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Separation of Protactinium Employing Sulfur-Based Extraction Chromatographic Resins

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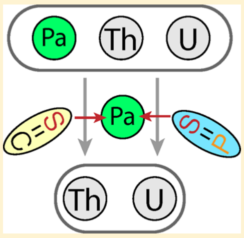
ABSTRACT: Protactinium-230 ($t_{1/2}$ = 17.4 d) is the parent isotope of ^{230}U ($t_{1/2}$ = 20.8 d), a radionuclide of interest for targeted alpha therapy (TAT). Column chromatographic methods have been developed to separate no-carrier-added ^{230}Pa from proton irradiated thorium targets and accompanying fission products. Results reported within demonstrate the use of novel sulfur bearing chromatographic extraction resins for the selective separation of protactinium. The recovery yield of ^{230}Pa was 93 ± 4% employing a $R_3P{=}S$ type commercially available resin and 88 ± 4% employing a DGTA (diglycothioamide) containing custom synthesized extraction chromatographic resin. The radiochemical purity of the recovered ^{230}Pa was measured via high purity germanium γ-ray spectroscopy to be >99.5% with the remaining radioactive contaminant being ^{95}Nb due to its similar chemistry to protactinium. Measured equilibrium distribution coefficients for protactinium, thorium, uranium, niobium, radium, and actinium on both the $R_3P{=}S$ type and the DGTA resin in hydrochloric acid media are reported, to the best of our knowledge, for the first time.



Actinide element protactinium plays a role in many applications such as nuclear forensics,[1−3] environmental chemistry,[4−8] nuclear medicine,[9−12] and molten-salt nuclear reactors.[13−16] Nuclear forensics and environmental applications of protactinium relate to the field of radiochronometry, where age dating of materials is accomplished by the determination of $^{231}Pa/^{235}U$ ratios. As a source of alpha emitting ^{230}U ($t_{1/2}$ = 20.8 d), the radioisotope ^{230}Pa ($t_{1/2}$ = 17.4 d) is of interest to nuclear medicine for targeted alpha therapy applications. Protactinium-233, on the other hand, is an intermediate of fissile ^{233}U in the breeding process within the thorium fuel cycle. Separation of protactinium from thorium and uranium in addition to fission products and bulk materials is mandatory for the aforementioned applications. Protactinium readily hydrolyzes and polymerizes in aqueous solution complicating the development of robust and reliable separation procedures.[17−19] Rather limited research has been conducted into the fundamental chemistry of protactinium that would aid in the design of effective separation methodologies. Reported methods that have historically been used for the separation of protactinium from these systems include ion exchange chromatography,[20−24] liquid−liquid extraction,[17,25−30] silica gel,[2] and solid phase extraction chromatography.[3,31−33]

Emerging interest in ^{230}Pa for medical applications has provided a motivation for development of an improved Pa/Th/U separation methodology. Protactinium-230 ($t_{1/2}$ = 17.4 d) partially (7.8% branching ratio) decays via β^- to ^{230}U ($t_{1/2}$ = 20.8 d). Uranium-230, in turn, possesses therapeutic properties, both for direct use as a longer-lived alpha emitter ($t_{1/2}$ = 20.8 d) for targeted alpha therapy[34] and indirectly as a continuous source of short-lived alpha emitter ^{226}Th ($t_{1/2}$ = 30.6 m), as realized in a $^{230}U/^{226}Th$ radionuclide generator system.[11] The decay scheme for $^{230}Pa/^{230}U/^{226}Th$ is shown in Figure 1.[35]

Protactinium-230 can be made through proton or deuteron induced reactions on thorium nuclei, that is, $^{232}Th(p,3n)^{230}Pa$[9] and $^{232}Th(d,4n)^{230}Pa$.[10] Moreover, long-lived ^{231}Pa ($t_{1/2}$ = 32760 a) can be used as a target material to make ^{230}U directly through the proton and deuteron induced reactions: $^{231}Pa(p,2n)^{230}U$[11] and $^{231}Pa(d,3n)^{230}U$.[12] All pathways to the production of ^{230}Pa or ^{230}U involve the separation of protactinium, uranium, and thorium in addition to proton and deuteron induced fission products.

