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Analytical Radiochemical Method Development for Mark 18A Program

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EXECUTIVE SUMMARY

The Savannah River National Laboratory Nuclear Measurements Group was tasked by the Mark 18A Program team with developing three analytical characterization methods. These methods will support process and waste characterization of the Mark 18A program material. While methods already existed for most analytes of interest to the Mark 18A program team, the Nuclear Measurements Group developed and refined methods to quantify the Cf isotopes, ^{107}Pd, and ^{121m}Sn. The results of that effort are presented in this work. Methods were successfully developed to characterize the Mark 18A samples for the needed isotopes and the NMG is ready to receive Mark 18A program samples.

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LIST OF ABBREVIATIONS

CP&C	Chemical Processing and Characterization
DGA	N,N,N',N'-tetra-n-octyldiglycolamide
DMG	Dimethylglyoxime
DWPF	Defense Waste Processing Facility
HCL	Hydrochloric acid
HDEHP	di(2-ethylhexyl)orthophosphoric acid
HNO_3	Nitric Acid
Ln	Lanthanides
LSC	Liquid scintillation counting
NMG	Nuclear Measurements Group
SRNL	Savannah River National Laboratory

1.0 Introduction

The Mark-18A team requested that Savannah River National Laboratory (SRNL) Chemical Processing and Characterization (CP&C) group evaluate the feasibility of the analytical work required once the Mark-18A mission enters production (1). Based on the list of analytes provided by the Mark-18A team three methods required development in preparation for the Mark-18A program. A method previously developed for ^{121m}Sn for samples from the Defense Waste Processing Facility (DWPF) was adapted to the Mark-18A project sample matrix. The ^{107}Pd method was refined to ensure that the detection limit is low enough to quantify ^{107}Pd in the Pu oxide material stream. The existing Cf method was modified to analyze some additional californium isotopes within the Mark-18A matrix that are not routinely measured in CP&C.

The Mark-18A targets used a feedstock from an irradiated Mark 42 targets to generate ^{242}Pu. The ^{242}Pu oxide was mixed with an aluminum oxide. The Mark-18A targets were manufactured with ^{242}Pu and then irradiated under high neutron flux in K-Reactor at the SRS from 1968 to 1978. The fission product challenges from the dissolved Mark-18A target material will be like the challenges of measuring the various fission products in the Canyon dissolvers. The CP&C Nuclear Measurements Group (NMG) will measure samples from the plutonium product stream following the Reillex separation, from the americium/curium stream calcined from a DGA column, the waste stream and likely other steps throughout the process as requested by the Mark-18A program team. The data quality requirements for shipping were the most stringent, so they were the focus of the study. Other process samples will be submitted for analytical characterization as outlined in the "Mark-18A Programmatic Sampling Strategy" (2).

As part of the "Mark 18A Feasibility Analysis" (1) several assumptions were made about the samples that would be received for analytical characterization from each Mark 18A process stream. Those assumptions are given in Table 1-1. The work presented here is based on these same assumptions.

Table 1-1. Mark 18A Material Stream Assumptions for Analytical Characterization

Mark 18A Material Stream	Assumptions
Am/Cm/Ln Stream	Am/Cm/Ln material stream is collected in a 750 mL (~280 g) column of DGA
	The activity (dpm/g) in the DGA resin containing the Am/Cm/Ln material stream will be diluted by a factor $4x10^3$ to reach $1x10^8$ dpm total alpha (or 0.2 mg of DGA)
	1 mL of sample solution will be used for each method
	If any detection limits need to be lower, additional sample could be used for a given analysis
Pu Oxide Stream	CP&C will receive a 20 mL sample containing $1x10^9$ dpm alpha
	The activity in the Pu oxide will be diluted $3x10^4$ times to reach $1x10^9$ dpm alpha
	10 mL of solution will be used for ICP-ES
	1 mL of sample solution will be used for each radiochemistry method and mass spectroscopy
	If any detection limits need to be lower, additional sample could be used for a given analysis
	The Pd is expected to be retained on the Reillex column or sock filter and not elute with the Pu. (3).

