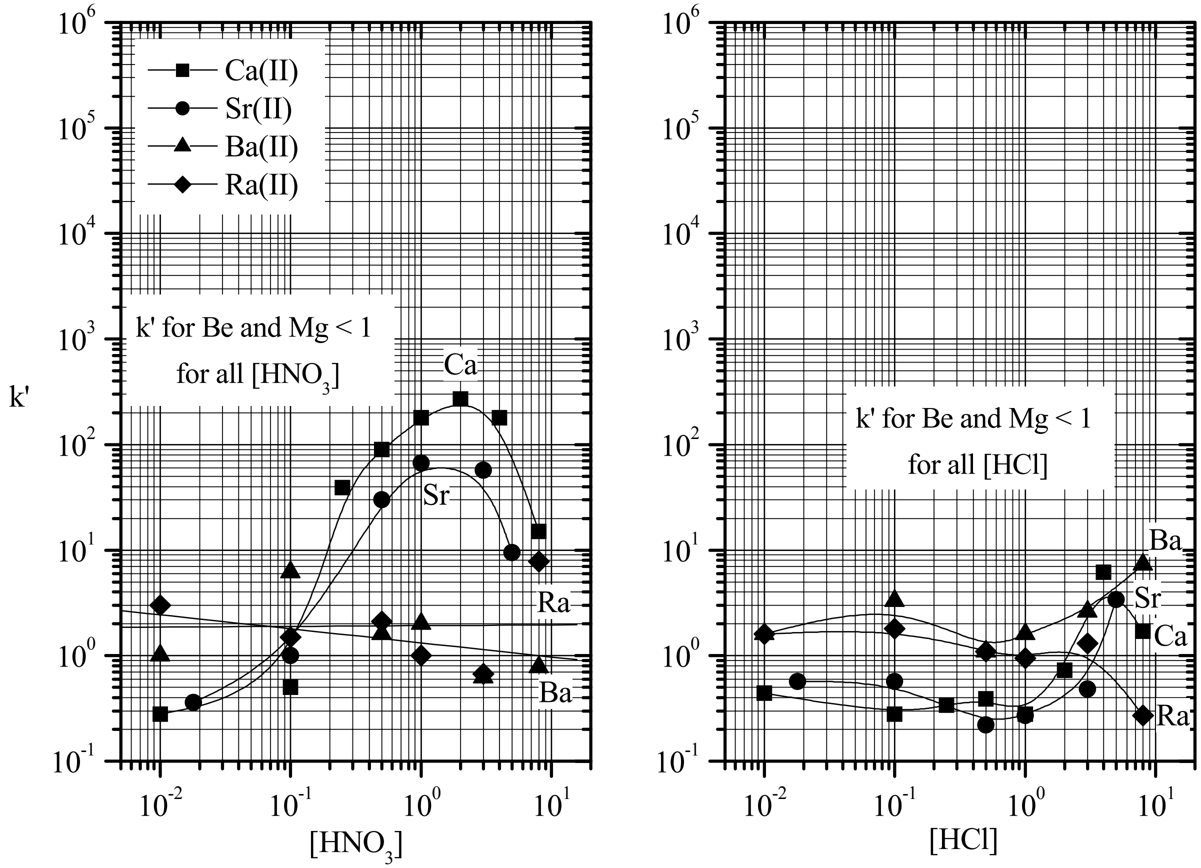

Figure 8. k′ for alkaline earth cations on TODGA resin (50-100 μm) versus HNO_3 and HCl, 1 hour equilibration time, 22(1)°C.