Sulfur-based extraction ligands find use for the separation of a variety of elements including actinides from lanthanides.[36−42] However, a thorough search of the literature revealed that to date this does not include protactinium separations. In preliminary studies, we decided to test sulfur-based systems as previous work has shown some actinide selectivity for these systems.[43−45] In this work, both a commercially available (CL resin) and a custom synthesized chromatography resin were studied. Equilibrium distribution coefficients for these two sulfur-based extraction chromatographic resins were measured for protactinium along with thorium(IV), uranium(VI), actinium(III), radium(II), and niobium(V). The two resin systems studied were CL resin and diglycolthioamide (DGTA) resin (Figure 2). CL resin is available from Triskem. The resin support carries an organic solution of alkyl phosphine sulfides ($R_3P{=}S$) primarily designed for the separation of chloride and

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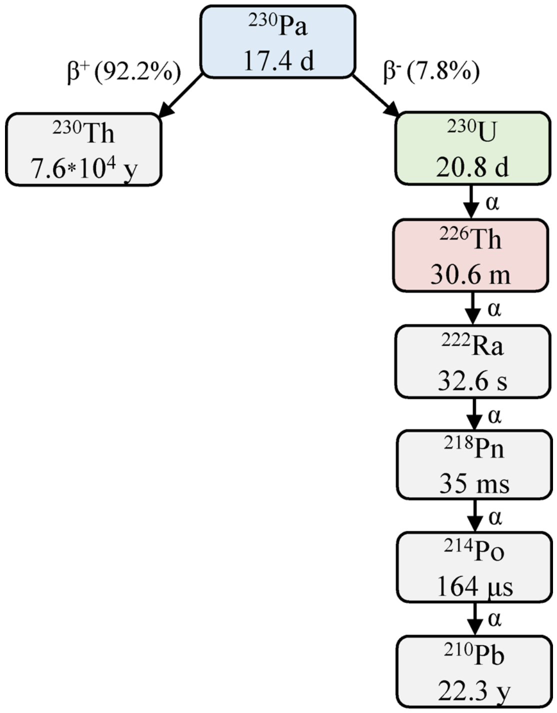

Figure 1. Decay scheme of ^{230}Pa.

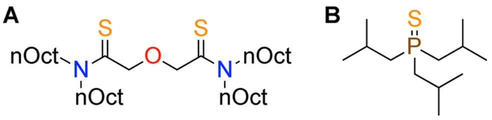

Figure 2. Structures of extractants in DGTA (A) and CL resin (B).

iodide ions from aqueous solutions after preloading the resin with silver ions.[46] DGTA resin, on the other hand, was prepared in-house: the DGTA extractant was first synthesized by modification of a previously published procedure;[47] the extractant was then adsorbed to an inert chromatographic support.

The separation of ^{230}Pa in high yield and purity from fission products and gram quantities of thorium was performed using both of the above-mentioned resin systems. Additionally, these resins were used to separate ^{230}U from ^{230}Pa in a radionuclide generator system after allowing sufficient time for the ingrowth of ^{230}U. The results from these separations in addition to the equilibrium distribution coefficients are reported within and have not been reported previously as determined by a thorough search of the literature.

■ EXPERIMENTAL SECTION

Reagents. All reagents used were trace metal grade unless specified elsewhere. Aqueous solutions were prepared with 18 MΩ water (Millipore). Thorium metal targets were manufactured at Los Alamos National Laboratory (LANL). Radionuclides used in this work as tracers were obtained from Oak Ridge National Laboratory or from in-house stocks. With the exception of ^{223}Ra and ^{227}Th, the radionuclides were obtained as byproducts from the proton irradiation of thorium targets for the production of ^{225}Ac.[22,48] Radium-223 and ^{227}Th were obtained via the decay of a ^{227}Ac source, and separated by published procedures.[49] *N,N,N′,N′*-Tetraoctyldiglycolamide extractant (Eichrom), Lawesson's reagent (Sigma-Aldrich), dry tetrahydrofuran (THF, Sigma-Aldrich), hexanes (Sigma-Aldrich), and silica gel (Sigma-Aldrich) were purchased. CG-71 resin was purchased from Dow chemical as a slurry in ethanol/water and converted to a dry form via filtration before use. DGA (50−100 μg) resin was obtained from Eichrom. Chloride (CL) resin (50−100 μg) was obtained from Triskem International.