The analytical characterization of the Am/Cm/Ln stream will support the Mark 18A program in shipping the material as a Type A shipment to ORNL. The estimated activities in the Am/Cm/Ln material were compared to estimated NMG detection limits based on the assumptions above for all isotopes of interest in a Type A shipment and to the Mark 18A program. The estimated activities were from reference (4) and were based the average ¼ target expected in the Mark 18A program. Two deficiencies were identified in the NMG analytical capabilities: a Cf method and a Sn-121m method. A Sn-121m method has already been developed by will need modified to reach the detection limits required for the Mark 18A program.

The analytical characterization of the Pu stream will support the Mark 18A program in shipping the material as a Type B shipment to ORNL. Similarly, to the Am/Cm/Ln stream, the estimated activities in the Pu Oxide product for ¼ targets were compared to detection limit estimates for the NMG methods for isotopes of interest. Again, the lack of a Cf method was an issue. It is estimated that there would be 4.64×10^8 dpm ^{107}Pd in a ¼ target. The detection limit for the ^{107}Pd method is 8×10^7 dpm/1/4 target. A detection limit this close to the expected value could result in process samples that have ^{107}Pd activities below the detection limit.

For process and waste samples, the aliquots used in the various methods may need to vary depending on the sampling point, but the method described below can remain the same. Further, other clean up steps, may be necessary and will require communication between the Mark 18A program and CP&C as to where the sample is from in the process. Samples from early in the process could have large ^{137}Cs and ^{90}Sr impurities that need removed. CP&C has well established methods to achieve these clean up steps. The goal of this work was to demonstrate the CP&C could characterize the samples to meet the shipping requirements.

1.1 Analytical Characterization and Method Development

The NMG at the SRNL is providing analytical support to the Mark-18A recovery program. While the NMG already provides radiochemical analyses for most of the isotopes of interest to the Mark-18A program, some research and development (R&D) was required to determine Cf activities in the Mark-18A matrix. Additionally, development work was needed to improve the ^{107}Pd and ^{121m}Sn methods to reach the required detection limits.

2.0 Cf method Experiments and Results

The proposed method involves a clean-up step with N,N,N',N'-tetra-n-octyldiglycolamide (DGA) followed by a dilute acid separation with Eichrom's LN resin.(1) Following the separation, the samples will be analyzed with gamma-ray spectroscopy. A portion of the R&D was focused on assessing the Eichrom's LN resin for the purpose of separating Cf from the Mark-18A matrix. The DGA clean up step will not be required, but can be utilized as needed, for the Mark 18A program samples already treated with DGA.

2.1 LN Resin

LN resin is made up of di(2-ethylhexyl)orthophosphoric acid (HDEHP) on an inert support.(1) For this work, ~2 mL (0.5 g) cartridges were prepared from 50 – 100 µm LN resin. LN resin has demonstrated success in the separation of lanthanides and actinides for decades. Figure 2-1 shows the k' values, or number of free column volumes to peak, for a variety of elements on LN resin (5). Generally, the lower the k' value the more likely the element is to elute from the column.