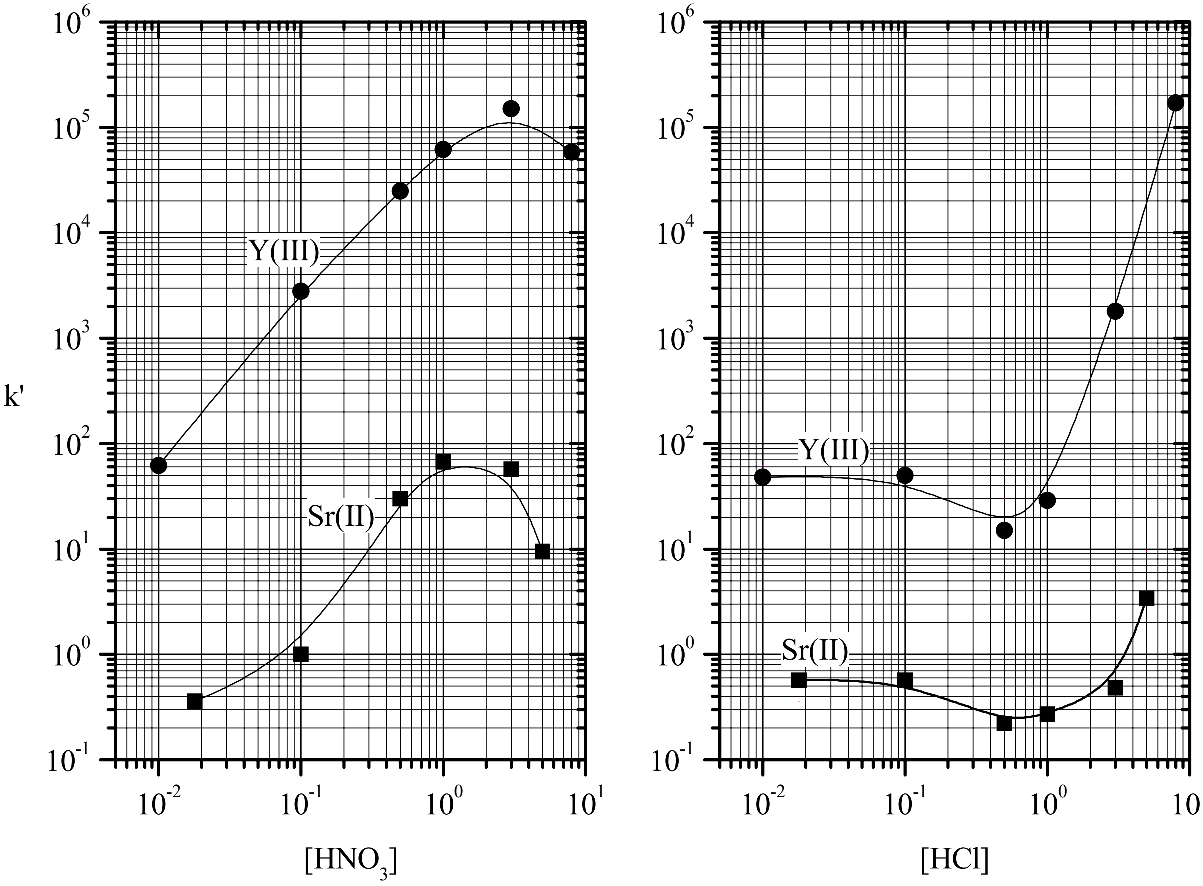

Figure 9. k′ for Y(III) and Sr(II) on TODGA resin (50-100 μm) versus HNO_3 and HCl, 1 hour equilibration time, 22(1)^{o}C.

