# Separation of Gold from Irradiated Actinide Material Utilizing a 2- Thenoyltrifluoroacetone Extraction Resin

Evan Warzecha[1,*], Nic E. Uhnak[1], Ean Arnold[1], Kirby P. Hobbs[1], Chelsie L. Beck[1]

[1]Pacific Northwest National Laboratory, 902 Battelle Blvd., Richland, WA 99352, USA

[*]Corresponding Author, email: evan.warzecha@pnnl.gov

Keywords: Gold, Extraction Chromatography, Nuclear Forensics

## Abstract

Post-detonation nuclear forensics capabilities depend on the ability to rapidly isolate radionuclides to improve measurement quality. In this work an extraction chromatography resin was developed utilizing thenoyltrifluoroacetone and 1-octanol supported on Eichrom prefilter resin. The resin was tested in nitric and hydrochloric acid matrices. In nitric acid the resin was able to extract zirconium, while in hydrochloric acid matrices it was possible to extract iron and gallium. In all acid conditions tested, gold was retained but can be eluted from the column with 10% thiourea.

## 1. Introduction

Separation techniques with high selectivity are useful in a multitude of applications. The various nuclear fields and applications have a particular need for highly selective, fast separation techniques not only for cost savings but also for the short half-lives of the separation targets.[1-4] Many techniques have been developed to effect chemical separations including precipitations, distillations, solvent extraction, and chromatography. Solvent extraction is an excellent method to effect chemical separation, however, it poses some challenges including the generation of organic liquid wastes. Solvent extraction is well suited to large-scale continuous process applications, but when done at a bench scale the technique-dependent variability can be large. Post-detonation nuclear forensics applications are generally done at the bench scale; therefore solvent extraction is not the most reproducible option for separations.

The drawbacks of solvent extraction at the bench scale can be mitigated via the use of extraction chromatography.[5, 6] Extraction chromatography effectively reproduces the process of solvent extraction by immobilizing the organic extractant on an inert solid support. This allows the selectivity found in solvent extraction to be translated to a column chromatography context and minimizes the generation of organic solvent wastes.[7] Over the last several decades increasing interest has been applied towards extraction chromatography in the context of radiochemical separations.

Extensive effort into reprocessing, remediating, and analyzing nuclear fuels has produced a large body of research into extractants and extraction systems, largely targeting the removal of actinides and lanthanides from a system for reprocessing.[8] Organophosphates have been widely studied and modified to produce optimal separation conditions, resulting in the use of tributyl phosphate (TPB) in the PUREX (Plutonium Uranium Reduction EXtraction) process and similar phosphates have been used in post-PUREX or alternative solvent extraction schemes as well as in Eichrom's LN resins.[9-11] Diglycolamides have been successfully implemented into actinide-

selective processes like Diamex-Sanex or ALSEP (Actinide Lanthanide SEParation), and also have been also adapted to a successful extraction resin in Eichrom's DGA resin.[12-15]

The extractant of focus of this study, 2-thenoyltrifluoroacetone (TTA), did not make it into the major uranium or plutonium reprocessing schemes in modern use as it was outcompeted by the PUREX process extractants, largely TBP. Modern-designed systems also tend to target only CHON-containing extractants for environmental safety and sustainability concerns.[16] As TTA contains sulfur it is less favorable for consideration. Extensive study of its extraction ability and use was published based on this work and remains a valuable resource and remains a potential candidate in alternative extraction techniques such as supercritical fluid extraction.[17-20] TTA is an acidic $\beta$-diketone (pkA ~ 6.5) allowing it to behave as an extractant of a very large range of analytes through ion-exchange mechanisms while at appropriately high pH values for a given analyte. As the pH decreases TTA becomes a much more selective extractant, preferring to extract tetravalent ions such as $Zr^{4+}$, $Hf^{4+}$, $Np^{4+}$, $Pu^{4+}$, and $Th^{4+}$.[21] This increase in selectivity is driven by the decrease in the α proton lability, with increasing $H^+$ concentration. While most metal ions have greater affinity for TTA with increasing pH, notable exceptions exist with gold, iron, molybdenum, and technetium, which each have higher retention at very low pH and decreases with increasing pH.[19]

Gold is an attractive target for low-concentration harvesting due to its high value and low natural abundance. Mining techniques utilizing mercury are highly effective at extracting elemental gold and cyanide processes are effective at extracting gold from ores.[22] Gold harvesting from seawater has been successfully pursued utilizing $Mn_2O_3$ nanoparticles.[23] Electronic waste recycling, which can contain much higher concentrations of gold and other precious metals than ores, has been actively pursued for decades with several commercially successful processes developed.[24-26] These processes generally combine a physical separation like grinding or delamination with organic solvents to separate the metallic components, followed by isolation of gold through cyanide leaching or pyrometallurgy.[24, 27] Alternative leachate solutions including thiosulfate, thiourea, and $Cl_2$ in HCl have been utilized, however cyanide remains the most efficient.[28] Radiochemical separations of gold have focused on the precipitation via reduction to metal utilizing carrier methods or ion exchange chromatography.[22, 29] Recently an effective but low-yield separation of gold from a complex fission and activation product sample was demonstrated utilizing Sr resin.[30] A comparison of the major methods to the method presented in this work is shown in Table 1.

This existing body of knowledge makes TTA an ideal candidate for use in extraction chromatography. One previous publication utilized TTA embedded on a polyurethane support and thoroughly examined the thermodynamics of europium extraction, however the analysis of other analytes was limited to the separation from europium at pH 3.5.[31] This concept is expanded here where we examine an extraction resin consisting of TTA deposited on Eichrom prefilter resin and its use in and optimization of separation schemes for the isolation of $Fe^{3+}$, $Ga^{3+}$, $Au^{3+}$, and $Zr^{4+}$ from fission and activation product samples. High selectivity was determined by testing with a suite of stable analytes in nitric and hydrochloric acids. The effectiveness of the separations developed was verified by testing with irradiated fission and activation product samples.

## 2. Methods

## 2.1. Materials

Single and mixed-element standards were National Institute of Standards and Technology (NIST)-traceable from Inorganic Ventures. Deionized (DI) water was 18 MΩ from an in-house Millipore filtration system. TTA was obtained from Sigma-Aldrich and 1-Octanol was obtained from Fisher Chemical. All chemicals were used as received with no purifications.

## 2.2. Resin Synthesis

TTA/Octanol resin was prepared in 10 g batches by physical adsorption of the extractants to the resin support. A round-bottom flask was charged with 10 grams of pre-filter resin, 1.5 g each of TTA and 1-octanol, and enough acetone to fully cover the resin. Due to the light-sensitive nature of TTA, all containers were wrapped in foil to minimize the exposure of the resin to light and the final product was stored at 4 °C. The mixture was slowly spun on stirred on a rotary evaporator for 1 hour before the vacuum was activated to ensure an even coating. Once the resin appeared as a loose, free-flowing powder it was removed from the rotary evaporator and placed under vacuum for further drying. Synthesis of resin material was confirmed by electrothermal vaporization mass spectrometry measurement as described in section 2.7.2. After 72 hours the mass ceased changing and the resin was removed from vacuum. Prior to use, the TTA/Octanol resin was hydrated in DI water, 0.1 M $HNO_3$, or 0.1 M HCl for a minimum of 1 hour.