High Purity Germanium Detector Analyses. All yields and purities from separation experiments were determined via γ-ray spectroscopy using an EG&G Ortec Model GMX-35200-S HPGe detector system in combination with a Canberra Model 35-Plus multichannel analyzer. Detector diameter was 50.0 mm, detector length was 53.5 mm, Be window thickness was 0.5 mm, and outer dead-layer thickness was 0.3 μm. Detector response function determination and evaluation were performed using standards of radionuclide mixtures containing ^{241}Am, ^{109}Cd, ^{57}Co, ^{139}Ce, ^{203}Hg, ^{113}Sn, ^{137}Cs, ^{88}Y, and ^{60}Co, traceable to the National Institute of Standards and Technology (NIST) and supplied by Eckert and Ziegler. The detector was a p-type Al-windowed HPGe detector with a measured fwhm at 1333 keV of approximately 2.2 keV and a relative efficiency of about 10%. Relative total source activity uncertainties ranged from 2.6% to 3.3%. Counting dead times were kept below 10%.

Synthesis of *N,N,N′,N′*-Tetraoctyldiglycolthioamide (DGTA) Extractant. To a stirred solution of *N,N,N′,N′*-tetraoctyldiglycolamide (1.5 g, 2.6 mmol) in 150 mL of dry THF, Lawesson's reagent (2.1 g, 5.2 mmol) was added. A drying tube was attached and the slurry was stirred at room temperature overnight (∼16 h) with a drying tube. The resultant yellow cloudy solution was filtered through a medium porosity frit and the solvent removed with rotary evaporation to give a gummy beige solid. This solid was then extracted with hexanes (3 × 10 mL) and the combined extracts were filtered through a short silica gel column (5 cm). The column was washed with 2 × 10 mL fractions of hexanes, and the solvent was removed by rotary evaporation to give *N,N,N′,N′*-tetraoctyldiglycolthioamide as a malodorous, viscous, yellow oil (790 mg, 50% yield). Subsequent batches (3 total) had yields varying from 50 to 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.57 (s, 4H), 3.90−3.78 (m, 4H), 3.64−3.53 (m, 4H), 1.77−1.58 (m, 8H), 1.39−1.20 (m, 40H), 0.95−0.83 (m, 12H).

Preparation of DGTA Extraction Chromatographic Resin. A total of 790 mg DGTA was added to a slurry of 1.8 g CG-71 resin in 15 mL of ethanol. The mixture was stirred on a rotary evaporator for 5 min before the solvent was slowly removed under vacuum. Note: when near dryness, use the minimal amount of vacuum necessary for solvent removal, as the fine resin is prone to severe bumping and loss into the rotary evaporator. The resulting free-flowing resin is approximately 30% w/w DGTA. The resin was then treated by high-vacuum and gentle heating (10 mTorr, 40 °C) overnight, giving 2.4 g of DGTA resin (there were slight losses due to transfer loss and bumping of the material under vacuum). Though unlikely, we cannot eliminate the possibility of remaining traces of ethanol.

Equilibrium Distribution Coefficients Measurements. Equilibrium distribution coefficients were determined for protactinium(V), uranium(VI), thorium(IV), niobium(V), radium(II), and actinium(III) using the batch mode. Each condition was run in triplicate. Approximately 50 mg chloride resin (CL resin) or diglycolthioamide resin (DGTA resin) were added to preweighed and tared 2 mL centrifuge tubes. A total of 1 mL of liquid phase (HCl variable concentrations ranging from 0.1 to 10 M) along with a 5 μL aliquot containing 5−15 kBq of ^{233}Pa, ^{230}U, ^{227}Th, ^{95}Nb, ^{223}Ra, and ^{225}Ac in 0.1 M HCl were added to each tube and weighed. The mixtures were vortexed and allowed to equilibrate for 24 h on a rocker at ambient temperature. The mixtures were filtered with 4 mm nonsterile hydrophilic polytetrafluoroethylene (PTFE) syringe filters 4 mm (0.2 μm, EMD Millipore), and the characteristic γ-ray lines (Table 1) of ^{233}Pa, ^{230}U, ^{227}Th, ^{95}Nb, ^{223}Ra, or ^{225}Ac in the filtrate were measured with a high purity germanium (HPGe) detector. Determination of ^{230}U and ^{225}Ac was performed by waiting 5−8 h to allow secular equilibrium to form between ^{230}U/ ^{226}Th or ^{225}Ac/^{213}Bi, respectively, and measuring characteristic ^{226}Th or ^{213}Bi γ-ray lines due to ^{230}U and ^{225}Ac having very weak γ-ray lines. The main γ-ray line for ^{226}Th coincides with an X-ray of ^{233}Pa; therefore, equilibrium distribution coefficients for ^{230}U were performed separately. The total activity in the aqueous phase was calculated from the filtered solution; the activity adsorbed on the resin was determined by subtraction of total aqueous activity from the total original activity added. Distribution coefficients were calculated using eq 1, where A_i is the initial activity, A_{eq} is the equilibrium activity in the aqueous phase, V is the volume of the equilibrium liquid phase (mL), and m is the mass of the resin (g). Considering the detection limit as dictated by signal-to-noise ratio, detector efficiency and reasonable counting time, the maximum distribution coefficient that could be measured under the experimental circumstances described above was ~10^5 mL·g^{-1} for Pa (V) and Nb (V) and ~10^4 mL·g^{-1} for all other isotopes measured.