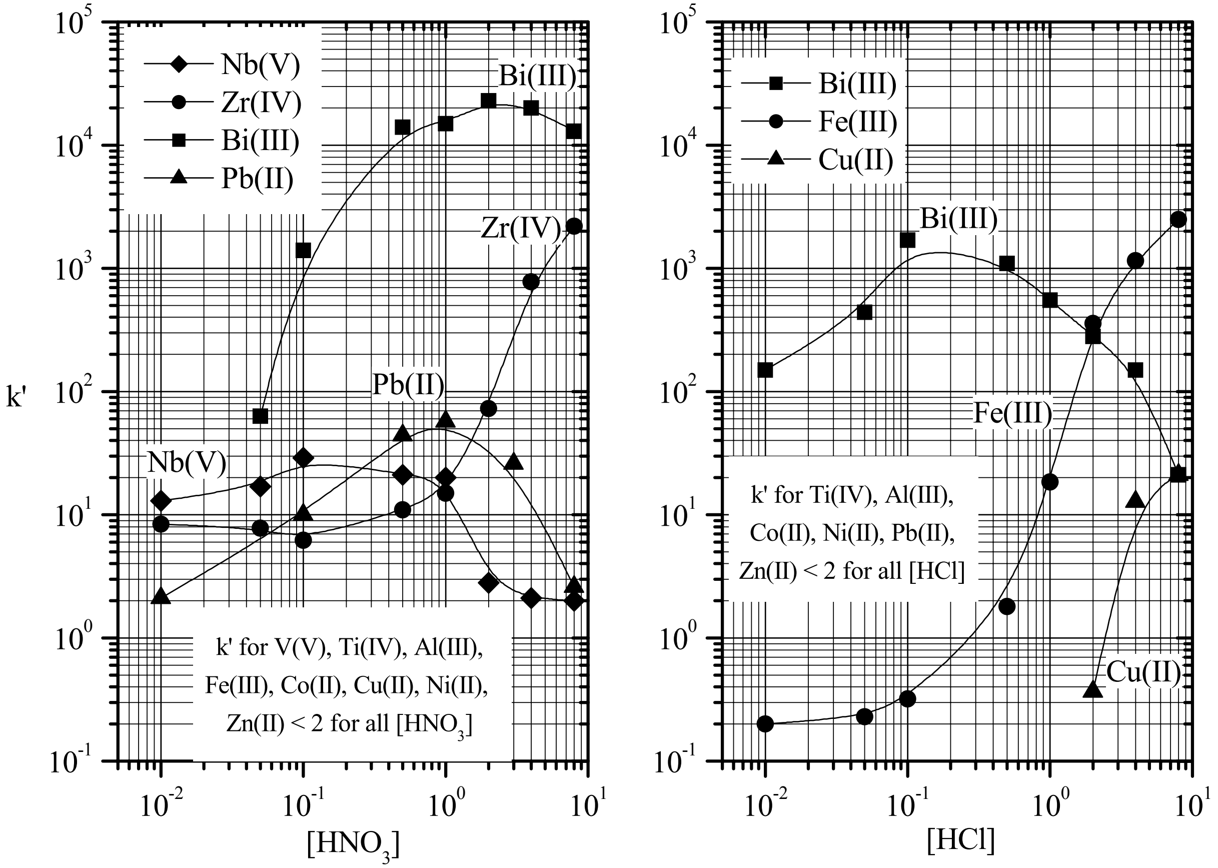

Figure 10. k′ for selected transition and post transition elements on TODGA resin (50-100 μm) vs. HNO_3 and HCl, 1 hour equilibration time, 22(1)°C.