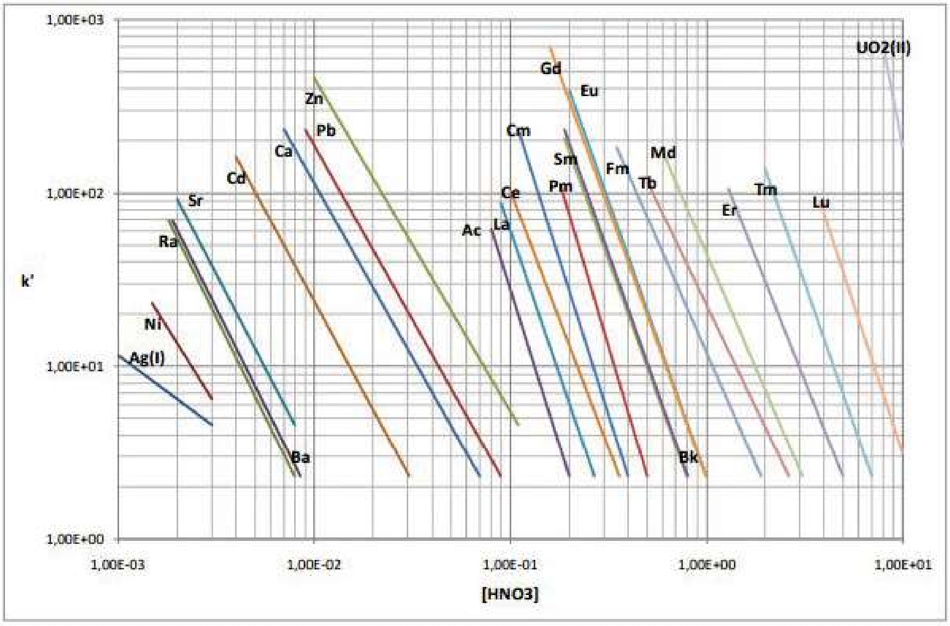

Figure 2-1. k' values of different elements on LN resin as a function of nitric acid concentration (5)

2.2 Characterization of stable lanthanides on LN resin

To characterize the LN resin, a series of stable lanthanides were extracted from a reference solution on an LN resin cartridge. The reference solution was prepared by combining the following in 0.2 M HNO_3:

- 1 mL of Eu solution (1 mg/mL)
- 0.5 mL of Nd solution (2 mg/mL)
- 0.5 mL of Ce solution (2 mg/mL)
- 0.5 mL of Sm solution (2 mg/mL)
- 1 mg of Gd
- 1 mg of Tb
- 1 mg of Ho
- 1 mg of Er.

The lanthanide solutions were evaporated to dryness before being reconstituted in 0.2 M HNO_3. The solvent for each of the lanthanide solutions was DI water. The procedure for that experiment is as follows:

1. Loaded two 2 mL LN resin cartridges, in series, with ~ 100 ppm each of 8 stable lanthanides (Ce, Nd, Sm, Eu, Gd, Tb, Ho, and Er) in 10 mL of 0.2 M HNO_3
2. Rinsed with an acid series from 0.20 M to 0.40 M HNO_3
    1. Additional 50 mL of 0.2 M HNO_3 (60 mL Total)
    2. 90 mL of 0.25 M HNO_3
    3. 90 mL of 0.30 M HNO_3
    4. 150 mL of 0.35 M HNO_3
    5. 150 mL of 0.40 M HNO_3
3. Analyzed rinses using ICP-MS

The two 2 mL cartridges provided a bed volume of 4 mL of resin. The column rinses were collected in 30 mL increments. Each rinse volume was analyzed by ICP-MS. The primary focus of this test was the Lns that eluted between 0.25 and 0.35 M HNO_3, where the Cf is expected. The larger rinses at the end were done to encourage the elution of the more well retained Lns. The results are consistent with prior characterizations of LN resin. Figure 2-2 shows the elution curves for the lanthanides from the LN resin. The measured k' values agree with those in the literature. Resin cartridges were used as they provide flexibility in adjusting the bed volume, if needed, with minimal additional waste and safety risk to the worker.