Table 1. Characteristic γ-ray Lines of Radionuclides Used for Equilibrium Distribution Coefficients[35]

radionuclide	half-life (d)	identifying γ-ray emissions (keV) [% Intensity]
^{233}Pa	26.97	312 [38.6]/300 [6.62]
^{230}U (^{226}Th)	20.8	111 [3.29]
^{227}Th	18.68	235 [12.3]
^{95}Nb	34.99	765 [100]
^{223}Ra	11.44	269 [13.7]/154 [5.62]
^{225}Ac (^{213}Bi)	10.0	440 [26.1]

$$K_d = \frac{C_{eq1}}{C_{eq2}} = \frac{A_i - A_{eq}}{A_{eq}} \cdot \frac{V}{m} \qquad (1)$$

Separation of Protactinium from Bulk Thorium and Fission Products. Fission product and ^{230}Pa radionuclides used in this work were obtained from Oak Ridge National Laboratory (ORNL) as byproducts within a U.S. Department of Energy funded collaboration for the development of therapy isotope ^{225}Ac ($t_{1/2}$ = 10.0 d) by proton irradiation of thorium targets.[50] As proton-induced fission coincides with the formation of ^{230}Pa through the ^{232}Th(p,3n)^{230}Pa reaction, separation studies included fission products previously identified in high energy irradiations of thorium targets.[22,48] For ^{230}Pa separation studies, approximately 1 g of thorium metal (>99% purity as determined via X-ray fluorescence spectroscopy) was dissolved in 40 mL of 10 M HCl/0.01 M HF. This solution was then spiked with a small aliquot of fission products as well as ~185 kBq ^{230}Pa and contacted with a column containing 1 mL CL or DGTA resin equilibrated with 10 M HCl. The eluent was collected (fraction 1). An additional 20 mL of 10 M HCl in 5 mL fractions (fractions 2−5) was added to the column and each fraction was collected. Protactinium-230 was then eluted with 10 mL of 4 M HCl/0.1 M HF in two 5 mL fractions (fractions 6 and 7). Fractions 6 and 7 contained the radionuclide contaminant ^{95}Nb. Niobium-95 separation from these fractions was obtained by converting them to 10 mL of 10 M HNO_3 and adding to a column containing 1 mL of DGA resin equilibrated with 10 M HNO_3. The eluent was collected (fraction 8), and 20 mL of 1 M HNO_3 in 5 mL fractions (fractions 9−12) was added to the column to remove ^{95}Nb. Protactinium-230 was then eluted with two 5 mL fractions (fractions 13−14) of 4 M HCl/0.1 M HF. Each fraction was analyzed via HPGe for radiochemical analysis. A schematic of the separation is shown in Figure 3.

