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Extraction of Pm-147 from Savannah River Site nuclear material management programs

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Abstract

The Savannah River Site (SRS) processes used-nuclear fuel to recover uranium. There are many interesting fission products lost in the raffinate from this separation including ^{147}Pm. The goal of this work was to recover ^{147}Pm from SRS waste solutions. A radiochemical separation method typically used for the determination of ^{147}Pm and ^{151}Sm was modified to purify significant quantities of ^{147}Pm from the H Canyon waste solutions. The developed scheme was tested on a small aliquot of waste solution from the processing of used fuel from the High Flux Isotope Reactor at Oak Ridge National Laboratory.

Keywords

radiochemical separation, promethuim-147, Savannah River Site, used nuclear fuel

Introduction

As part of ongoing nuclear materials management missions, the Savannah River Site (SRS) regularly receives highly enriched used nuclear fuel from foreign and domestic nuclear reactors. While awaiting processing, used fuel is stored in L Basin, the disassembly basin for the no-longer-operational L Reactor. H Canyon, SRS's radiologically-shielded chemical separations facility, processes the used fuel. SRS uses a modified PUREX process to extract uranium from the used fuel. First, the fuel assemblies are dissolved in nitric acid. Then, the solution is contacted with tributyl phosphate (TBP) multiple times to extract the uranium [1]. The extracted uranium is blended with natural uranium to reach commercial reactor grade enrichment specifications. The raffinate, which contains fission products, is transferred to SRS's liquid waste treatment facilities for disposal. It is either vitrified at the SRS Defense Waste Processing Facility or grouted on site in the SRS Saltstone Facility [1].

The raffinate is the focus of this work because it contains many fission products that are of scientific interest and are difficult to access elsewhere. One isotope of interest in the raffinate is ^{147}Pm [2, 3]. Promethium has no stable isotopes but is a prominent fission product. Recently, the Savannah River National Laboratory's Nuclear Measurements Group (NMG) was challenged to extract ^{147}Pm from SRS used fuel processing rather than dispose of it in the SRS liquid waste system.

The NMG provides boutique radioanalytical analyses for SRS, Department of Energy (DOE), and Department of Homeland Security (DHS) customers. These analyses require the development of novel radiochemical separations and counting techniques to measure radionuclides that cannot be assayed by commercial laboratories. The NMG has been analyzing high-activity waste for ^{147}Pm and ^{151}Sm for SRS customers for many years. In this work, that method was modified to purify significant quantities of ^{147}Pm from the H Canyon waste solutions.

SRS used-fuel raffinate from H Canyon processing is a high-dose and complicated matrix. The solutions have a high whole-body dose from ^{137}Cs and high extremity dose rate from ^{90}Sr and its daughter, ^{90}Y. The first step in many of the NMG's methods is to remove these high dose isotopes, often in the SRS Shielded Cells Facility. On top of the radioactivity, the chemistry of the SRS high level waste adds another degree of complexity. Promethium is one of many trivalent elements in SRS high level waste. Other prominent trivalent elements present in the H Canyon waste solutions include yttrium, americium, samarium, europium, and cerium. The goal of this work was to purify Pm from an H Canyon waste solution, so a scheme was developed to separate Pm from these trivalent elements.

Theory

The NMG Pm/Sm determination method uses Eichrom's LN Resin to separate the trivalent actinides [4]. The primary extractant in LN resin is di(2-ethylhexyl)orthophosphoric acid (HDEHP). Many researchers have demonstrated that the retention of the lanthanides on HDEHP is highly sensitive to the molarity of nitric acid (HNO_3) used in the extraction [5, 6, 7, 8]. Promethium is well retained on the LN resin in nitric acid concentrations less than 0.2M, but begins to elute as the concentration increases to 0.25M HNO_3. The retention of Pm on LN resin decreases with increasing concentration of HNO_3. In 0.20 M HNO_3 the k' value for Pm is approximately 20. In 0.30 M HNO_3 the k' is approximately 6.[6] LN resin has successfully been used for the separation of Pm by the NMG and others [9, 10, 11, 12]. Other methods to separate promethium from radioactive waste have also been tested and include batch solvent extraction with 50% tributyl phosphate and n-dodecane and ion exchange [13, 14].