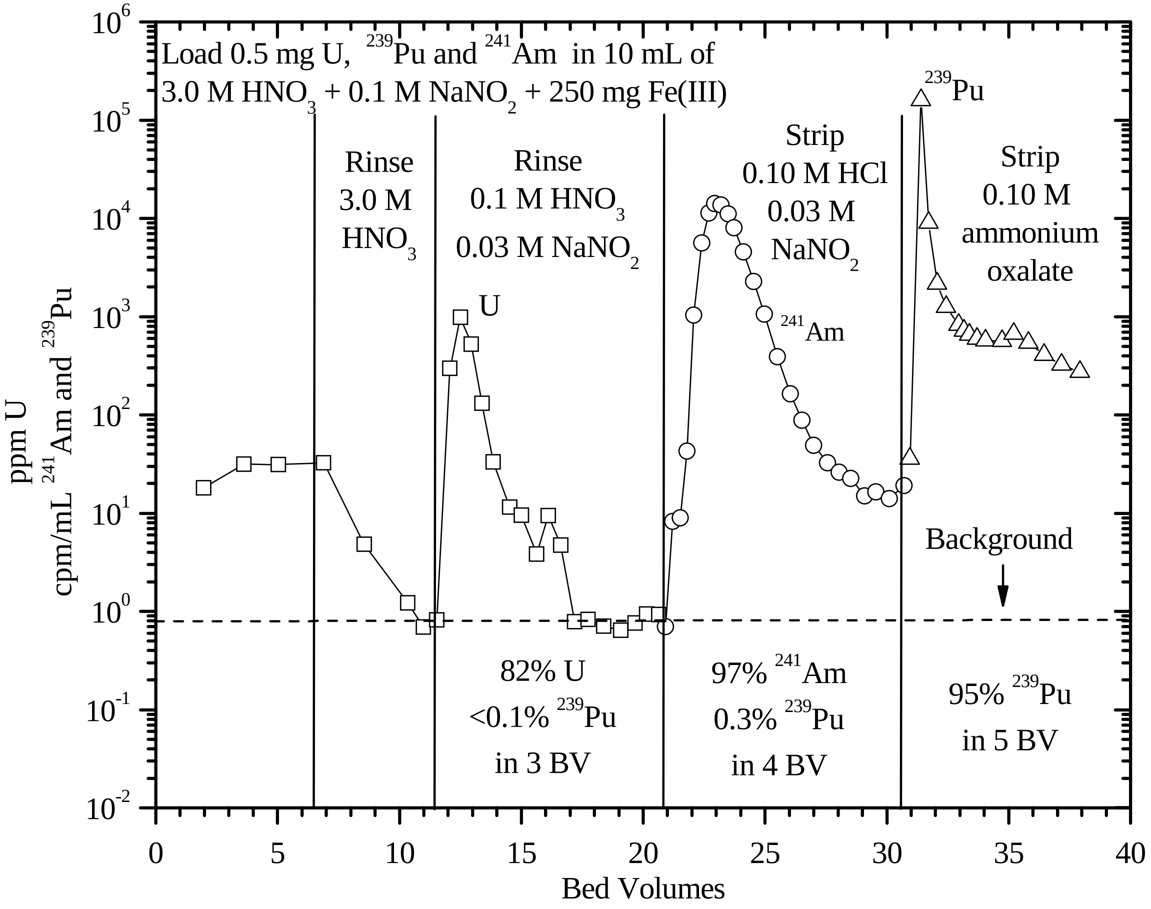

Figure 11. Separation of U(VI), Am(III) and Pu(IV) on TODGA resin (50-100 µm), 2.0 mL bed volume, flow rate equals 2 mL/min load/rinse, 1 mL/min strip, 22(1)°C.