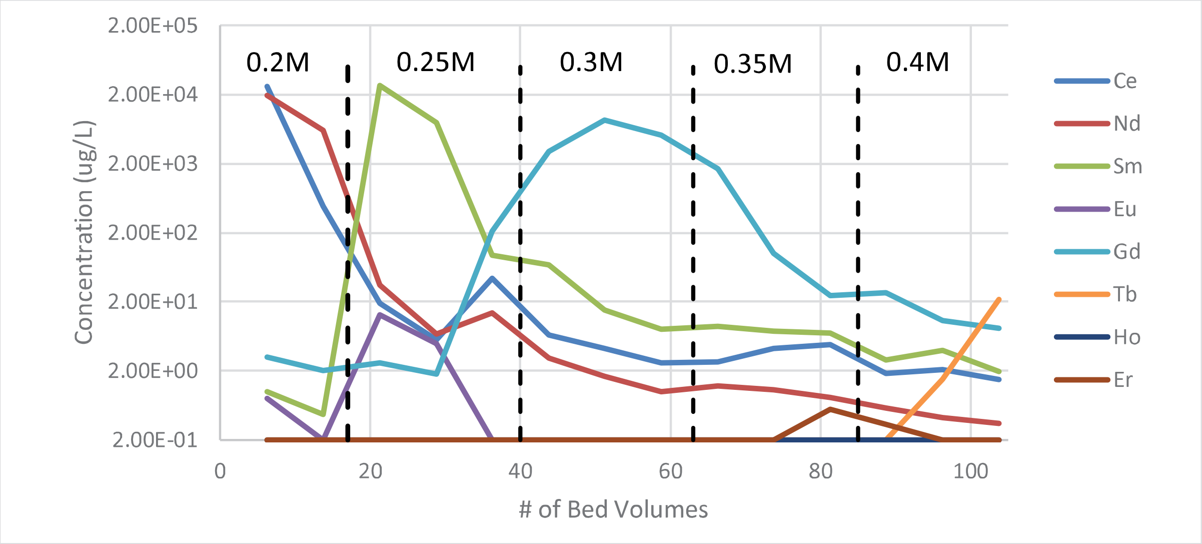

Figure 2-2. Concentration of lanthanides (ug/L) vs # of bed volumes from the separation of 8 stable lanthanides with LN resin

2.3 Separation of Cf, Eu, and Am

An experiment was performed to evaluate the retentions of Cf, Am, and Eu in a reference solution on the LN resin. The reference solution consisted of 1.08×10^4 dpm of ^{249}Cf, 3.57×10^4 dpm of ^{154}Eu (Standard Eckert and Zeigler ^{154}Eu, 1480-93-9 Dilution #2), 5.40×10^3 dpm of ^{241}Am (Standard Amersham ^{241}Am Solution S3/21/5 Dilution #1) in 1 M HNO_3. Before the standard solution was loaded on the column it was reconstituted in 0.2 M HNO_3. The procedure was based on the one used in the Ln test described above and was as follows:

1. Loaded two 2 mL LN resin cartridges, in series, with ^{249}Cf, ^{241}Am, and ^{154}Eu in 10 mL 0.2 M HNO_3
2. Rinsed with an acid series from 0.20 M to 0.40 M HNO_3
    1. Additional 50 mL of 0.2 M HNO_3 (60 mL Total)
    2. 90 mL of 0.25 M HNO_3
    3. 90 mL of 0.30 M HNO_3
    4. 90 mL of 0.35 M HNO_3
    5. 90 mL of 0.40 M HNO_3
3. Analyzed rinses using gamma-ray spectroscopy
4. Repeated separation with narrower acid concentration 0.26 M – 0.3 M to further assess Eu and Cf separation

As expected, ^{241}Am eluted from the column with the 0.2 M rinse. Only 60 mL of 0.2 M HNO_3 were used because previous work had demonstrated that the Cf would not elute in 0.2 M HNO_3 and the ^{241}Am eluted readily. ^{154}Eu began eluting after 30 bed volumes of 0.25 M HNO_3. All the ^{249}Cf eluted with the 0.30 M rinse. There is significant overlap between the Eu and Cf elutions. The presence of Eu in the Cf stream, raised the background in the gamma measurement. This can be compensated for by doing additional rinses with the 0.25 M HNO_3 flush.

The pre-existing Am/Cm method, with some tailoring based on the information learned from the studies shown above and knowledge of the process sampling point, will provide the necessary decontamination and recoveries for Cf. The method is described below.

A DGA cleanup step will be required to separate the trivalent elements, including Am, Cm, and Cf, from other fission products in the sample as needed based on the process sampling point. The samples will be evaporated to dryness and reconstituted in dilute (0.1 M) nitric acid. Then, they will be loaded on to Ln resin in 0.1 M HNO_3. The Am can be separated with 40 mL rinses of 0.25 M HNO_3. Then, the Cf eluted in 40 mL of 0.3 M HNO_3. The eluted liquid will be evaporated to dryness and redissolved in 6 mL of 1.0 M HNO_3. A 5 mL gamma sample will be prepared and 2 alpha plates to check and correct for contaminants.