## 2.3. Screen Tests

Screen tests were performed utilizing mixed element standards and a 0.5 mL column of TTA/Octanol resin with an inner diameter of 0.8 cm. 100 µg of each analyte was combined and transposed into 1 mL of the target matrix (1, 3, and 9 molar solutions of HCl and $HNO_3$) to create a load solution. The load solution was added to the column and washed with 2.5 mL of the same matrix. Following the load fraction, several 2 mL rinses of varying matrices were flushed through the column and collected. All fractions were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis.

## 2.4. Sample Preparation

### 2.4.1. Stable test samples

Tests utilizing non-radioactive analytes were performed utilizing mixtures of multi-element tracers from Inorganic Ventures. Prior to use, aliquots of the mixed standards containing 530 µg per sample were transposed to the target load matrix by drying and redissolving in the target matrix. This was repeated a minimum of three times. After transposition was complete, an aliquot of the sample was prepared for analysis by ICP-OES to ensure initial loading conditions.

### 2.4.2. Fission product samples

Fission product-only samples were produced by irradiating highly enriched uranium (HEU) foils at the Massachusetts Institute of Technology Reactor. Aliquots for column samples contained $1x10^{12}$ fissions and were traced with 400 µg stable Inorganic Ventures standard for yielding.

### 2.4.3. Fission and activation product samples

A 7.7 mg HEU foil was double encapsulated in quartz ampules. Activation products were produced by irradiating Ir, Zn, Ta, W, Ga, Ni, Cr, Cu, and Au as salts in ½ dram polypropylene vials by drying down single element ICP-OES standards from Inorganic Ventures. Fe and Pt were irradiated as metal wires singly encapsulated in quartz ampules. The activation products and HEU were placed in the same port at the Dodgen Research Facility TRIGA reactor at Washington State University and exposed to a thermal fluence of 7.49*1015 N*cm-2 over 2 hours, as determined by analyzing several metal wires that were included in the outer ampule as flux monitors. Fluence was determined using the PNNL STAYSL software program21 after high purity germanium (HPGe) gamma analysis of the flux monitor wires. The samples were transported to PNNL for dissolution and initial screening via ICP-OES and HPGe. Each column sample was comprised of 1x1012 fissions and 1x108 atoms of activation products. Samples were transposed to immediately before addition to the column and were traced with 400 µg stable Inorganic Ventures standard for yielding. Fe and Pt were not traced in this way as the irradiated sample contained enough stable metal to yield with ICP-OES.

#### 2.4.4. Actinide test samples

Load solutions containing Th-232, U-238, Np-237, Pu-242, and Am-243 were generated by combining PNNL owned standard solutions of these isotopes, bringing the resulting solution to near dryness, and reconstituting them in 0.1 M $HNO_3$. The initial solutions contained Th-232 and U-238 at 1 ng/g while Np-237, Pu-242, and Am-243 were present at 1 pg/g. The load solutions were adjusted to pH 2 or pH 4 utilizing $NH_4OH$. Immediately prior to loading the solutions 0.05 mg $NaNO_2$ was added.

### 2.5. Column Separations

All separations were performed in triplicate and accompanied by a reagent blank containing no sample. Separations with fission products or fission and activation products were also accompanied by a tracer blank which included only the stable tracers. All blanks received identical processing to the samples.

#### 2.5.1. Stable, fission product, and mixed fission and activation product sample separations

Column separation experiments were carried out using Bio-Rad Poly-Prep® chromatography columns with 2 mL resin volumes and an 0.8 cm inner diameter. Prior to use, each column was conditioned by passing 5 mL of the acid matrix of the loading solution through the column. Conditioning was performed no more than one hour in advance of loading the column with sample. Loading solution for all samples was 5 mL in volume and followed by 3 times with 2 mL rinses to ensure transfer of the entire sample. The total volume for all collected fractions was between 10 and 20 mL. Elution schemes A and B were utilized for fission and activation product tests and samples and are shown in Table 2. Five percent of each fraction was prepared for ICP-OES analysis, while the rest of the sample was sent to gamma counting by HPGe or NaI detectors.

#### 2.5.2. Actinide Samples

Column separation experiments were carried out using Bio-Rad Poly-Prep® chromatography columns with 0.5 mL resin volumes. Prior to use, each column was conditioned by passing 2 mL of pH 2 or pH 4 $HNO_3$ matched to the loading solution. The samples were loaded and quantitatively transferred onto the column with 3 mL total volume. All subsequent rinses were 2.5 mL in volume. Table 3 shows rinse sequences for this experiment denotated as C and D. All samples were diluted to 2% $HNO_3$ with a total volume of 10 mL and analyzed by inductively coupled plasma mass spectrometry (ICP-MS).

### 2.6. ICP-OES

Yielding of stable analytes was done by ICP-OES utilizing a Thermo iCAP7600 with Qtegra software. Quantitation was performed using external matrix-matched standards for all analytes and accompanying check standards.

### 2.7. ICP-MS/MS

#### 2.7.1. Actinide Measurements

Analysis of the actinides was done via ICP-MS/MS using an Agilent 8900. The instrument was equipped with an integrated autosampler, a 100 µL·min-1 microflow PFA nebulizer (Elemental Scientific, Omaha, NE, USA), and a quartz double-pass spray chamber. The instrument was configured with an s-lens and Ni sampler/skimmer cones and was tuned maximize sensitivity at the high *m/z* range. The instrument was operated with Q1 as an ion guide and Q2 as a mass filter. Quantitation was performed using external matrix-matched standards for all analytes.

#### 2.7.2. Resin Synthesis Verification

Electrothermal vaporization (ETV) ICP-MS/MS was used to verify TTA/Octanol resin synthesis by using sulfur as a proxy for the presence of TTA. A Spectral Systems 4000d ETV was connected directly to the torch of an Agilent 8900. The instrument was configured with the same cones/lens as outlined above. Oxygen was used as a reaction gas in the collision reaction cell to mass shift S to SO with Q1 set to m/z = $M^+$ (32, 33, 34) and Q2 set to m/z = $MO^+$ (48, 49, 50). Pyrolytically coated graphite tubes and boats were used. A slow heat ramp (200 °C/min up to 1000 °C) was used due to the high amounts of sulfur expected from the TTA.

The pre-filter resin had no detectable amounts of sulfur above the background of the instrument (see Fig. 1). The TTA resin exhibited a sulfur peak from 100-300 °C that is ~30 times higher than the background spectrum when compared to the pre-filter resin. The sulfur peak appears at the boiling temperature of TTA at 100 °C confirming that TTA resin successfully adsorbed to the pre-filter resin.