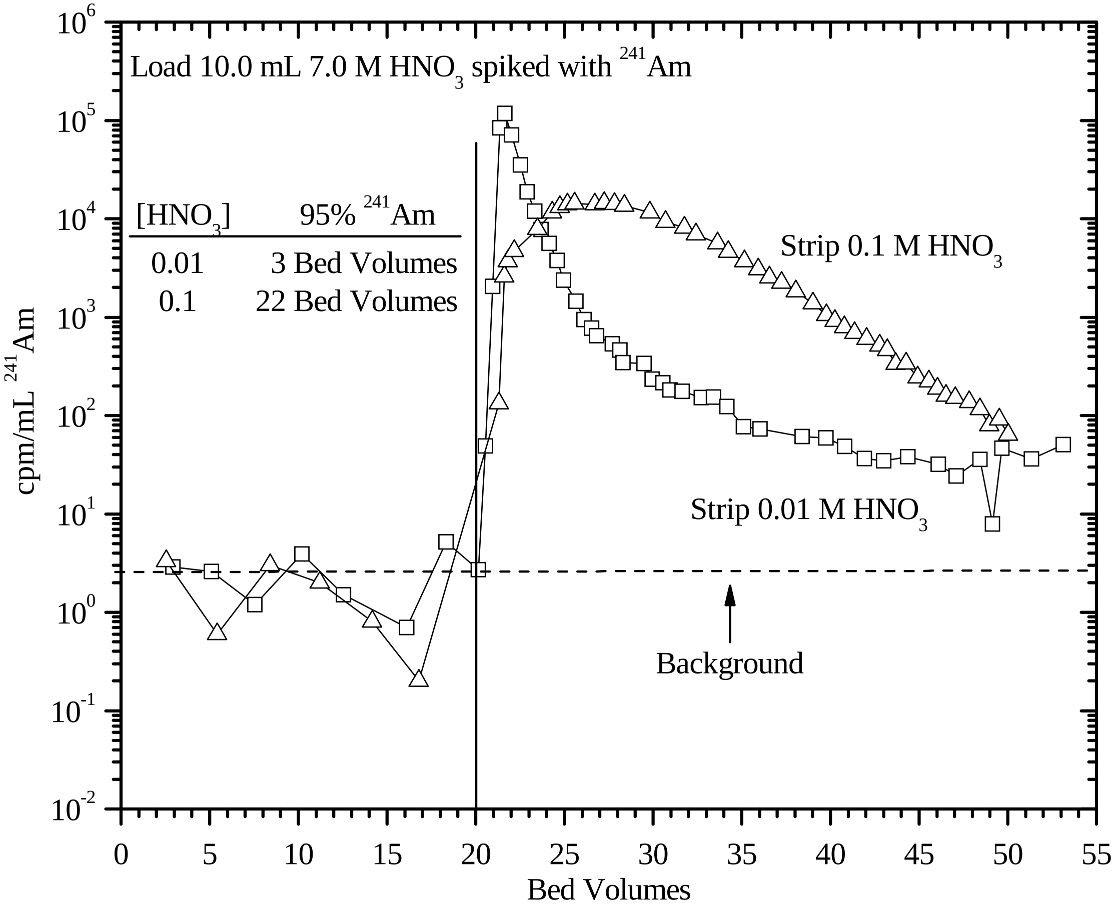

Figure 12. Elution of Am(III) on TEHDGA resin (50-100 μm) with 7.0, 0.1 and 0.01 M HNO_3, 0.5 mL bed volume, flow rate equals 2 mL/min load/rinse, 1 mL/min strip, 22(1)°C.

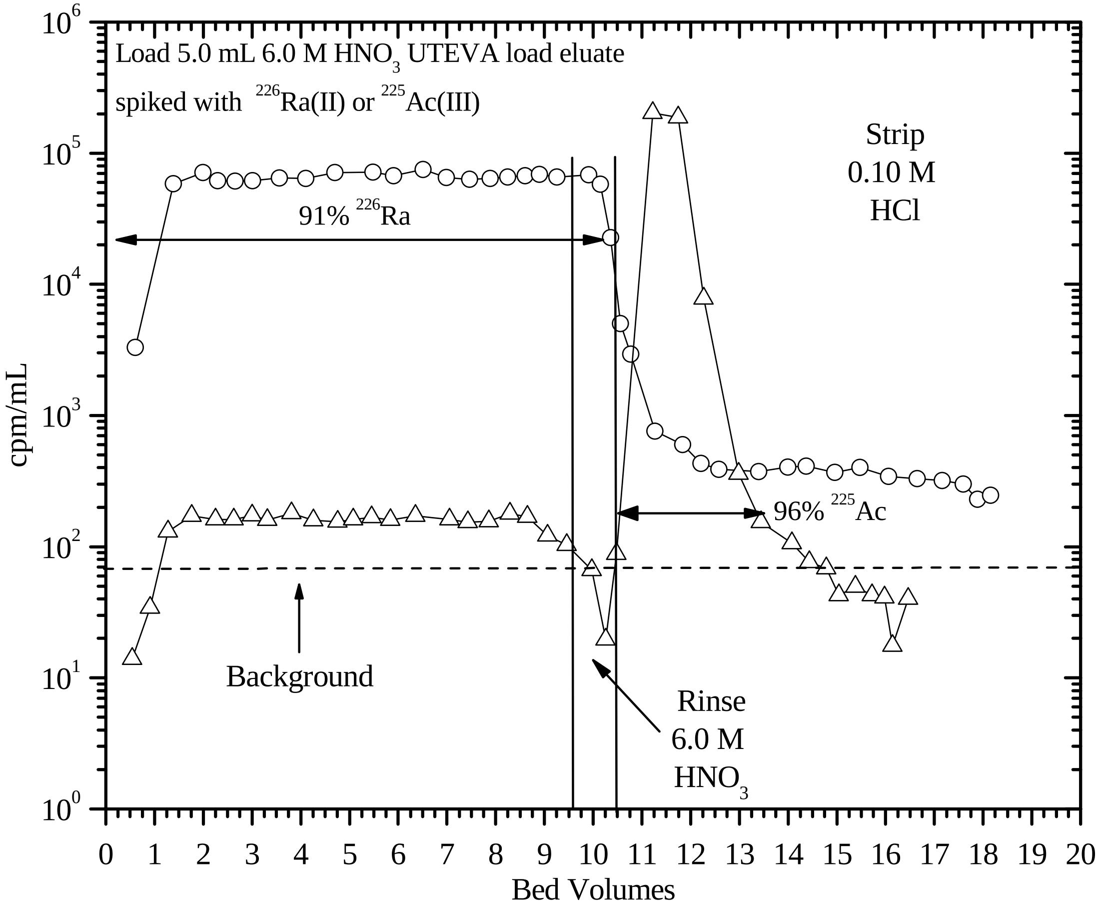

Figure 13. Separation of Ac(III) and Ra(II) on TODGA resin (50-100 μm) with 6.0 M HNO_3 and 0.1 M HCl, 0.5 mL bed volume, flow rate equals 2 mL/min load/rinse, 1 mL/min strip, 22(1)^{o}C.