Experimental

All resins were purchased from Eichrom Technologies and used as received. The 20 – 50 µm LN resin was used in this work. Cartridges and accessories (caps, frits, etc) were purchased from Eichrom Technologies and used without modification. Reagent or Optima grade HNO_3 was purchased from Fisher Scientific. The cartridges used in this work were prepared by packing ~ 0.5 grams of resin into an empty 2 mL cartridge from Eicrhom Technologies to form an approximately one-inch long resin bed.

The original NMG procedure for the Pm/Sm separation method is given in Fig. 1. The entire procedure, from digestion to detection, is shown. The sample is loaded onto the DGA resin (N,N,N',N'-tetra-n-octyldiglycolamide) in 2.5M HNO_3 to retain the trivalent rare earth elements and Am(III,IV, VI). Most other fission products are not retained on the DGA resin. The additional rinsing of the column ensures other fission products are not retained. The trivalent elements are eluted from the column with 0.1 M hydrochloric acid (HCl). Eichrom Technologies' RE resin is also oftern used instead of DGA resin at this stage. RE resin retains more Fe(III) in 2.5 M HNO_3 than DGA [15,16], so DGA is preferred for samples with high iron content.

This work focuses on the modification of this procedure to purify Pm and will focus on changes to the "Eichrom LN extraction" step. Typically, the Pm and Sm are eluted together with 0.35 M nitric acid. However, the goal of the work reported here was to separate the Pm from other trivalent elements, including Sm. To achieve this, the nitric acid molarity had to be carefully tailored.

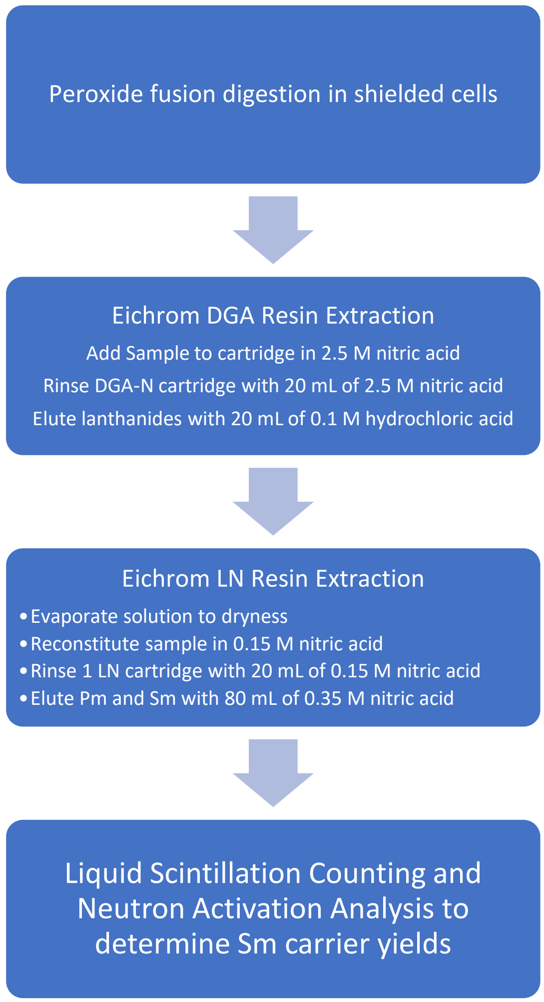

Fig. 1 Procedure for Typical Pm/Sm determinations in SRS High Activity Waste

Liquid Scintillation Counting

^{147}Pm is a pure beta emitter with Q_β of 224 keV [17]. The results given below are from liquid scintillation counts (LSC) of the samples. All LSC samples were counted on a Packard Tricarb. Each count was 10 minutes long. A blank containing 2 mL of nitric acid in 18 mL of Ultima Gold AD liquid scintillation cocktail was used counted with each sample set and background subtracted from each sample. Three regions were established in the LSC protocol. Region A ranged from 3.0 to 25.0 keV, region B ranged from 25.0 to 224.0 keV, and region C covered the whole range from 3.0 to 2000.0 keV. Region B was selected to identify the ^{147}Pm.