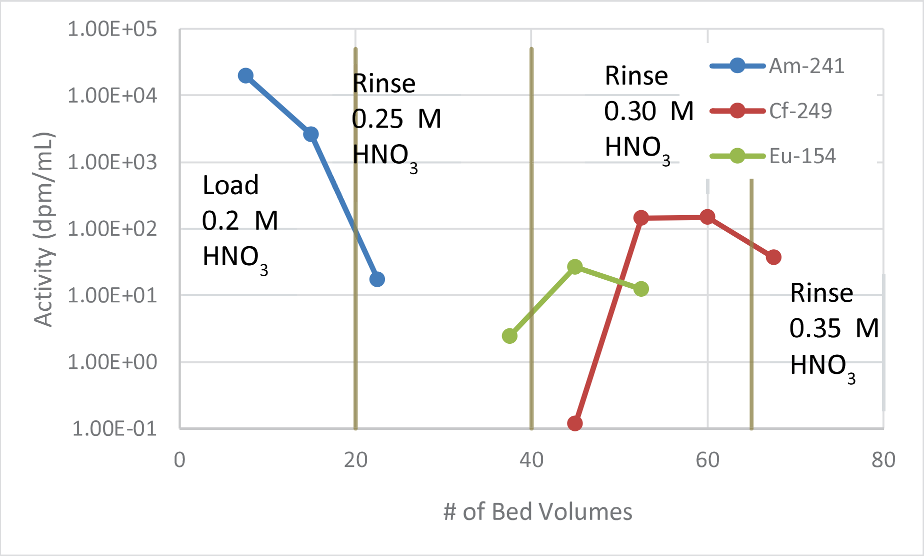

Figure 2-3. Activity (dpm/mL) vs number of Bed volumes for the separation of ^{241}Am, ^{249}Cf, and ^{154}Eu on LN Resin.

3.0 ^{107}Pd method Experiments and Results

^{107}Palladium is a pure beta emitter with a long half-life of 6.5×10^6 years. It is typically found in the presence of ^{108}Ag, also a beta emitter which convolutes the beta spectrum. These two need to be separated to quantify ^{107}Pd. Palladium is known to complex with dimethylglyoxime (DMG) in low concentrations of HCl.(6) A DMG based resin cartridge is commercially available from Eichrom (7), that is marketed for the separation of nickel. Pd forms a similar complex to the one shown below for Ni. The method will be traced with natural Pd to correct for any losses of Pd in the extraction due to competing species from the matrix or incomplete collection of the Pd on the resin.at

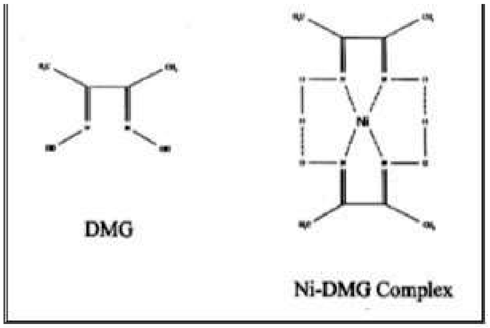

Figure 3-1. DMG structure and complex with Ni (7)

Table 3-1 shows the experimental conditions tested in the development of the Pd method. The ideal conditions were identified as loading the cartridge with the samples in 0.01 N hydrochloric acid (HCl), rinsing the cartridges with 0.01 N HCl, and eluting the Pd with 8 M nitric acid. The results with these conditions are highlighted in the table below with a blue border. The Pd yield under these conditions was >60%. The 8 M HNO_3 solution breaks down the Pd-DMG complex. Recoveries of 60 – 90% have been measured using this procedure. After the separation, the 8 M HNO_3 solution is evaporated to dryness, the Pd is redissolved in 10 mL of 0.1 N HCl and submitted to mass spectroscopy for analysis. The NMG also maintains the capabilities to analyze for ^{107}Pd through liquid scintillation, in conjunction with neutron activation for carrier recovery quantification.