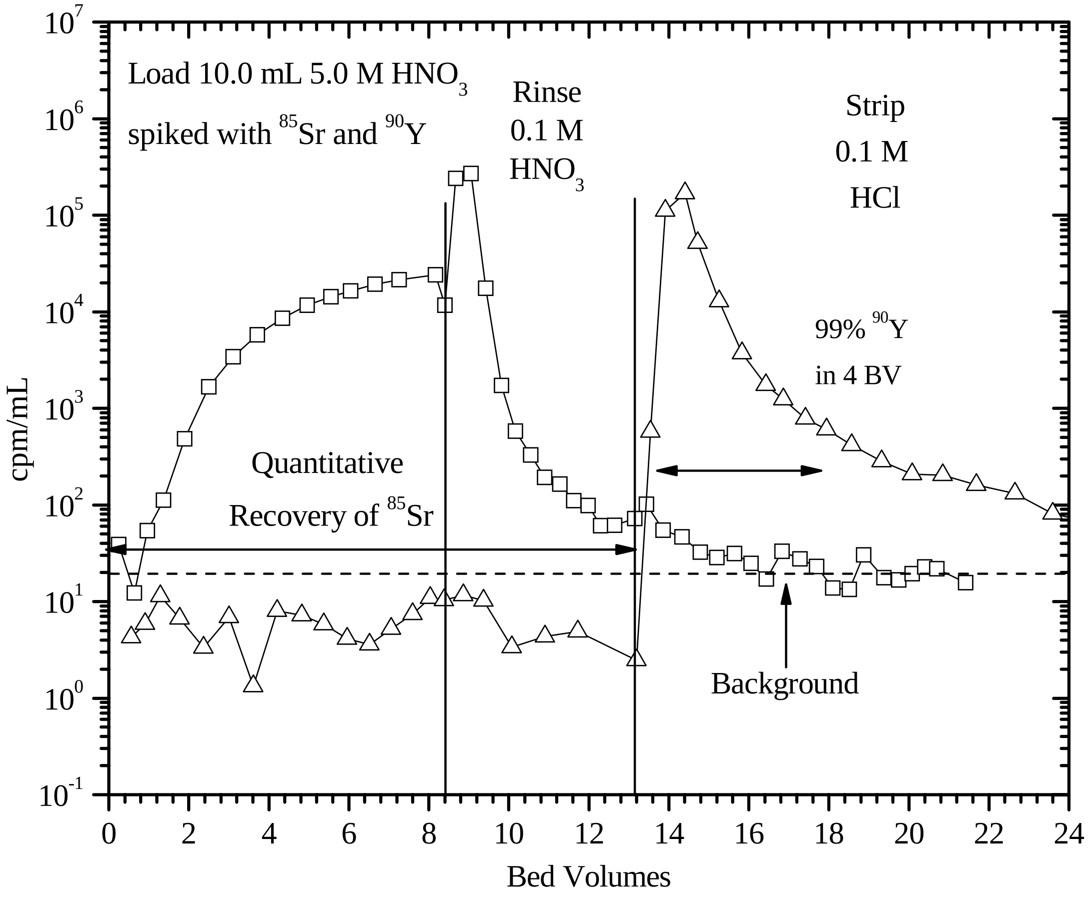

Figure 14. Separation of Y(III) and Sr(II) on TODGA resin (50-100 μm) with 5.0 M HNO_3, 0.1 M HNO_3 and 0.1 M HCl, 1.0 mL bed volume, flow rate equals 2 mL/min load/rinse, 1 mL/min strip, 22(1)°C.