Method Development

A series of standards were tested to optimize the procedure and determine the nitric acid molarity necessary separate promethium from other trivalent elements. ^{241}Am and ^{151}Sm are used to demonstrate the methods ability to separate Pm from other trivalent elements in the matrix. ^{241}Am is retained on LN resin at the similar rate to Nd [6] at a given concentration of HNO_3. As such, if a procedure successfully separates Am and Pm, it can be expected to separate Nd and any lighter trivalent lanthanides. Sm is more strongly retained than Pm on LN resin at a given concentration of HNO_3 [6]. Previous work has shown that Eu through Lu are more strongly retained that Sm on LN resin at a given HNO_3 concentration. The successful separation of Pm from Sm indicates that heavier lanthanides (Eu-Lu) would be separated from Pm as well.

^{241}Am and ^{147}Pm Standard Test

To determine the acid concentration necessary to separate Am from Pm, 2 mL of a ^{147}Pm standard and 1 mL of ^{241}Am standard were dissolved in 10 mL of 0.15 M nitric acid. The ^{147}Pm and ^{241}Am standards were purchased from Amersham. The standard volumes were selected to provide an activity of approximately $1x10^5$ dpm,

The solution was passed through the LN resin cartridge under vacuum at a rate of 3 mL /minute. All 10 mL of solution were collected. Each rinse was labeled by its molarity and a sequential number, so this collected fraction was labeled 0.15-1. The column was rinsed with an additional 10 mL of 0.15 M nitric acid. This 10 mL was also collected (labeled 0.15-2) and analyzed. Then, the column was rinsed ten times with 10 mL of 0.22 M nitric acid. Each 10 mL rinse was collected. Finally, the column was rinsed with 10 mL of 0.35 M nitric acid.

To prepare each sample for LSC analysis, 2 mL from each rinse was added to 18 mL of Ultima Gold AB liquid scintillation cocktail. Fig. 2 shows the LSC results from the ^{147}Pm/^{241}Am test. The plot shows the activity of each analyte that was collected in a given fraction. The collected fractions are labeled by nitric acid molarity and rinse number. There were two rinses at 0.15 M nitric acid, ten at 0.22 M nitric acid, and one at 0.35 M nitric acid.

The ^{241}Am activity was identified by counts above 224.0 keV (region C minus regions A and B) and ^{147}Pm activity was identified by counts in the 3.0 to 224.0 keV region (region B). The Am eluted quickly with nearly 100% of the ^{241}Am detected in fraction 0.22-1. The Pm also began eluting with the first rinse of 0.22 M nitric acid. By the fifth 0.22 M nitric rinse, all the Pm had eluted from the column. To achieve improved separation of Am, additional rinses with 0.15 M nitric acid were added to future experiments. The recoveries of both ^{241}Am and ^{147}Pm were greater than 90%.