### 2.8. Gamma detection

Gamma counting performed using Mirion HPGe detector systems utilized Canberra Genie 2000 V3.4.1 and APEX software. HPGe detectors are calibrated utilizing NIST traceable multi-isotope standards from Eckert and Ziegler. Gamma counting utilizing NaI detectors were performed with a PerkinElmer Wizard$^2$ system.

## 3. Results and Discussion

### 3.1. Screen tests

As a $\beta$-diketone, TTA can exist in the ketone form, an enol form, and an enolate form as shown in Fig. 2 The pKa value of TTA is 6.2, therefore in 1 M or greater acid concentrations examined here the enolate form is not expected to be the dominate confirmation. Excluding the enolate form from the coordination, should limit the coordination to a very limited selection of analytes. To confirm this, screening experiments were performed by passing a solution containing 100 µg of 40 transition metal and lanthanide elements each through a column at several $HNO_3$ and HCl concentrations. Different speciation conditions between $HNO_3$ and HCl lead to differences in extractability that can be leveraged for separations. When loading conditions of 1, 3, and 9 M $HNO_3$ matrices were tested, only gold showed strong retention in all conditions. There was some retention for $Tl^{2+}$, $Ir^{2+}$, and $Pt^{2+}$, however increasing rinse volume from two column volumes should allow for quantitative elution and prevent fractionation. Loading in HCl concentrations of 1 M and greater show similar results, with $Au^{3+}$ being quantitatively retained at all loading concentrations. The high affinity for sulfur bonds may explain the difference in behavior between gold and the rest of the analytes examined. $Tl^{2+}$ shows greater retention in HCl and is not completely eluted until $HNO_3$ rinses are used. 9 M HCl loading condition showed quantitative retention of $Fe^{3+}$ and $Ga^{3+}$. These results were used to develop separation schemes A and B (Table 1) depending on the initial sample conditions.

### 3.2. Column Separations

Separation A is intended for isolating gold from a sample in 3 M $HNO_3$. Loading this sample in 3 M $HNO_3$ allows most of the analytes to elute while gold will be retained. The following 9 M HCl rinse allows for recovery of any $Ag^{+}$ that was precipitated by the presence of trace $Cl^{-}$. Most analytes other than gold should have eluted from the column, allowing gold to be extracted by thiourea on its own. Thiourea is unstable in the presence of high acid concentrations, so a 0.1 M HCl rinse is added to protect the thiourea. Thiourea is effective at both dissolution of metallic gold and has a very strong affinity for coordination with $Au^{3+}$. This allows for the recovery of gold if the extraction method of gold by TTA resin is either coordination with the TTA extractant or reduction to metal on the column.[25, 32] The separation was tested with stable tracers with the results shown in Fig. 3. Unlike the screen tests, approximately 25% of the Pd was retained passed the load fraction and was recovered in the 9 M HCl fraction. The Pd retention was consistent at 25% over initial Pd concentrations of 290 to 520 µg/mL, suggesting it is not Pd plating out on the column being redissolved in later fractions. All other analytes behaved as expected, with only gold retained on the column until it was stripped by a 10% thiourea solution.

Separation A was also tested with a fission sample irradiated at the MIT Reactor. As detection limits can be much lower for radiometric counting techniques compared to ICP-OES, testing with radioactive analytes can reveal tailing not seen in stable testing. For example, 0.01% of a peak fission product like Mo-99 or Ba-140 would not be detected by ICP-OES but can interfere with isotopes with less favorable counting statistics or lower yields. As seen in Fig. 4, no radioactive materials were detected in the 10% Thiourea fraction where gold elutes.

An interesting artifact of using stable tracers is revealed in this experiment. The Zr-95 was retained in the fission sample test where Zr is not retained in the stable element tests. This discrepancy can be attributed to the presence of HF in the tests utilizing non-radioactive analytes. The mixed element tracer containing Zr and Nb has small amounts of HF to maintain the solution stability of those analytes. While the tracers are transposed before use, small amounts of HF likely remained due to its very strong coordination between $F^-$ and the Zr and Nb. Reports on the use of TTA as an extractant for Zr and Nb show that the presence of small amounts of HF inhibit the binding of TTA to Zr and Nb.[17] As HF was not present in the fission sample experiment, therefore Zr was able to be bound by the TTA extractant.

Separation B is intended for the isolation of $Fe^{3+}$, $Ga^{3+}$, and gold from a sample in 9 M HCl. Loading in 9 M HCl allows for the retention of $Au^{3+}$, $Fe^{3+}$, and $Ga^{3+}$. The $Fe^{3+}$ and $Ga^{3+}$ are then eluted in the 0.1 M HCl fraction. A test separation was performed using stable tracers; the results for this second separation are shown in Fig. 5. While only 62% of the $Fe^{3+}$ was eluted in this fraction, this can be improved by increasing rinse volumes and in future tests the rinse volumes were increased to 20 mL for all fractions. The $Ga^{3+}$ was recovered quantitatively, and no other elements were detected in this fraction. Neither gold nor $Tl^{3+}$ are recovered in either the load or initial rinse. Further testing revealed large retention of $Tl^{3+}$, therefor a 3 M $HNO_3$ rinse was added to ensure all $Tl^{3+}$ was removed prior to $Au^{3+}$ elution with 10% Thiourea.

Separation B was further tested using a freshly irradiated HEU produced at WSU in combination with several activation products and prepared as described in section 2.4.3. Additional rinses and increased rinse volumes were added to this separation to elute the Tl and Au separately and improve the Fe recovery. The stable yielding results are shown in fig. 6. The increased rinse volumes produced quantitative recovery of both Fe and Ga, but also prompted fractionation of the Tl between the first three fractions. No Tl was found in the 10% Thiourea fraction with the Au. The largest contaminant of the 0.1 M HCl fraction is the Tl, with small amounts of Mo, Ti, and W also found in this fraction.

The 0.1 M HCl fractions and 10% Thiourea fractions were sent for HPGe analysis. The Fe-59 was measured directly in the 0.1 M HCl fraction. The 10% thiourea fraction was dominated by Au-198 and Au-199. Small amounts of peak fission products (<0.1%) were present but did not interfere with the measurement of either gold isotope by either HPGe or NaI detector. Both separations A and B allow for the isolation of gold from radiochemically complex solutions while preventing fractionation of nearly all analytes examined in this work. This allows for the use of TTA resin in sequential separation schemes targeting many analytes. Ion exchange chromatography allows this to some degree, but the number of analytes is much more limited.

Retention of the actinides was not seen in the previous experiments, however literature reports suggest that some separation of the actinides can be achieved with TTA in solvent extraction when starting at high (>3) pH.[21] Separating a mixture of Th, U, Np, Pu, and Am was attempted utilizing the TTA/Octanol resin utilizing separations C and D. Fig. 7 shows the results of separation C while Fig. 8 shows the results of separation D. Loading the column at pH 4 should allowed for the retention of the actinides, while loading at pH 2 should have allowed the trivalent and pentavalent actinides to elute.

