Lawrence Livermore National Laboratory

New NBL Pu Isotopic Standards C137A and C136A as Working Reference Materials for Radiochronometry in Nuclear Forensics

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Lawrence Livermore National Laboratory (LLNL) and the NBL Program Office (NBL PO) are collaborating on production of purified sub-units of the former NBS 936, 937 and 938 plutonium isotopic reference materials, which will be certified for plutonium isotopic composition and sold as certified reference materials (CRMs) C136A, C137A, and C138A, respectively. These reference materials are used throughout the United States and international community as standards for isotopic measurement method calibration and quality control and were first produced over 50 years ago. To reduce quantities of in-grown daughter products and potentially enable their use as Pu radiochronometry reference materials, the materials undergo a two-stage anion exchange purification to significantly reduce the quantities of U, Am, and Np in the source material. The purified Pu is aliquoted into ~1 mg units in the nitrate form, which will facilitate easier shipping and use compared to the 0.25 g parent units. The production process has been completed for the high- and medium- burnup isotopic standards C137A and C136A and will soon be performed for the weapons-grade Pu standard C138A. This report describes the measurement of trace actinide progeny of the Pu isotopes (^{234}U, ^{235}U, ^{236}U, ^{241}Am and ^{237}Np) in purified C137A and 136A isotopic standards to provide informational values and assess the possibility of their use as working reference materials for radiochronometry.

Aliquoting of Prepared Standard Units

As specified in the Project Plan for production of the new units of the plutonium standard reference materials: during dispensing of the units, three aliquots representing one unit each were dispensed into 125 mL FEP bottles for analyses of Pu and trace actinide concentration. The tare weights of the empty FEP bottles were measured and the Pu standard units were diluted with 2 M HNO_3 + 0.01 M HF. The weighing data for these three solutions, designated as the X, Y, and Z “Primary”, are given in Table 1.

The trace actinide progeny of the Pu isotopes (^{234}U, ^{235}U, ^{236}U, ^{241}Am and ^{237}Np) were measured in samples of these primary solutions.

Table 1. Weights of the Primary Solutions measured on the balances in B151, R1334.

Date	125 mL FEP Tare	Wt. (g)	Std. Uncert.
6-Oct-21	C137A Unit X	42.0309	0.001
6-Oct-21	C137A Unit Y	42.3654	0.001
6-Oct-21	C137A Unit Z	42.2861	0.001
13-Jul-22	C136A Unit X	43.3027	0.001
13-Jul-22	C136A Unit Y	42.7726	0.001
13-Jul-22	C136A Unit Z	42.5924	0.001
	Diluted Units		
13-Oct-21	C137A Unit X	171.2136	0.001
13-Oct-21	C137A Unit Y	172.1304	0.001
13-Oct-21	C137A Unit Z	171.9648	0.001
15-Jul-22	C136A Unit X	173.0743	0.001
15-Jul-22	C136A Unit Y	169.8245	0.001
15-Jul-22	C136A Unit Z	170.3992	0.001
	Primary Solution		
13-Oct-21	C137A Unit X	129.1827	0.0014
13-Oct-21	C137A Unit Y	129.7650	0.0014
13-Oct-21	C137A Unit Z	129.6787	0.0014
15-Jul-22	C136A Unit X	129.7716	0.0014
15-Jul-22	C136A Unit Y	127.0519	0.0014
15-Jul-22	C136A Unit Z	127.8068	0.0014

The purification times are defined as the end of the 10M HCl wash from the second column and the subsequent start of Pu elution using mixed HCl/HI.

The purification time for C137A was 28-Sept-2021 at 8 PM PDT.

The purification time for C136A was 29-Jun-2022 at 9:25 PM PDT.

The C137A units were dispensed on 11-Oct-2021 and the C136A units were dispensed on 15-Jul-2022. Details of the purification chemistry and production can be found in the revised project plan[1] and in the individual production reports for each isotopic standard.