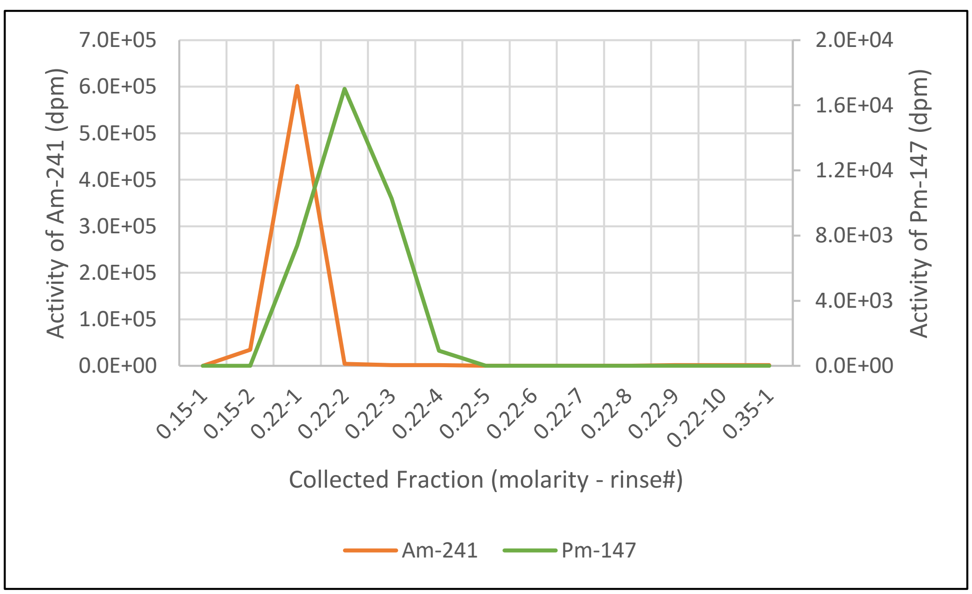

Fig. 2 Activity, in dpm, collected in a given fraction during the separation of ^{147}Pm and ^{241}Am for each analyte. The orange line depicts the ^{241}Am activity fraction and the green line depicts the ^{147}Pm activtiy fraction

^{151}Sm and ^{241}Am Standard Test

A second standard solution was used to test the separation of Am and Sm. Again, a 1 mL solution of an ^{241}Am standard was used. This time it was combined with 1 mL of a 3.8x10^{4} dpm/mL of ^{151}Sm standard from Eckert & Ziegler. As in the Pm/Am test, the standards were diluted in 10 mL of 0.15 M nitric acid. The procedure was similar to the Pm/Am test, except four rinses with 0.15 M nitric acid were used instead of two. The extra rinses were added to elute more of the Am before the 0.22 M nitric acid was used to elute the Sm. The results of this experiment are shown in Fig. 3.

^{151}Sm activity is identified by counts in the 3.0 – 25.0 keV region. The Am eluted quickly with the 0.15 M nitic acid. The majority of the ^{241}Am eluted with the 0.15 M rinses, only 34% of the ^{241}Am activity was detected in the first rinse of 0.22M nitric acid. The Sm was first detected in the after the third rinse of 0.22 M nitric acid. This was not favorable to separating Pm and Sm in the solution. An adjustment was necessary to cleanly separate Pm from Sm. For the final test, with all three standards, the molarity of the nitric acid was lowered from 0.22 to 0.20 M to slow the elution of Pm and Sm and give a more complete separation. Both standards were recovered well during the separation. The ^{241}Am recovery was 99% and the ^{151}Sm recovery was 94%.

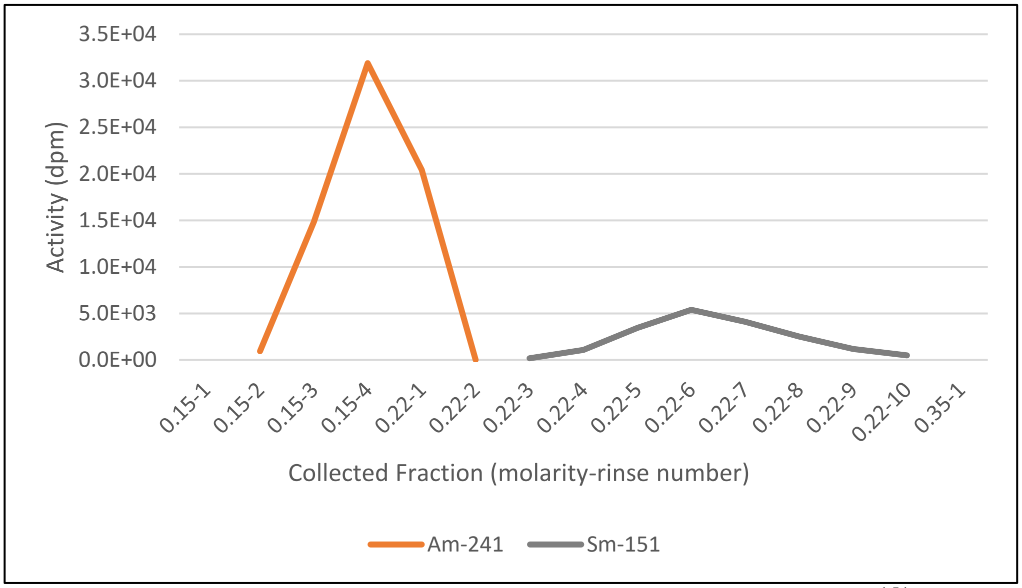

Fig. 3. Activity, in dpm, collected in a given fraction during the separation of ^{151}Sm and ^{241}Am. The orange line depicts the ^{241}Am activity fraction and the gray line depicts the ^{151}Sm activtiy fraction

^{147}Pm, ^{151}Sm, ^{241}Am Standard Test

For this experiment all three of the standard solutions were combined and diluted in 10 mL of 0.15 M nitric acid. The procedure was the similar to the Sm/Am test. The volume of each of the 0.15 M nitric acids rinses was increased from 10 mL to 20 mL. The molarity of the nitric acid used to elute the Pm and Sm was reduced from 0.22 M to 0.20 M.