A shown by Fig. 7, none of the elements are quantitatively retained past the load fraction when loading with pH 2 $HNO_3$ in separation C. Best retained were Th-232 and U-238. Despite the addition of $NaNO_2$ to the load solution prior to the separation, the behavior of Pu indicates that there was incomplete oxidation state control. A comparison to separation D in Fig. 8 shows that the TTA/Octanol resin has the capacity to retain the actinides and a separation should be possible, however controlling the plutonium oxidation state and solubility was a difficult proposition at these higher pH conditions. Absent the presence of plutonium the rest of the actinides can be separated from each other utilizing separation scheme D. As Pu is an important analyte for nuclear forensics, optimizing the actinide separation schemes was not pursued and efforts were instead focused on modifying the extractant to facilitate the actinide separations including plutonium. These efforts are the focus of ongoing work and will be described elsewhere.

## 4. Conclusions

Two separations tailored towards post-detonation nuclear forensics applications have been developed for Au, Fe, Ga, and Zr utilizing an extraction resin containing 2-thenolyltrifluoroacetone and 1-octanol as the extractants. All acid conditions tested provided effective extraction of gold. Three molar nitric acid effectively extracted Zr, however the presence of fluoride blocks this extraction. Nine molar HCl allowed the extraction of Fe and Ga. The separation schemes were tested on fission samples from irradiated uranium foils as well as mixtures of fission and activation product samples. The high selectivity for the very limited number of analytes preserves the rest of the sample for continued analysis after this separation, allowing for the use of this resin in situations where sample quantity is limited. Separation of actinides with the TTA/octanol resin was attempted, however the difficulties of managing plutonium oxidation states at the pH ranges needed for extraction prevents this resin from being a good candidate for an actinide separation scheme.

## 5. Competing Interests

The authors declare no competing or conflicting interests.

## 6. Acknowledgements

This work was supported by the Office of Defense Nuclear Nonproliferation Research and Development within the U.S. Department of Energy's National Nuclear Security Administration and Pacific Northwest National Laboratory, which is operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC05-76RLO1830.

## 7. References

(1) Metz, L. A.; Payne, R. F.; Friese, J. I.; Greenwood, L. R.; Kephart, J. D.; Pierson, B. D. Experimental measurements of short-lived fission products from uranium, neptunium, plutonium and americium. *Journal of Radioanalytical and Nuclear Chemistry* **2009**, *282* (2), 373-377. DOI: 10.1007/s10967-009-0225-1.

(2) Finn, E.; Metz, L.; Greenwood, L.; Pierson, B.; Friese, J.; Kephart, R.; Kephart, J. Short-lived fission product measurements from >0.1 MeV neutron-induced fission using boron carbide.

*Journal of Radioanalytical and Nuclear Chemistry* **2012**, *293* (1), 267-272. DOI: 10.1007/s10967-012-1652-y.
(3) Pierson, B. D.; Finn, E. C.; Friese, J. I.; Greenwood, L. R.; Kephart, J. D.; Kephart, R. F.; Metz, L. A. Identifying and quantifying short-lived fission products from thermal fission of HEU using portable HPGe detectors. *Journal of Radioanalytical and Nuclear Chemistry* **2012**, *295* (3), 1881-1885. DOI: 10.1007/s10967-012-2109-z.
(4) Arrigo, L. M.; Greenwood, L. R.; Pierson, B. D.; Metz, L. A.; Friese, J. I. Radiochemical separations and experimental measurements of short-lived fission products from 14 MeV irradiation of depleted uranium. *Journal of Radioanalytical and Nuclear Chemistry* **2018**, *318* (1), 353-360. DOI: 10.1007/s10967-018-6115-7.
(5) Tranter, T. J. 13 - Solid-phase extraction technology for actinide and lanthanide separations in nuclear fuel reprocessing. In *Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment*, Nash, K. L., Lumetta, G. J. Eds.; Woodhead Publishing, 2011; pp 377-413.
(6) Lumetta, G. J.; Wester, D. W.; Morrey, J. R.; Wagner, M. J. PRELIMINARY EVALUATION OF CHROMATOGRAPHIC TECHNIQUES FOR THE SEPARATION OF RADIONUCLIDES FROM HIGH-LEVEL RADIOACTIVE WASTE. *Solvent Extraction and Ion Exchange* **1993**, *11* (4), 663-682. DOI: 10.1080/07366299308918180.
(7) Philip Horwitz, E.; McAlister, D. R.; Dietz, M. L. Extraction Chromatography Versus Solvent Extraction: How Similar are They? *Separation Science and Technology* **2006**, *41* (10), 2163-2182. DOI: 10.1080/01496390600742849.
(8) Hill, C. 11 - Development of highly selective compounds for solvent extraction processes: partitioning and transmutation of long-lived radionuclides from spent nuclear fuels. In *Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment*, Nash, K. L., Lumetta, G. J. Eds.; Woodhead Publishing, 2011; pp 311-362.
(9) Herbst, R. S.; Baron, P.; Nilsson, M. 6 - Standard and advanced separation: PUREX processes for nuclear fuel reprocessing. In *Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment*, Nash, K. L., Lumetta, G. J. Eds.; Woodhead Publishing, 2011; pp 141-175.
(10) Nash, K. L. The Chemistry of TALSPEAK: A Review of the Science. *Solvent Extraction and Ion Exchange* **2014**, *33* (1), 1-55. DOI: 10.1080/07366299.2014.985912.
(11) Philip Horwitz, E.; Kalina, D. C.; Diamond, H.; Vandegrift, G. F.; Schulz, W. W. THE TRUEX PROCESS - A PROCESS FOR THE EXTRACTION OF THE TKANSURANIC ELEMENTS EROM NITRIC AC In WASTES UTILIZING MODIFIED PUREX SOLVENT*. *Solvent Extraction and Ion Exchange* **1985**, *3* (1-2), 75-109. DOI: 10.1080/07366298508918504.
(12) Pourmand, A.; Dauphas, N. Distribution coefficients of 60 elements on TODGA resin: Application to Ca, Lu, Hf, U and Th isotope geochemistry. *Talanta* **2010**, *81* (3), 741-753. DOI: 10.1016/j.talanta.2010.01.008.
(13) Baron, P.; Hérès, X.; Lecomte, M.; Masson, M. Separation of the minor actinides: the DIAMEX-SANEX concept. In GLOBAL 2001, Paris, France; 2001.
(14) Gelis, A. V.; Lumetta, G. J. Actinide Lanthanide Separation Process—ALSEP. *Industrial & Engineering Chemistry Research* **2014**, *53* (4), 1624-1631. DOI: 10.1021/ie403569e.
(15) Madic, C.; Boullis, B.; Baron, P.; Testard, F.; Hudson, M. J.; Liljenzin, J. O.; Christiansen, B.; Ferrando, M.; Facchini, A.; Geist, A.; et al. Futuristic back-end of the nuclear fuel cycle with the partitioning of minor actinides. *Journal of Alloys and Compounds* **2007**, *444-445*, 23-27. DOI: 10.1016/j.jallcom.2007.05.051.