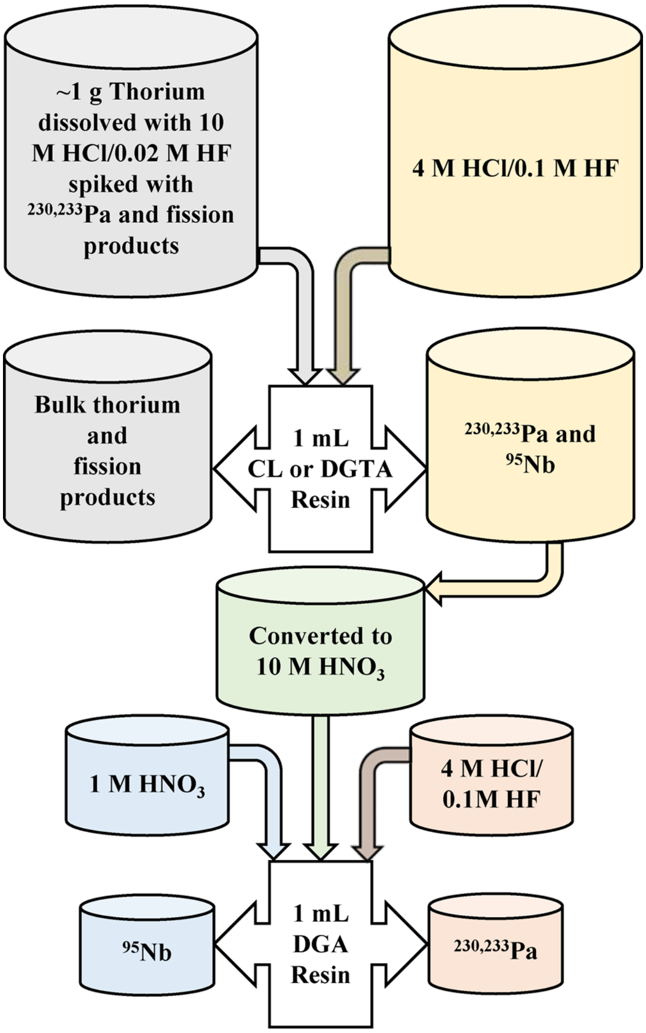

Figure 3. Schematic for the separation of $^{230/233}$Pa from bulk thorium and fission products.

■ RESULTS AND DISCUSSION

Synthesis of DGTA Ligand and DGTA Extraction Chromatographic Resin. By modification of previously published procedures,[47] the DGTA extractant was synthesized in reasonable yield (~50%). As compared to the previously published method, we avoided any aqueous workup or chromatographic separation beyond a simple silica gel filtration. The DGTA extraction chromatographic resin was prepared

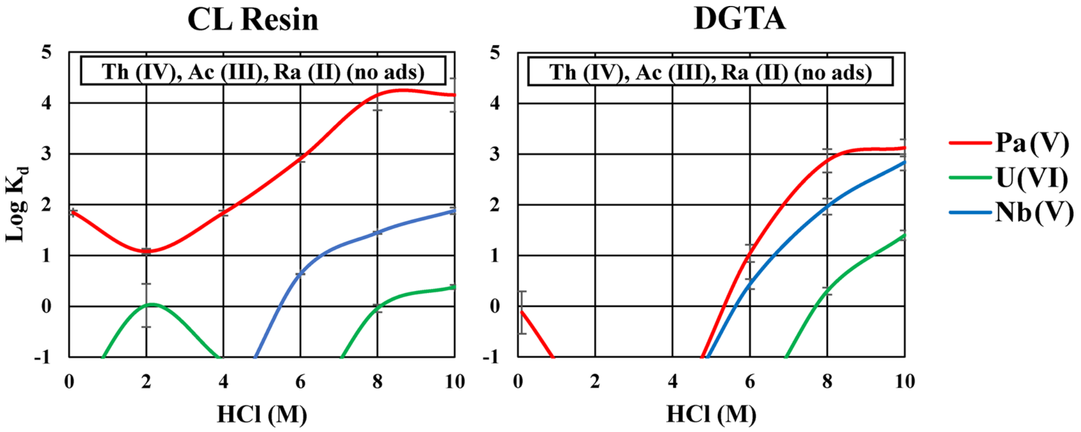

Figure 4. Equilibrium distribution coefficients K_d/[mL·g^{-1}] for Pa, U, Th, Ac, Ra, and Nb on CL and DGTA resin in hydrochloric acid concentrations ranging from 0.1 to 10 M. Thorium(IV), actinium(III), and radium(II) did not adsorb onto the resin.

analogously to DGA resin,[51] with only a minor solvent change due to the insolubility of DGTA in methanol.