The results are shown in Fig. 4. As above, the horizontal axis gives the collected fraction number, shown as molarity-rinse number. The vertical axis shows the activity, in dpm/mL, of each analyte. With the increased rinse volume, all the ^{241}Am eluted in the 0.15 M nitric acid rinses. The ^{147}Pm began eluting with the first rinse of 0.20 M nitric acid. By the fourth 0.20 M nitric acid rinse all the ^{147}Pm had eluted. The ^{151}Sm began slowly eluting with the fourth rinse with 0.20 M nitric acid and peaked in the fifth rinse. These results show excellent separation of the three analytes. The same procedure was used for the separation of ^{147}Pm from a sample from H Canyon.

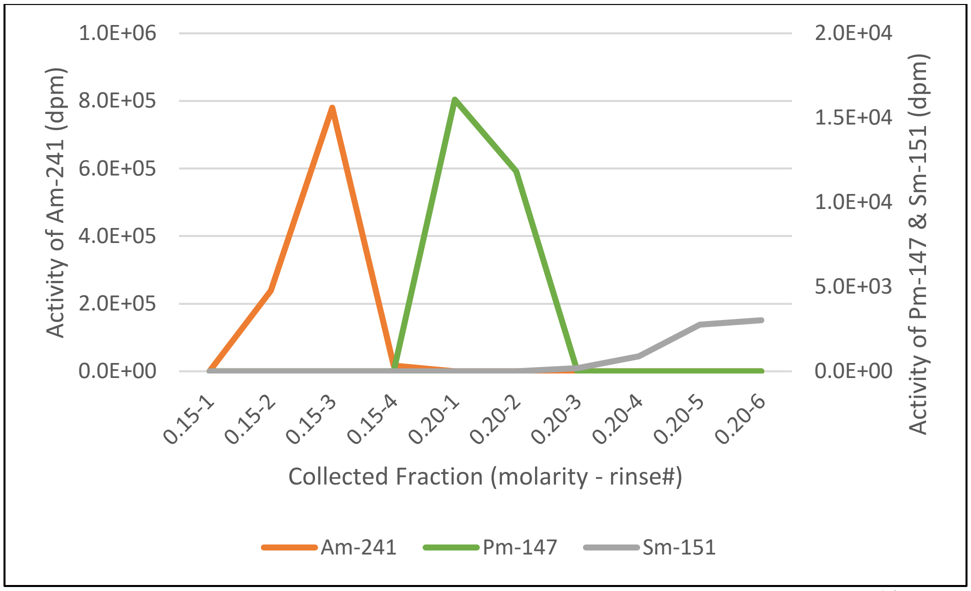

Fig. 4 Activity, in dpm, collected in each fraction during the separation of ^{147}Pm, ^{151}Sm, and ^{241}Am. The orange line depicts the ^{241}Am activity fraction, the green line depicts the ^{147}Pm activtiy fraction and the gray line depics the ^{151}Sm activity fraction

Results and discussion

^{147}Pm Separation from H Canyon Tank 12.3 Sample

The SRNL NMG had several milliliters of material from the chemical processing of fuel from the High Flux Isotope Reactor (HFIR). The fuel was processed in SRS H Canyon facility. The samples came from H Canyon Tank 12.3. The material in Tank 12.3 has already been through the dissolution process but has yet to go through the PUREX process. This sample had a 0.015 Rem/hr whole body dose and an 8 Rem/hr extremity dose. In this experiment, 1 mL of the sample from Tank 12.3 was used. This material was removed from the reactor roughly 10 years ago. This volume of material should contain approximately $1x10^8$ dpm/mL of ^{147}Pm. This is estimated based on the age of the material and the activity of other fission products present in the sample. Fresher material (3-5 years old) would be necessary to purify significant quantities of ^{147}Pm from nuclear materials management programs waste. This sample is high in other dissolved trivalent metals (i.e. Al, Fe, etc…) so DGA resin was used instead of RE resin. ^{147}Pm is primary Pm isotope present in this material.