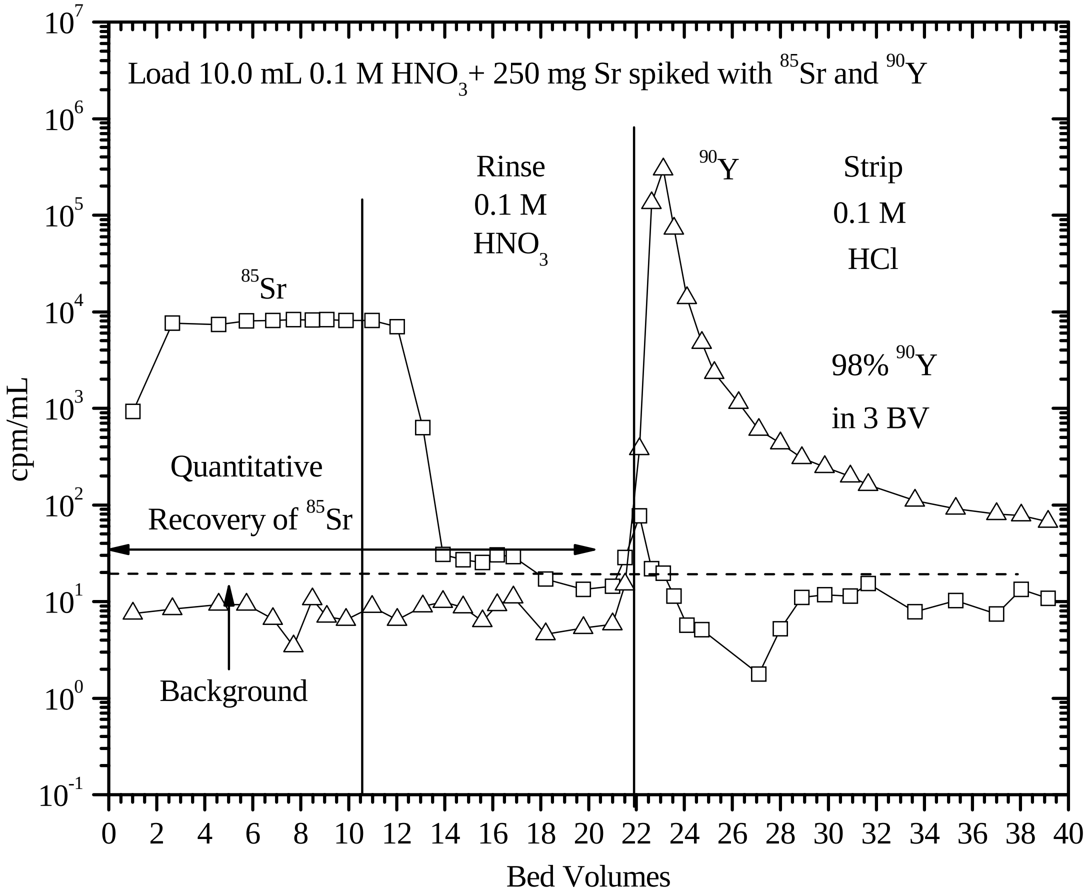

Figure 15. Separation of Y(III) and Sr(II) on TODGA resin (50-100 μm) with 0.1 M HNO_3 and 0.1 M HCl, 1.0 mL bed volume, flow rate equals 2 mL/min load/rinse, 1 mL/min strip, 22(1)°C.