(16) Commission, E.; Research, D.-G. f.; Innovation; Hudson, M.; Madic, C. *High-level liquid waste partitioning by means of completely incinerable extractants*; Publications Office, 1998.
(17) Marsh, S.; Maeck, W.; Booman, G.; Rein, J. Improved 2-Thenoyltrifluoroacetone Extraction Method for Radiozirconium. *Analytical Chemistry* **1961**, *33* (7), 870-872.
(18) Poskanzer, A. M.; Foreman, B. M. A summary of TTA extraction coefficients. *Journal of Inorganic and Nuclear Chemistry* **1961**, *16* (3-4), 323-336. DOI: 10.1016/0022-1902(61)80507-1.
(19) Jackson, W. M.; Gleason, G. I. Distribution Studies of Radium and Other Metallic Elements between Thenoyltrifluoroacetone in Methyl Isobutyl Ketone and Aqueous-Solutions. *Analytical Chemistry* **1973**, *45* (12), 2125-2129. DOI: DOI 10.1021/ac60334a024.
(20) Wai, C. M.; Wang, S. F. Supercritical fluid extraction: metals as complexes. *Journal of Chromatography A* **1997**, *785* (1-2), 369-383. DOI: Doi 10.1016/S0021-9673(97)00679-1.
(21) Cary, S. K.; Livshits, M.; Cross, J. N.; Ferrier, M. G.; Mocko, V.; Stein, B. W.; Kozimor, S. A.; Scott, B. L.; Rack, J. J. Advancing Understanding of the +4 Metal Extractant Thenoyltrifluoroacetonate (TTA(-)); Synthesis and Structure of M(IV)TTA(4) (M(IV) = Zr, Hf, Ce, Th, U, Np, Pu) and M(III)(TTA)(4)(-) (M(III) = Ce, Nd, Sm, Yb). *Inorg Chem* **2018**, *57* (7), 3782-3797. DOI: 10.1021/acs.inorgchem.7b03089 From NLM PubMed-not-MEDLINE.
(22) Emery, J.; Leddicotte, G. W. *The Radiochemistry of gold*; Oak Ridge National Lab., Tenn., 1961. https://library.lanl.gov/cgi-bin/getfile?rc000062.pdf.
(23) Koyanaka, H.; Takeuchi, K.; Loong, C. K. Gold recovery from parts-per-trillion-level aqueous solutions by a nanostructured Mn2O3 adsorbent. *Separation and Purification Technology* **2005**, *43* (1), 9-15. DOI: 10.1016/j.seppur.2004.09.005.
(24) Rao, M. D.; Singh, K. K.; Morrison, C. A.; Love, J. B. Challenges and opportunities in the recovery of gold from electronic waste. *RSC Adv* **2020**, *10* (8), 4300-4309. DOI: 10.1039/c9ra07607g From NLM PubMed-not-MEDLINE.
(25) Syed, S. Recovery of gold from secondary sources—A review. *Hydrometallurgy* **2012**, *115-116*, 30-51. DOI: 10.1016/j.hydromet.2011.12.012.
(26) Bigum, M.; Brogaard, L.; Christensen, T. H. Metal recovery from high-grade WEEE: a life cycle assessment. *J Hazard Mater* **2012**, *207-208*, 8-14. DOI: 10.1016/j.jhazmat.2011.10.001 From NLM Medline.
(27) Manigandan, S.; Rajmohan, K. S.; Varjani, S. Current trends in gold recovery from electronic wastes. In *Current Developments in Biotechnology and Bioengineering*, 2020; pp 307-325.
(28) Wen, Q.; Wu, Y.; Wang, X.; Zhuang, Z.; Yu, Y. Researches on preparation and properties of sodium polysulphide as gold leaching agent. *Hydrometallurgy* **2017**, *171*, 77-85. DOI: 10.1016/j.hydromet.2017.04.008.
(29) Douglas, M.; Friese, J. I.; Greenwood, L. R.; Farmer, O. T.; Thomas, M. L.; Maiti, T. C.; Finn, E. C.; Garofoli, S. J.; Gassman, P. L.; Huff, M. M.; et al. Separation and quantification of chemically diverse analytes in neutron irradiated fissile materials. *Journal of Radioanalytical and Nuclear Chemistry* **2009**, *282* (1). DOI: 10.1007/s10967-009-0263-8.
(30) Herman, S.; Warzecha, E.; Stene, R.; Emerson, H.; Arbova, D.; Allen, C.; Uhnak, N.; RisenHuber, M.; Seiner, B.; Metz, L.; Beck, C. Evaluation of SR/ TEVA/ TRU triple stack for separation of activation products. *Journal of Radioanalytical and Nuclear Chemistry* **2024**. DOI: 10.1007/s10967-024-09379-9.
(31) Saeed, M. M. Adsorption profile and thermodynamic parameters of the preconcentration

of Eu(III) on 2-thenoyltrifluoroacetone loaded polyurethane (PUR) foam. *Journal of Radioanalytical and Nuclear Chemistry* **2003**, *256* (1), 73-80. DOI: 10.1023/a:1023300109423.
(32) Li, K.; Zhang, Y.; Li, Q.; Liu, X.; Yang, Y.; Jiang, T. Role of foreign ions in the thiourea leaching of gold. *Minerals Engineering* **2023**, *202*. DOI: 10.1016/j.mineng.2023.108265.

Table 1 Comparison of different methods for the isolation and recovery of gold

| Separation Method | TTA/Octanol Resin | Ion Exchange | Cyanide Leaching | Mercury Amalgamation | Selective Dissolution |
|---|---|---|---|---|---|
| Typical Gold Sample Form | Nuclear forensic samples | Aqueous waste, nuclear forensics samples | Gold-containing ores | Environmental samples | Electronic wastes |
| Final Gold Form | Thiourea solution | Acidic Solution | Cyanide Solution | Elemental Gold | Aqua Regia solution |
| Main Chemical Hazards | Strong acids | Strong acids | Cyanide exposure | Mercury exposure | Strong acids |
| Main Advantages | High recovery, High purity, fast separation | High purity | High recovery | Large scale collection | Large scale collection |

Table 2 Elution schemes for isolating gold

| | A | B |
|---|---|---|
| Load | 3 M $HNO_3$ | 9 M HCl |
| Rinse 1 | 9 M HCl | 0.1 M HCl |
| Rinse 2 | 0.1 M HCl | 3 M $HNO_3$ + DI $H_2O$ |
| Rinse 3 | 10% Thiourea | 10% Thiourea |

Table 3 Elution schemes tested for the separation of actinides. pH 2 and pH 4 solutions had $NO_3^-$ concentrations of 0.1 M.

| | C | D |
|---|---|---|
| Load | pH 2 $HNO_3$ | pH 4 $HNO_3$ |
| Rinse 1 | 0.01 M $HNO_3$ | pH 4 $HNO_3$ |
| Rinse 2 | 0.1 M $HNO_3$ + 0.1 M Ascorbic Acid | 0.01 M $HNO_3$ |
| Rinse 3 | 1 M $HNO_3$ | 0.1 M $HNO_3$ |
| Rinse 4 | 3 M $HNO_3$ | 1 M $HNO_3$ |