Plutonium Content of the Prepared Standard Units

Dilutions of each standard were prepared by adding 500 mL of 2 M HNO3 + 0.01 M HF to approximately 0.5 ml of primary solution in pre-cleaned polyethylene bottles (Table 2). The Pu contents of the dilution-1 solutions were characterized by isotope dilution mass spectrometry (IDMS) using an ultra-high-purity (UHP) ^{244}Pu spike prepared and calibrated at LLNL using methods described by Essex *et al*. [2].

Table 2. The weighing data for preparation of Dilution-1

Date	500 mL poly bottle tare	Wt. (g)	Std. Uncert.
16-Oct-21	C137A Unit X Dil-1	59.2061	0.0017
16-Oct-21	C137A Unit Y Dil-1	58.1024	0.0013
16-Oct-21	C137A Unit Z Dil-1	59.2699	0.0018
15-Jul-22	C136A Unit X Dil-1	57.9586	0.0016
15-Jul-22	C136A Unit Y Dil-1	57.9503	0.0008
15-Jul-22	C136A Unit Z Dil-1	57.7264	0.0010
	Primary Solution		
17-Oct-21	C137A Unit X	0.592882	0.000016
17-Oct-21	C137A Unit Y	0.518114	0.000014
17-Oct-21	C137A Unit Z	0.688690	0.000021
18-Jul-22	C136A Unit X	0.574742	0.000019
18-Jul-22	C136A Unit Y	0.50339	0.000011
18-Jul-22	C136A Unit Z	0.475026	0.000020
	Poly bottle with Dilutions		
17-Oct-21	C137A Unit X Dil-1	591.2540	0.001
17-Oct-21	C137A Unit Y Dil-1	594.8867	0.001
17-Oct-21	C137A Unit Z Dil-1	597.3003	0.001
18-Jul-22	C136A Unit X Dil-1	605.2660	0.001
18-Jul-22	C136A Unit Y Dil-1	578.1927	0.001
18-Jul-22	C136A Unit Z Dil-1	601.6188	0.0016
	Dilution-1 Solution		
17-Oct-21	C137A Unit X Dil-1	532.0479	0.0020
17-Oct-21	C137A Unit Y Dil-1	536.7843	0.0016
17-Oct-21	C137A Unit Z Dil-1	538.0304	0.0021
18-Jul-22	C136A Unit X Dil-1	547.3074	0.0019
18-Jul-22	C136A Unit Y Dil-1	520.2424	0.0013
18-Jul-22	C136A Unit Z Dil-1	543.8924	0.0019

Table 3. The calculated concentrations of the primary solutions in Dilution-1

	g-Primary / g-Dil-1	Std. Uncert.
C137A Unit "X" Dilution-1	0.001114340	0.000000030
C137A Unit "Y" Dilution-1	0.000965218	0.000000026
C137A Unit "Z" Dilution-1	0.001280020	0.000000039
	g-Primary / g-Dil-1	**Std. Uncert.**
C136A Unit "X" Dilution-1	0.001050126	0.000000034
C136A Unit "Y" Dilution-1	0.000967607	0.000000020
C136A Unit "Z" Dilution-1	0.000873382	0.000000037

Table 4. The ^{244}Pu concentration of the LLNL UHP ^{244}Pu spike used for Pu IDMS

Pu244 Spike Aug-2016	
244Pu atoms /g	**Std. Uncert.**
4.4204E+12	4.7E+09

Table 5. The weights of the Dilution-1 solutions for PuID

Date	Dilution-1 for Pu IDMS	Wt. (g)	Std. Uncert.
18-Oct-21	C137A X-PuID	0.623302	0.000018
18-Oct-21	C137A Y-PuID	0.570134	0.000016
18-Oct-21	C137A Z-PuID	0.694682	0.000016
19-Jul-22	C136A X-PuID	0.440012	0.000023
19-Jul-22	C136A Y-PuID	0.688312	0.000018
19-Jul-22	C136A Z-PuID	0.485890	0.000021

Table 6. The weights of the ^{244}Pu spike added

Date	Pu244 Spike Aug-2016	Wt. (g)	Std. Uncert.
18-Oct-21	C137A X-PuID	2.311324	0.000017
18-Oct-21	C137A Y-PuID	2.412760	0.000027
18-Oct-21	C137A Z-PuID	2.936222	0.000020
19-Jul-22	C136A X-PuID	2.050358	0.000012
19-Jul-22	C136A Y-PuID	2.178648	0.000016
19-Jul-22	C136A Z-PuID	2.134202	0.000023

The PuID samples were refluxed in capped Savillex PFA vials with rounded interior on a hotplate to equilibrate the spike with the sample. These solutions were diluted further at the instrument and analyzed by multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS). The analyses of the PuID samples were made using the same Faraday multi-collection method that was used to measure

the Pu isotopic compositions[3]; instrumental mass bias was corrected using bracketing analyses of C128. Two analyses of each PuID sample were made. The average is given in Table 7.