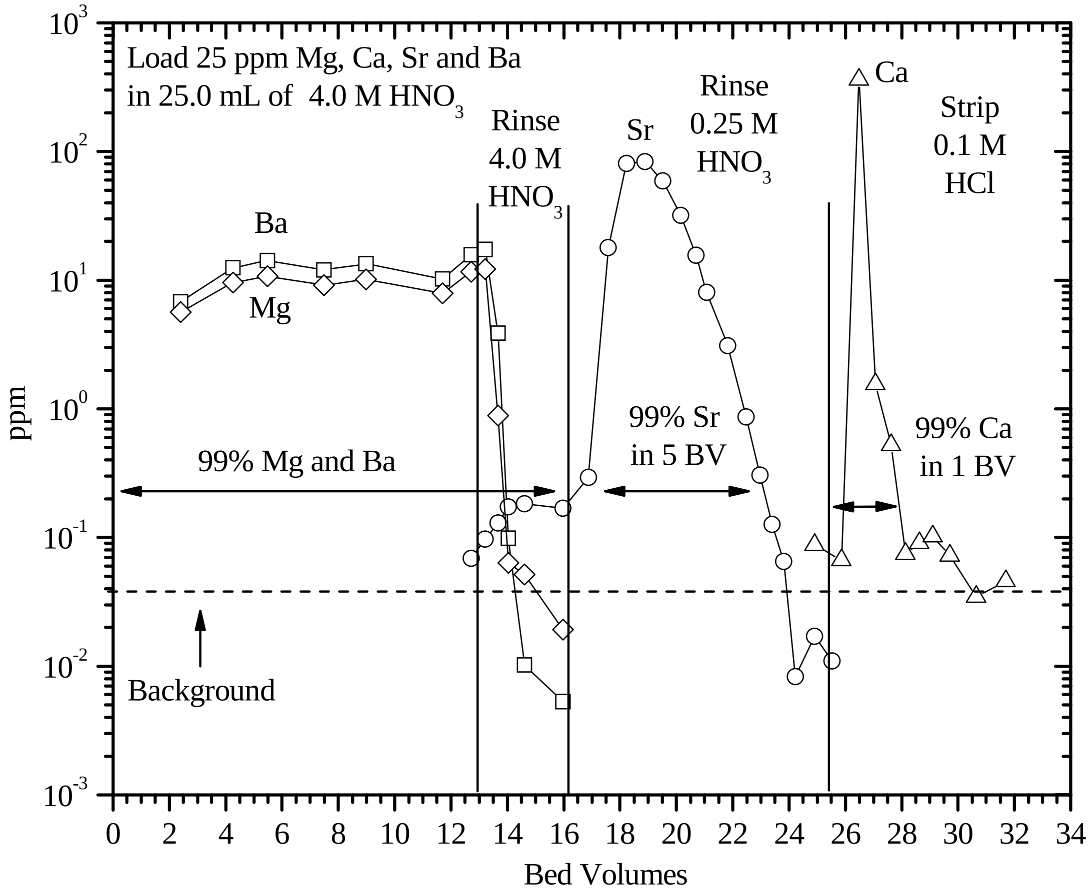

Figure 16. Separation of alkaline earth cations on TODGA resin (50-100 μm) with 4.0 M HNO_3, 0.25 M HNO_3 and 0.1 M HCl, 2.0 mL bed volume, flow rate equals 2 mL/min load/rinse, 1 mL/min strip, 22(1)^{o}C.

Table 1. Parameters employed for metal ion determination by ICP-AES

Analyte	Peak (nm)	Window (nm)	Analyte	Peak (nm)	Window (nm)	Analyte	Peak (nm)	Window (nm)
Al	396.152	0.080	Fe	259.940	0.040	Sr	407.771	0.080
Ba	455.403	0.080	Gd	342.247	0.040	Tb	350.917	0.040
Be	234.861	0.040	Ho	345.600	0.040	Th	283.730	0.040
Ca	393.366	0.080	La	379.478	0.040	Ti	334.941	0.080
Ce	413.765	0.080	Lu	339.707	0.040	Tm	313.126	0.040
Co	228.616	0.060	Mg	279.553	0.040	U	385.958	0.080
Cr	267.716	0.040	Nb	316.340	0.040	V	292.402	0.040
Cu	324.754	0.040	Nd	406.109	0.040	Y	371.030	0.040
Dy	259.940	0.040	Ni	231.604	0.060	Yb	369.419	0.040
Er	337.271	0.040	Pr	414.311	0.040	Zn	213.856	0.027
Eu	381.967	0.040	Sm	359.260	0.040	Zr	343.823	0.040

Integration time:	3.00 seconds	Sample uptake delay:	25 seconds
Replicates:	3	Pump rate:	15 rpm
Power:	1 kW	Instrument stabilization:	15 seconds
Viewing height:	10 mm	Rinse time:	30 seconds

Table 2. Physical Constants of Slurry-Packed Columns of DGA Resin

	TODGA	TEHDGA
Extractant Density (g/mL)	0.88	0.89
Bed Density (g/mL)	0.38	0.38
Resin Density (g/mL)	1.13	1.13
v_s	0.17	0.17
v_m	0.66	0.66
v_s/v_m	0.26	0.26
D_v conversion factor (C_1)[a]	2.20	2.23
k' conversion factor (C_2)[b]	0.57	0.58

[a] $D_v = D_w \times C_1$

[b] $k' = D_w \times C_2$

Table 3. Extractant leaching of TODGA and TEHDGA resins at 25°C

		% Extractant Lost/Bed Volume	
	BV	TODGA	TEHDGA
Load/Rinse[a]	10	3.6×10^{-5}	4.6×10^{-5}
Strip[b]	5	3.6×10^{-5}	1.3×10^{-5}
Strip with guard[b,c]	5	1.5×10^{-5}	0.7×10^{-5}

[a] 6 M HNO^3

[b] 0.1 M HCl for TODGA, 0.1 M HNO_3 for TEHDGA

[c] The strip solution was passed through a column of Amberchrom CG71m