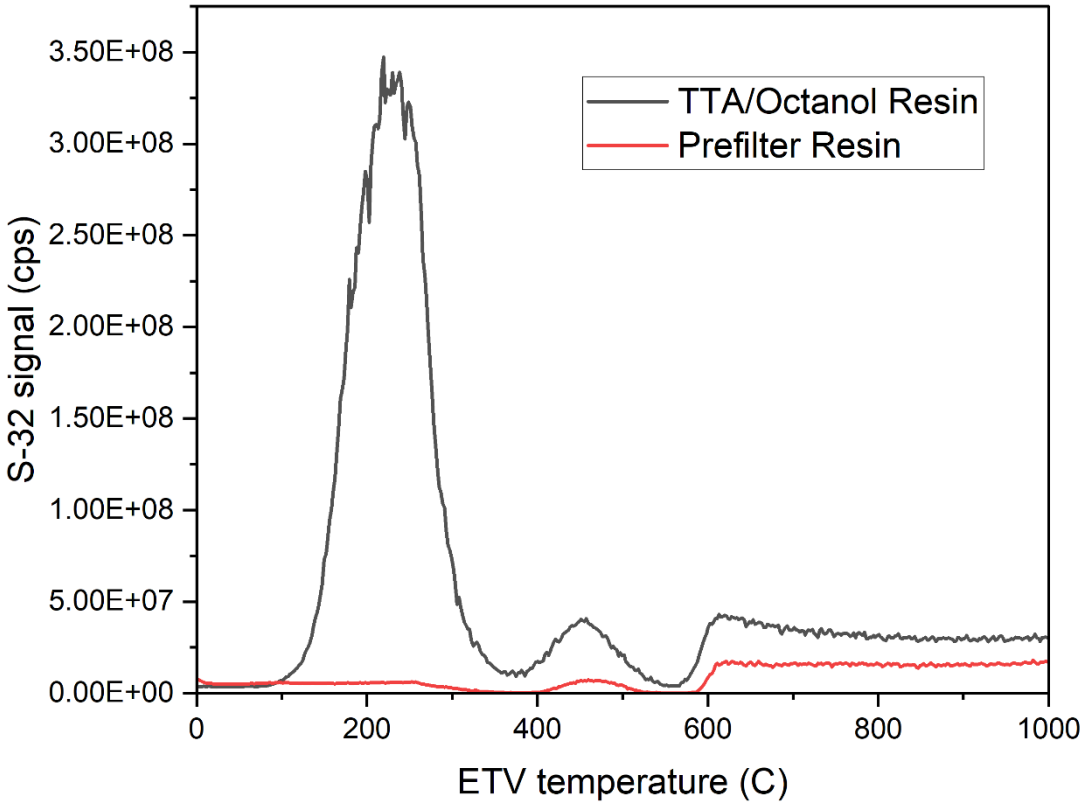


Fig. 1. Time-resolved analysis of sulfur in the Prefilter and TTA/Octanol resin. The x-axis is the temperature setpoint of the ETV calculated from the 200 °C/min heat ramp.

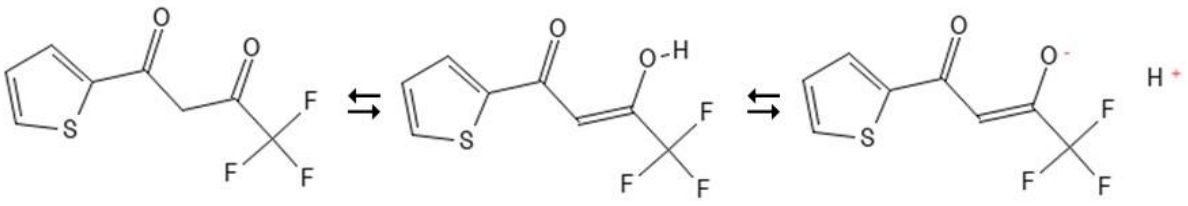


Fig. 2. Structure of TTA in solution. In the conditions examined in this work TTA likely exists in the enolate form

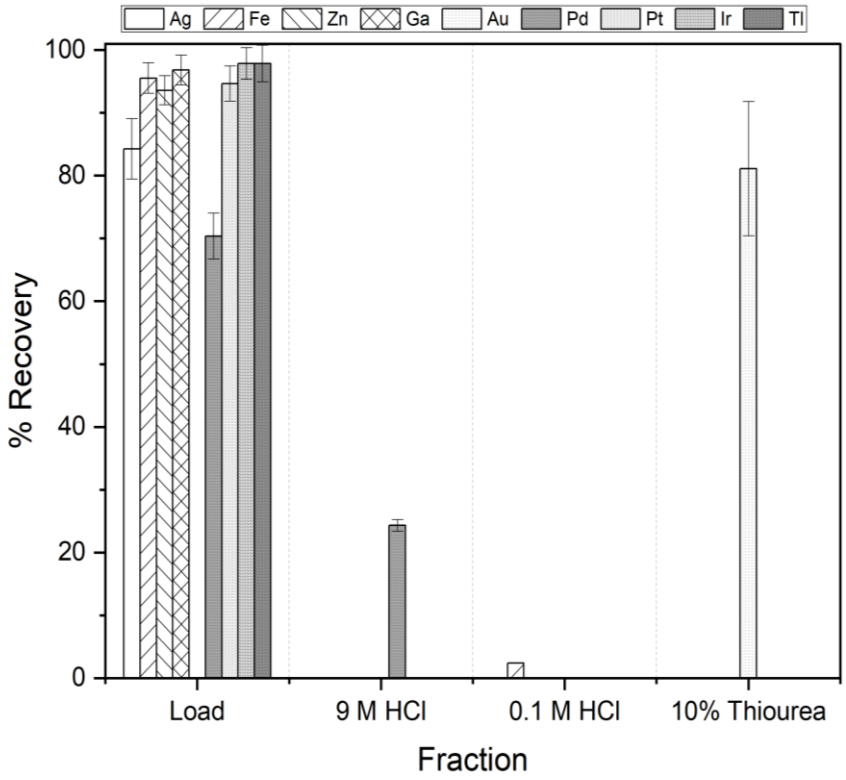


Fig. 3 The results of cold testing the TTA/Octanol resin separation A. Only a small selection of analytes are shown. The analytes that follow were also analyzed for but are only present in the load fraction: Ba, Be, Cd, Ce, Co, Cr, Cu, Eu, Hf, La, Li, Lu, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Ru, Sc, Sm, Sr, Ta, Tb, Ti, Tm, W, Y, Zr