Table 7. The measured 244Pu/239Pu atom ratio of the PuID samples

Analysis Date	Sample ID	244Pu/239Pu	Std. Uncert.
21-Oct-21	C137A X-PuID	0.91201	0.00024
21-Oct-21	C137A Y-PuID	1.20673	0.00061
21-Oct-21	C137A Z-PuID	0.90844	0.00032
21-Jul-22	C136A X-PuID	1.11226	0.00061
21-Jul-22	C136A Y-PuID	0.80411	0.00047
21-Jul-22	C136A Z-PuID	1.23945	0.00068

The concentration of ^{239}Pu per unit is calculated from the data in these tables as follows:

$$239Pu\ \left[\frac{atoms}{unit}\right] = \frac{244PuSpike\left[\frac{atoms}{g}\right] \times 244PuSpike(g) \times \left[\frac{Primary(g)}{unit}\right]}{\left[\frac{Primary(g)}{Dil1(g)}\right] \times IDMSDil1(g) \times \left[\frac{n244Pu}{n239Pu}\right]}$$

Table 8. The Pu IDMS results for the units of C137A

	239Pu atoms/Unit	Combined Std. Uncert.
C137A Unit X	2.08359E+18	2.28E+15
C137A Unit Y	2.08412E+18	2.45E+15
C137A Unit Z	2.08364E+18	2.33E+15
Average and Std. Deviation	2.08378E+18	2.92E+14

Using the LLNL measurements for the isotopic composition of C137A, which were decay corrected to the purification date (28-Sep-2021), the atomic weight of Pu is 239.28622; the weight fraction of ^{239}Pu is 0.7902747 and the average Pu concentration per unit is 1.0467 milligram.

Table 9. The Pu IDMS results for the units of C136A

	239Pu atoms/Unit	Combined Std. Uncert.
C136A Unit X	2.28855E+18	2.74E+15
C136A Unit Y	2.28472E+18	2.80E+15
C136A Unit Z	2.29236E+18	2.74E+15
Average and Std. Deviation	2.28854E+18	3.82E+15

Using the LLNL measurements for the isotopic composition of C136A, decay corrected to the purification date (29-Jun-2022), the atomic weight of Pu is 239.20017; the weight fraction of ^{239}Pu is 0.8635271 and the average Pu concentration per unit is 1.0520 milligram.

The Pu isotope atomic concentrations, calculated for the average unit on the purification date, were used to construct the ingrowth curves for the Pu decay-progeny that are used in the following sections to evaluate the efficacy of Pu purification from these trace actinide isotopes. These atomic concentrations are given in Table 10.

Table 10.

	C137A Units on 28-Sep-2021		C136A Units on 29-Jun-2022	
Isotope	**atoms/unit**	**Exp. U (k=2)**	**atoms/unit**	**Exp. U (k=2)**
Pu-238	5.51369E+15	1.92E+12	4.58893E+15	1.57E+13
Pu-239	2.08379E+18	5.87E+14	2.28858E+18	7.63E+15
Pu-240	5.01279E+17	1.41E+14	3.30483E+17	1.10E+15
Pu-241	1.11693E+16	3.52E+12	9.46659E+15	3.16E+13
Pu-242	3.24626E+16	9.72E+12	1.55119E+16	5.22E+13

The trace actinide concentrations were calculated on a per unit basis also, for calculation of the progeny/parent ratios. The individual analyses of the X, Y and Z primaries are each ratioed to these average unit Pu parent concentrations and are presented graphically (as atom ratios) in the following sections. The horizontal axes in Figures 1-10 are the days after purification of the Pu. That is, Day 0 is the CRM purification time and the solid blue lines trace the evolution of the progeny/parent ratios. The points are plotted at the time when the U, Am and Np isotopes were separated from their parents for analysis. In all cases, a second purification step occurred one-day after the first. So, while the first purification step may not have removed all parent, the second reduced this residual amount to a point where further change of the progeny concentration before analysis is minimal. To show this uncertainty in purification time on the graphs, the X, Y and Z analyses are plotted over a range which helps to distinguish one analysis from another.