Natural PdCl is used as a tracer for the method, so yields of around 60% are reasonable to provide the results needed by the Mark 18A program team. The natural Pd provides many Pd isotopes to trace the method through mass spectroscopy analysis.

Table 3-1. Experimental conditions, Yields, and Losses in Pd separation

	Yield	**Loss in Rinse**	**Left in Column**
Load Condition: 0.01 N HCl Rinse: 5 mL 0.01 N HCl Elute: 10 mL 6 M Nitic Acid	47.8%	0%	52.2%
Load Condition: 0.01 N HCl Rinse: 5 mL 0.01 N HCl Elute: 10 mL 8 M Nitic Acid	61.4%	8%	30.63%
Load Condition: 0.1 N HCl Rinse: 5 mL 0.1 N HCl Elute: 10 mL 6 M Nitic Acid	4.31%	17.26%	78.4%
Load Condition: 0.1 N HCl Rinse: 5 mL 0.1 N HCl Elute: 10 mL 8 M Nitic Acid	55.6%	7.0%	37.4%
Load Condition: 0.5 N HCl Rinse: 5 mL 0.5 N HCl Elute: 10 mL 6 M Nitic Acid	18.5%	23.5%	58.0%
Load Condition: 0.5 N HCl Rinse: 5 mL 0.1 N HCl Elute: 10 mL 8 M Nitic Acid	40.1%	34.3%	24.9%
Load Condition: 1 N HCl	23.8%	36.9%	39.3%

Rinse: 5 mL 1 N HCl Elute: 10 mL 6 M Nitic Acid			
Load Condition: 1 N HCl Rinse: 5 mL 1 N HCl Elute: 10 mL 8 M Nitic Acid	28.8%	32.2%	39.0%

Based on a literature review, it was determined that the Pd-DMG complex could be more effectively stripped from the resin column with 3 M nitric acid. An additional round of testing was performed to evaluate these conditions. A 6 M nitric acid elution was included for comparison. The yields given below are relative to the 6 M nitric system yield. This work showed that the 3 M system was not successful at stripping the Pd-DMG precipitate. The 0.01 M HCl / 8 M HNO_3 system will be used for the analysis, with yields great than 60% this procedure will for the determination of ^{107}Pd in the Mark 18A program samples.

Table 3-2. Yields for elution with 3 M nitric acid at various loading conditions

	Yield
Load Condition: 0.01 N HCl Rinse: 5mL 0.01 N HCl Elute: 10 mL 3 M Nitic Acid	6%
Load Condition: 0.1 N HCl Rinse: 5mL 0.1 N HCl Elute: 10 mL 3 M Nitic Acid	22%
Load Condition: 0.5 N HCl Rinse: 5 mL 0.5 N HCl Elute: 10 mL 3 M Nitic Acid	9%

4.0 ^{121m}Sn Method Experiment and Results

Two resins were tested for the separation of ^{121m}Sn: Eichrom's ZR resin and anion exchange resin. The ZR resin has a hydroxamate extractant (8).

Three Savannah River Site Nuclear Materials Management Programs samples were used to test the proposed Sn methods. Two samples were from the H-Canyon dissolver tanks: Tank 7.4 and 8.3. The third sample was from Salt Batch 7. These samples have similar components to the contaminates in the Mark-18A material.

For the Anion resin separation, 0.1 mL of the samples was dissolved in 20 mL of 6 M HCl. A spike of 0.2 mL ($6.23x10^4$ dpm) of a ^{113}Sn standard from Eckert and Ziegler was added to each of the samples to evaluate the Sn recovery from the separation. Two anion cartridges were connected in series and conditioned with 3 M HNO_3. After the samples were loaded on to the cartridges, the cartridges were rinsed twice with 20 mL of 3 M HNO_3 to separate other contaminants from the Sn. The Sn was then eluted with 20 mL of 1 M HNO_3. A gamma sample was then prepared from the separated Sn and counted on a semi-planar high purity germanium (HPGe) detector.