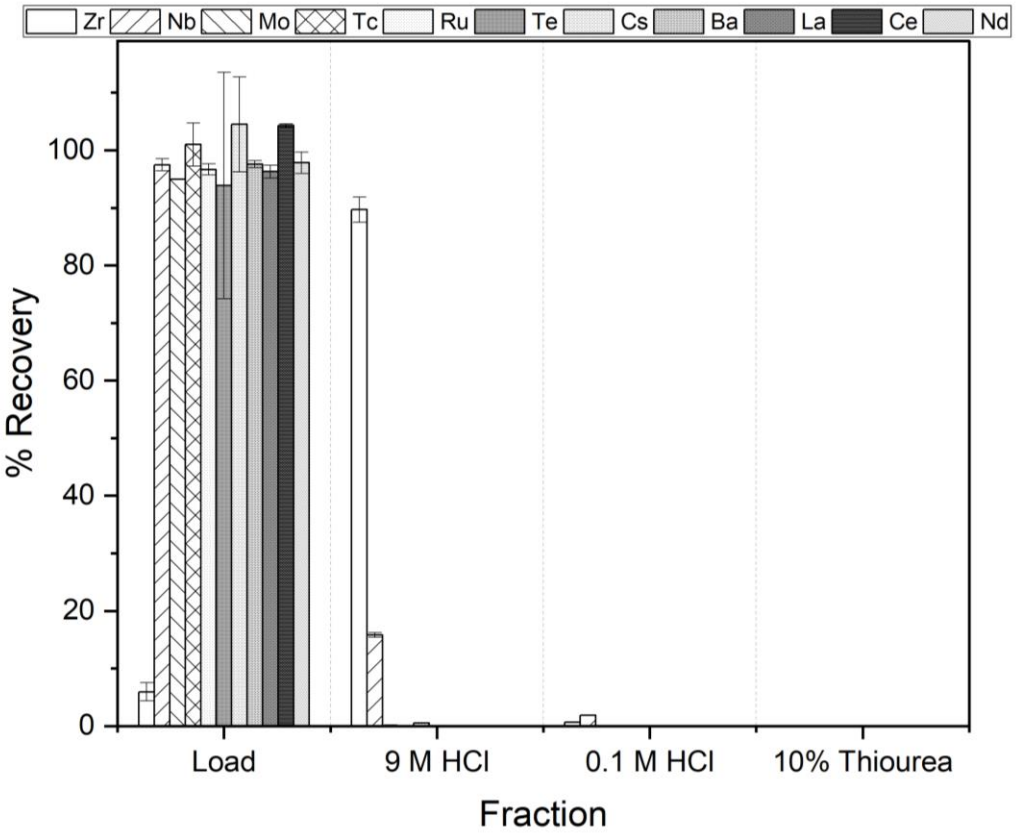


Fig. 4 Yield of measured isotopes by gamma emissions.

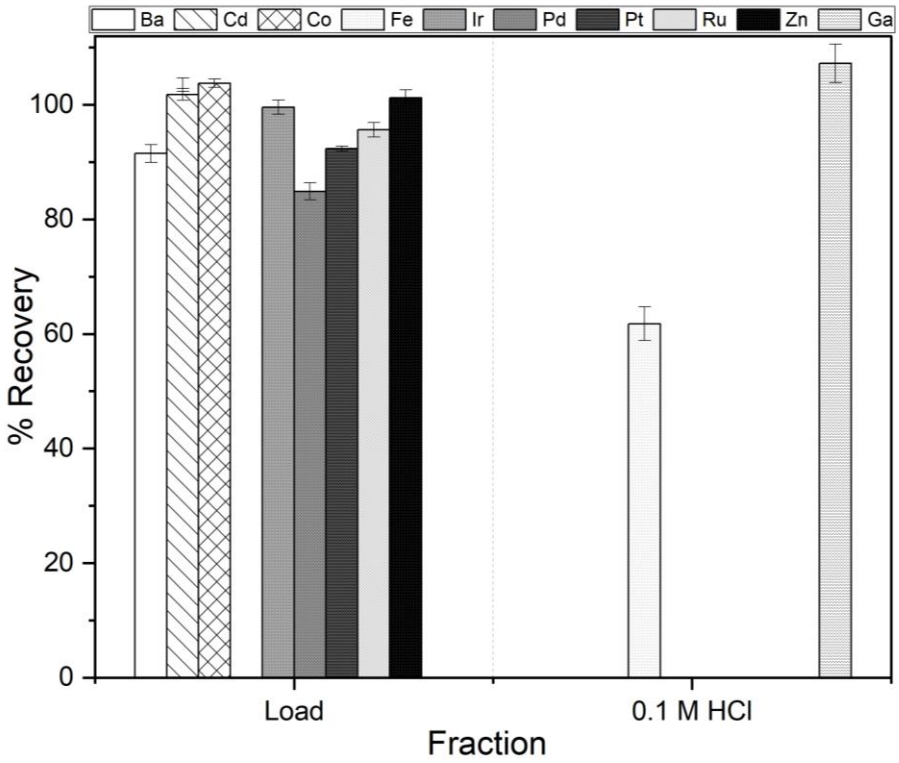


Fig. 5 The results of a test separation on TTA/Octanol resin. The load fraction consists of 16 mL 9 M HCl while the 0.1 M fraction is 10 mL in volume. The following analytes were also analyzed for but only detected in the load fraction: Be, Ce, Cr, Cu, Eu, La, Li, Lu, Mn, Na, Nd, Ni, Pb, Pr, Sc, Sm, Sr, Ta, Tb, Tl, Tm, W, Y. Au was also analyzed for but not detected in either fraction.

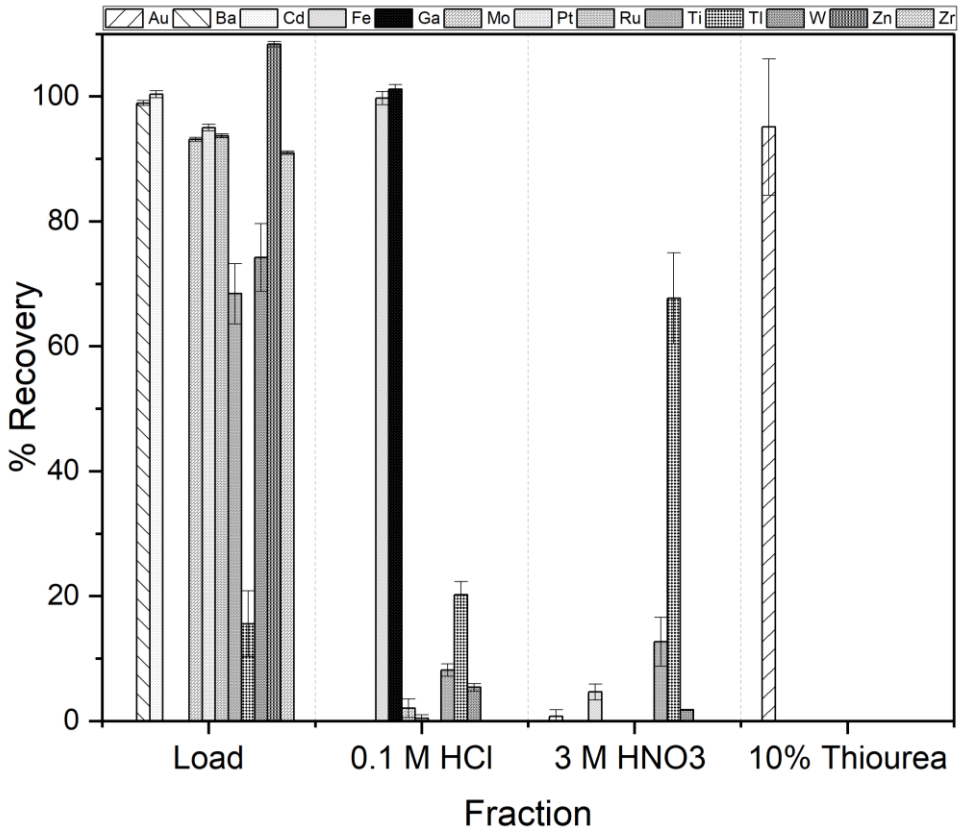


Fig. 6 Stable yielding results of separation B on a mixed fission and activation product sample. The following analytes were also analyzed for but only detected in the load fraction: Ag, Be, Ce, Co, Cr, Cu, Eu, Hf, Ir, La, Li, Lu, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pd, Pr, Sc, Sm, Sr, Ta, Tb, Tm, and Y.