The Uranium Isotopes

Samples of the X, Y and Z primary solutions were weighed and spiked with LLNL ^{233}U Spike 917 Dil-1 Oct-2020. The concentration of this spike is 1.77790 E+11 atoms/g and has a relative standard uncertainty of 0.089 %. It is the same high-purity ^{233}U described by Essex *et al.* [4] and was calibrated with NBL C112A.

It was found that the best method to purify trace uranium from Pu for these analyses was the same method used to purify the bulk Pu for preparation of the CRM units. That is, by sorbing the Pu on anion exchange resin in 8 M HNO_3 and catching the uranium that is rinsed through. Inevitably, some Pu is washed through with the uranium fraction and the purification must be repeated to avoid contaminating the mass spectrometer with excess Pu. The second purification was performed one day after the first, and the X, Y and Z analyses are placed on the horizontal axis over this time span.

The first column for the C137A samples was run on 2-Nov-2021 at 10:45 AM; 34.6 days after final purification of Pu for unit preparation. The C137A UID samples were analyzed twice: with a peak-jumping method using pulse-counting detectors on 6-Nov-21, and by a static Faraday multi-collection method on 7-Nov-21.

The first column for the C136A samples was run on 1-Sep-2022 at 12:40 PM; 63.6 days after final purification of Pu for unit preparation. The C136A UID samples were analyzed by a Faraday multi-collection method only, on 6-Sep-2022.

The combined expanded uncertainties (K=2) on the calculated ratios are plotted here. For C137A the error bars are slightly smaller than the plot symbols but are just discernible for C136A. The graphs of U-isotope ingrowth for C137A and C136A follow.