For the ZR resin separation, 1 mL of the samples was dissolved in 20 mL of 2 M HNO_3. Like the Anion resin procedure, a spike of 0.2 mL ($6.23x10^4$ dpm) of a ^{113}Sn standard from Eckert and Ziegler was added to each of the samples to evaluate the Sn recovery from the separation. A ZR resin cartridge was conditioned with 10 mL of 2 M HNO_3. After the samples were added to the cartridge, they were rinsed twice with 20 mL of 2 M HNO_3. The Sn was eluted with 30 mL of 10 M HNO_3. Then, a final rise of 10 mL of DI water was added to the cartridges. Samples of the separated Sn solution were prepared for gamma spectroscopy and counted on a coaxial HPGe detector.

The ^{113}Sn recoveries for both the anion resin and ZR resin procedures are given in Table 3-3. Generally higher and more consistent recoveries were achieved with the anion resin across all three samples, so the anion separation procedure will be used for the Mark-18 A sample analysis.

Table 3-4-1. Sn recoveries from separation procedures on SRS Nuclear Materials Management Programs Samples with Anion resin and ZR resin.

	Recovery	
	Anion	**ZR**
Canyon 7.4	58%	60%
Canyon 8.3	65%	49%
Salt Batch 7	58%	2%

4.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. Gamma spectroscopy measurements were performed in compliance with L16.1-ADS-2420 “High Purity Germanium Detector Gamma Pulse Height Analysis". Information and data associated with this report are recorded in the SRNL electronic laboratory notebook system as notebook/experiment number ELN #J1290-00319-27 Mark 18A Analytical Method Development.

5.0 Conclusions

Methods have been developed to quantify the Cf isotopes, ^{107}Pd and ^{121m}Sn in the Mark-18A matrix. The Cf method is based on the use of LN resin to separate trivalent materials and the Cf is detected by gamma spectrometry. DGA will be used to clean up other fission products from the samples and mass spectrometry can be used to compliment the gamma spectrometry results. The ^{107}Pd uses a DMG material to extract Pd. The ^{107}Pd is quantified by mass spectroscopy and liquid scintillation counting. The ^{121m}Sn method uses anion resin to separate Sn and quantifies ^{121m}Sn by liquid scintillation counting.

6.0 Recommendations, Path Forward or Future Work

Once the Mark-18A begins dissolving targets and submitting samples for analytical work, some adjustments to the methods described above may be necessary to adapt to the matrix conditions. As the Mark 18A program team begins sending samples for analytical characterization, samples for ^{107}Pd and ^{121M}Sn should be submitted to the methods that already exist in LIMS, PD_107 and SN_126_SN_121M, respectively. Samples needing the Cf method will be logged in under the existing AM_CM method. The Mark 18A program team should communicate with the Analytical CTF that they are submitting Mark 18A program samples so the appropriate analysis can be completed.

7.0 References

1) Fenker, K. “Mark 18A Analytical Feasibility Study” SRNL-RP-2020-00262 May 2020
2) Eldridge, H. " Mark-18a Programmatic Sampling Strategy" SRNL-L2250-2022-00001 1/18/2022.
3) Personal Communication, Dr. Kathryn Taylor-Pashow, 2/6/2023
4) Branney, S. B. Results of Mk 18A Target Irradiation Actinide Inventory Calculation. N-CLC-A-00084, April 2016.
5) “LN Resins”.https://www.eichrom.com/eichrom/products/ln-resins/
6) “The Radiochemistry of Pd”. https://library.lanl.gov/cgi-bin/getfile?rc000009.pdf
7) Eichrom Ni Columns. https://www.eichrom.com/eichrom/products/nickel-resin/
8) "Zirconium Separation of ZR resin." https://www.eichrom.com/wp-content/uploads/2018/11/AN-1808_ZR-Resin-1.pdf

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