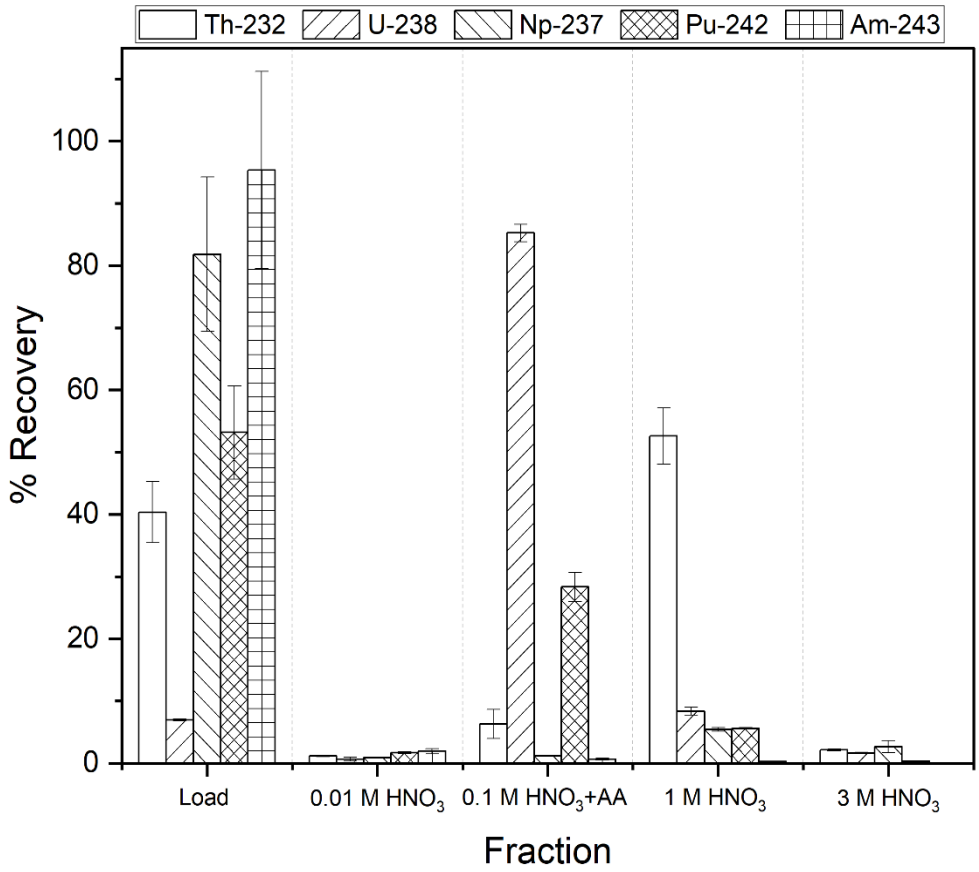


Fig. 7 Elution of actinides off TTA/Octanol resin loading with pH 2 $HNO_3$. AA is Ascorbic Acid.

494

495

496

497

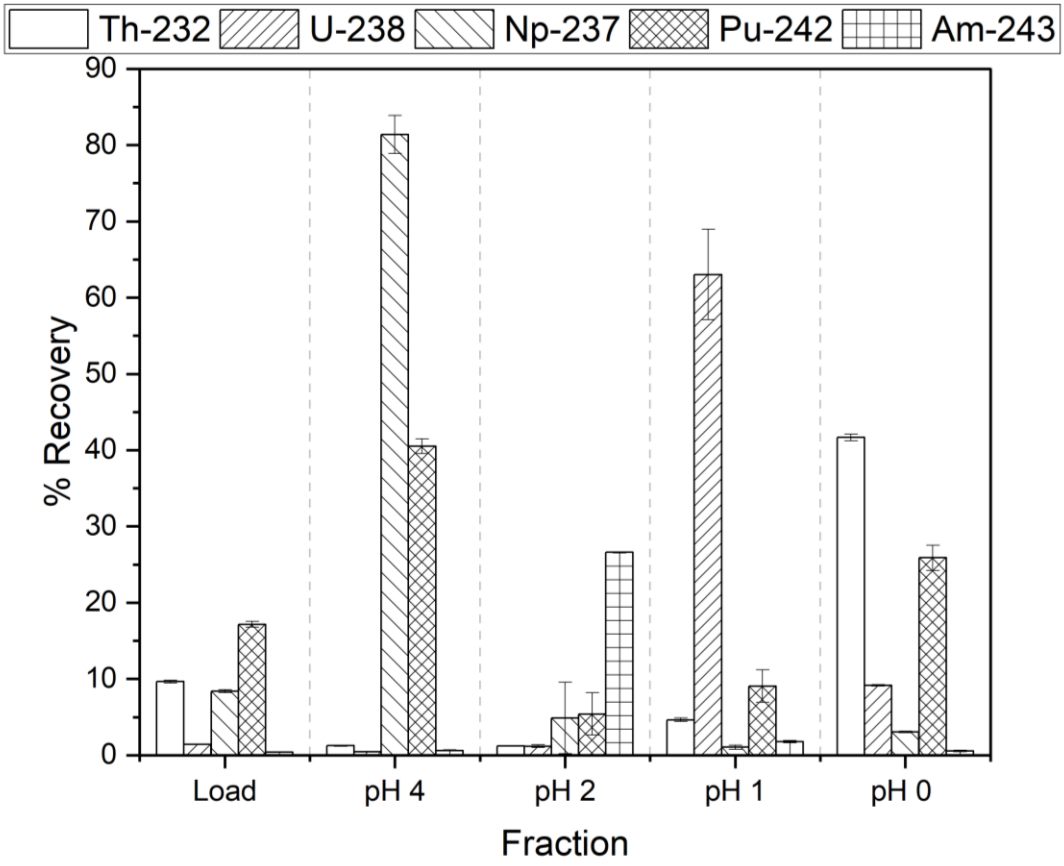


Fig. 8 Elution of actinides off TTA/Octanol resin loading with pH 4 $HNO_3$.

498

499

500