The procedure used to extract Pm from the Tank 12.3 material is shown in Fig. 5. The first step in separating the ^{147}Pm from the sample was to remove the ^{137}Cs. This was done by striking the sample with ammonium molybdophosphate (AMP). Removing the ^{137}Cs reduces the whole-body dose of the sample prior to loading it on the column. The large amount of ^{137}Cs in this sample necessitates a dedicated extraction step.

Then, the trivalent elements were separated from the uranium and any other fission products by contacting the samples with Eichrom's DGA normal resin. The trivalent elements are retained on DGA in 2.5 M HNO_3 while other fission products and uranium are not. The additional rinse with 20 mL of 2.5 M HNO_3 ensures only the trivalent elements remain on the column.

The DGA column is then rinsed with 0.1 M HCl to strip the trivalents off the of the column. Prior to the extraction on the LN resin, the sample was evaporated to dryness, to remove any residual HCl from the matrix, and reconstituted in 0.15 M HNO_3. The sample was then loaded on to the LN column. As shown in previous experiments for this work, Pm and Sm are retained on LN resin in 0.15 M HNO_3. The rinse volumes were increased to 30 mL to ensure Am, Y and Ce were stripped from the column. Pm and Sm were then eluted from the column in 0.20 M HNO_3. As shown above, Sm is more strongly retained on LN resin in 0.20 M HNO_3 so it eluted more slowly than the Pm. The elution with 0.20 M was done over six rinses of 30 mL each. Finally, Eu and other higher Z trivalent rare earth elements, which are more strongly retained on LN resin than Sm, were stripped from the column with 0.35 M HNO_3. ^{154}Eu activity is used to confirm that it was separated from the Pm.

The high activity in this sample resulted in some challenges in the separation. High dose points (8 Rem/hr extremity) were encountered as hot particles were filtered out of the sample by the AMP. When the trivalents were evaporated to dryness prior to eluting through the LN resin, the dose increased to 14 Rem/hour. The dose rate remained elevated, at 2 Rem/hr, while extracting the trivalent elements on the LN cartridge.