Equilibrium Distribution Coefficients. The equilibrium distribution coefficients for protactinium, uranium, thorium, niobium, radium and actinium in hydrochloric acid on CL and DGTA resin were measured and are shown in Figure 4. At high (≥8 M) hydrochloric acid concentrations, protactinium is strongly adsorbed onto both CL and DGTA resin with K_d values of ∼10^4 mL·g^{-1} and ∼10^3 mL·g^{-1} respectively. At low hydrochloric acid concentrations (≤4 M), K_d values for protactinium are significantly lower with DGTA having lower affinity (<0.1 mL·g^{-1}) than CL resin (<100 mL·g^{-1}). Niobium has less affinity for both resins; however, the K_d values are still significant at hydrochloric acid concentrations ≥8 M, limiting the ability to separate niobium from protactinium using these resins. Interestingly, DGTA resin shows higher affinity for niobium, with K_d values approaching 10^3 mL·g^{-1}, under these conditions than with CL resin. Additionally, uranium (most likely present in the form of uranyl UO_2^{2+}) has a K_d value >10 mL·g^{-1} in 10 M HCl on DGTA resin and on CL resin its k_d values remain less than 2 mL·g^{-1}. Thorium, radium, and actinium exhibited no affinity for either resin in any of the conditions tested. These results establish the feasibility of these resins to separate ^{230}Pa from ^{230}U and bulk thorium.

Separation of ^{230}Pa from Bulk Thorium and Fission Products. Protactinium-230/233 was separated from bulk thorium and fission products with average final recovery yields of 93 ± 4% and 88 ± 4% with CL resin and DGTA resin, respectively. Protactinium radionuclidic purity reached >99.5% using both methods. The only measurable radioactive impurity consisted of ^{95}Nb, contributing <0.5% of the total radioactivity. Due to its chemical similarity to protactinium(V), niobium(V) was difficult to separate and therefore a residual contaminant. Niobium(V), breakthrough from a ^{230}Pa/^{230}U radionuclide generator could be easily removed employing normal DGA extraction chromatographic resin.[52] All fission products, with the exception of ^{95}Nb, were quantitatively removed using either CL or DGTA column. Residual ^{95}Nb was finally removed by the use of a column containing DGA resin. Both CL and DGTA resin are optimal for separating protactinium from thorium, however CL resin holds a slight advantage over DGTA resin for the separation of uranium from protactinium as DGTA resin requires several more column volumes of 10 M HCl to recover uranium. The higher affinity of protactinium and uranium for CL resin over DGTA resin may be due to the difference in electron density of the sulfur in thiocarbonyls vs phosphine sulfides.

The advantage of the use of sulfur containing resins over other reported methods is the ability to separate protactinium from both uranium and thorium in addition to a wide variety of fission products in one step with one concentration of acid. Anion exchange chromatography in combination with extraction chromatography has been used to separate protactinium from these contaminants, however the method is more complex and requires varying acid concentrations and multiple columns to obtain a comparable purity.[22] The advantage over liquid—liquid extraction methods is the elimination of mixed waste (organic with radioactive), which can be costly to dispose of. Newer methods, such as the use of TK400 resin, have not demonstrated the ability to separate protactinium from a wide variety of fission products.[32,33]

The use of sulfur-containing extraction chromatographic resins has been shown to be valuable for the selective separation of protactinium from a wide variety of contaminants. To the best of our knowledge, this is the first time protactinium has been shown to have an affinity for sulfur containing ligands. This is a major advantage as these systems have little to no affinity for thorium or uranium making them optimal for the separation of protactinium(V) from uranium(VI) or thorium(IV). This is an interesting result, which highlights the need for better characterization of the fundamental chemistry of protactinium. Future work should focus on understanding the thermodynamic properties of protactinium—sulfur systems in addition to that of their oxo-analogs. Additionally, experiments that probe the *f*-orbital involvement of these interactions would be of interest as complexation with soft donor atoms such as sulfur is generally considered more covalent in nature than those with hard donor atoms and covalency among the *f*-elements is of significant interest.[53,54]

■ CONCLUSION

A novel method for the extraction of protactinium from proton irradiated thorium matrices has been presented in our study. One of the resins utilized in our study has been custom synthesized at Los Alamos for the purpose of efficient separation of small Pa quantities from bulk thorium. This appears to be the first published use of sulfur-containing extraction chromatographic resins for the separation of protactinium as determined by a thorough search of the literature. This method results in a final protactinium chemical recovery yield of 88−93% with a radiochemical purity of >99.5%.

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Notes

The authors declare no competing financial interest.

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