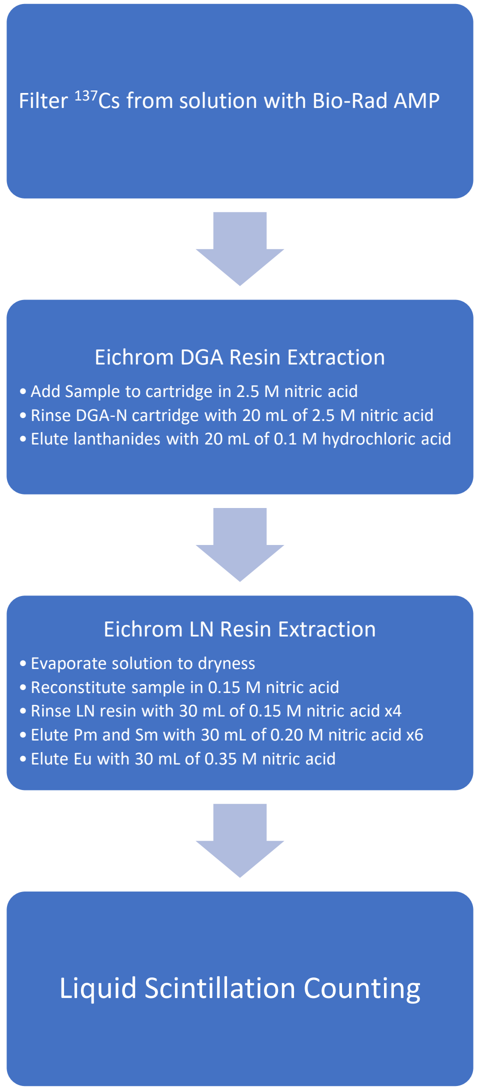

Fig. 5 Procedure for the separation of ^{147}Pm from a Tank 12.3 Sample

The results from this separation are shown in Fig. 6. The ^{241}Am eluted in the 0.15 M nitric acid rinses. The LSC results also indicate that other beta emitters such as ^{90}Y were eluted in the first 3 rinses. Gamma measurements identified ^{144}Ce in the first rinse and confirmed the presence of ^{241}Am in the first 3 rinses. The ^{147}Pm began eluting in the fourth rinse with 0.15 M nitic acid, though 99% of the recovered ^{147}Pm activity was detected in fractions 0.20-1 and 0.20-2. Combined they contain approximately 1.5x10^{8} dpm ^{147}Pm. This is a good recovery of the approximately 1x10^{8} dpm of ^{147}Pm expected in 1 mL of the sample from Tank 12.3. Approximately 3.6x10^{7} dpm of ^{147}Sm were collected in aliquots 0.20-4, 0.20-5, and 0.20-6. A final rinse was done with 0.35 M nitric acid and ^{154}Eu was detected in the eluate. Future work could further demonstrate the purity of the Pm fractions and demonstrate the removal of all other radioactive materials. This work demonstrates that the procedure given in Fig.5 can separate Pm from Am and Sm in a sample of material from the SRS Liquid Waste processing facilities.

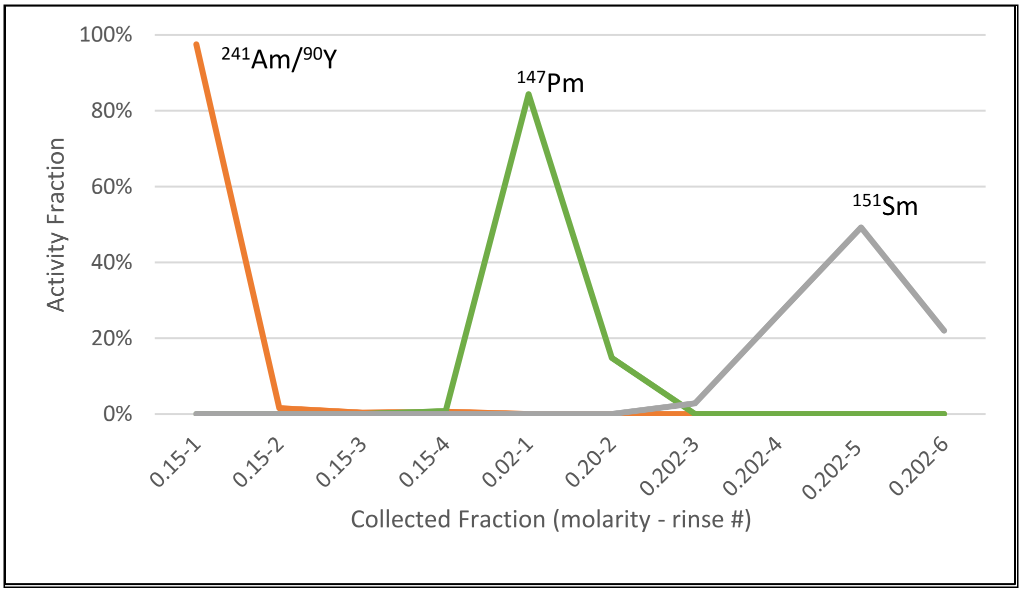

Fig. 6 Fraction of activity from each analyte that was collected in a given fraction during the separation of ^{147}Pm and ^{241}Am. The orange line depicts the ^{241}Am activity fraction and the green line depicts the ^{147}Pm activtiy fraction

Conclusions

The SRNL nuclear measurements group successfully modified a method designed to determine Pm and Sm in high activity waste to extract ^{147}Pm. Several standards tests were completed and concluded that 0.20 M nitric acid was ideal for separating Pm from the other trivalent elements in SRS high activity waste solutions. The method was used to extract 1.5×10^8 dpm of ^{147}Pm from material from SRS's H Canyon radiochemical reprocessing facility.

Acknowledgements

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Conflict of Interest Statement (COI)

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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