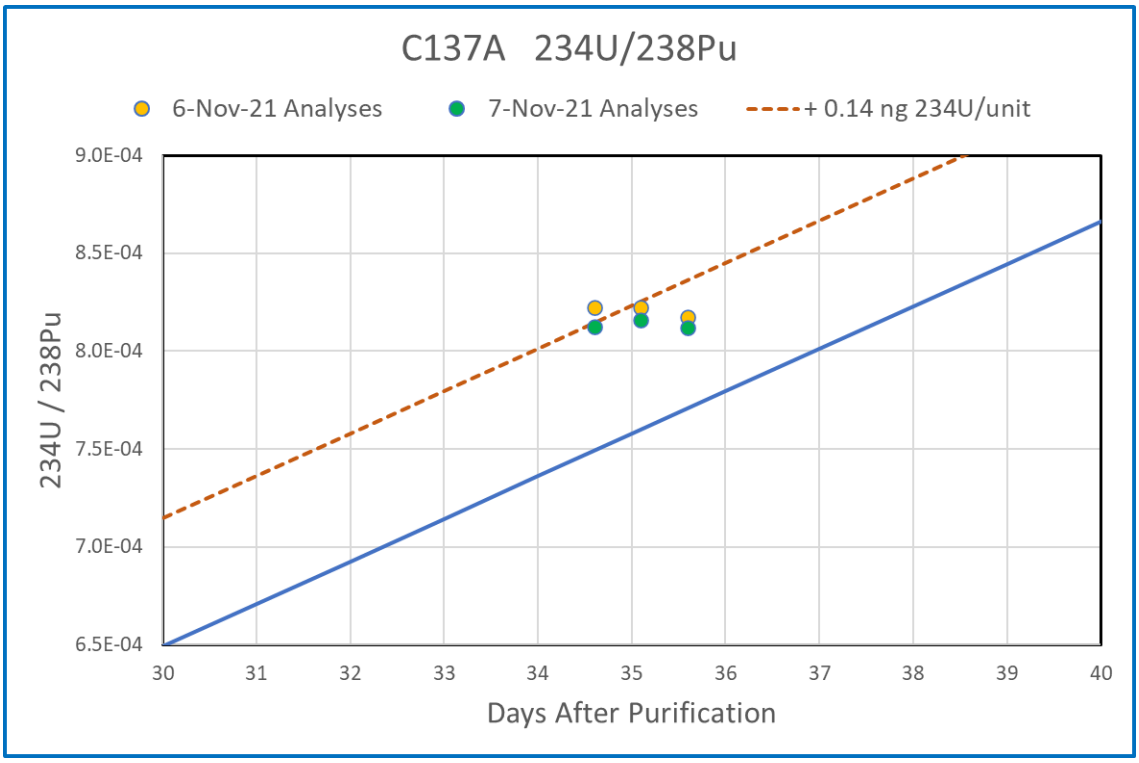

Figure 1. The C137A UID samples seem to have an excess of ^{234}U that give a ^{238}Pu-^{234}U model-date that is approximately three days before the purification date.

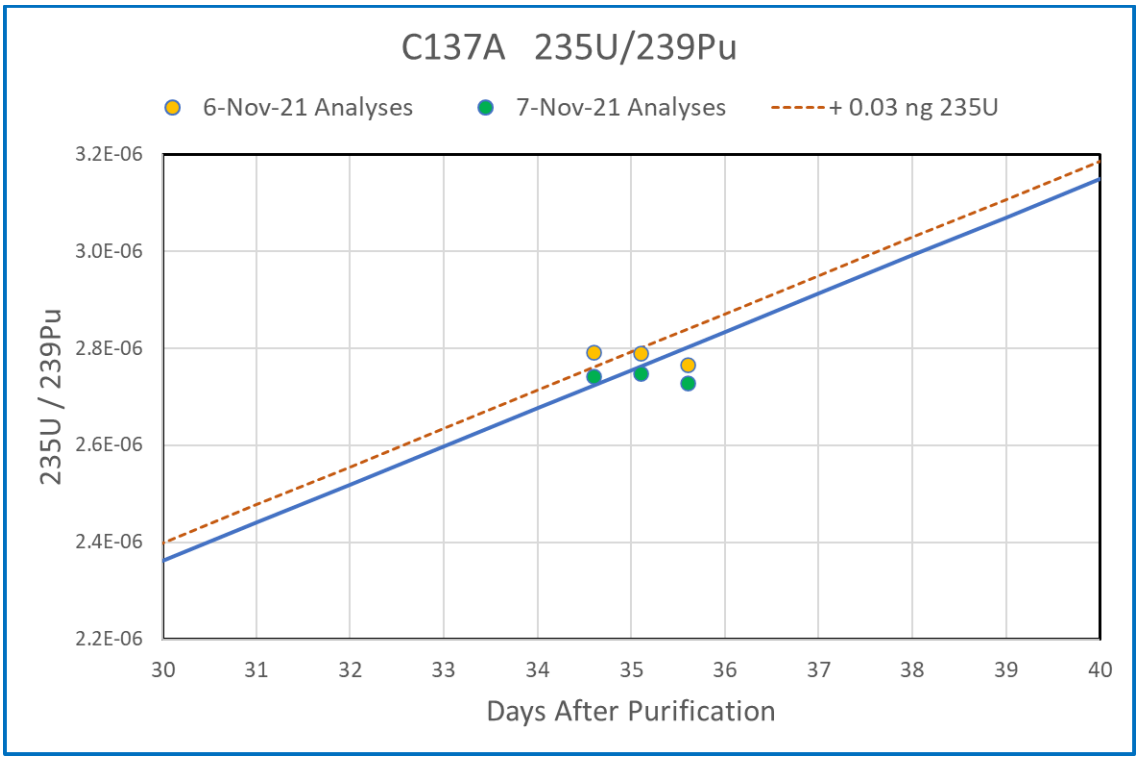

Figure 2. There is no indication of excess ^{235}U in these units. The ^{239}Pu-^{235}U model-age is concordant with the final purification date (28-Sept-2021 at 8 PM PDT).

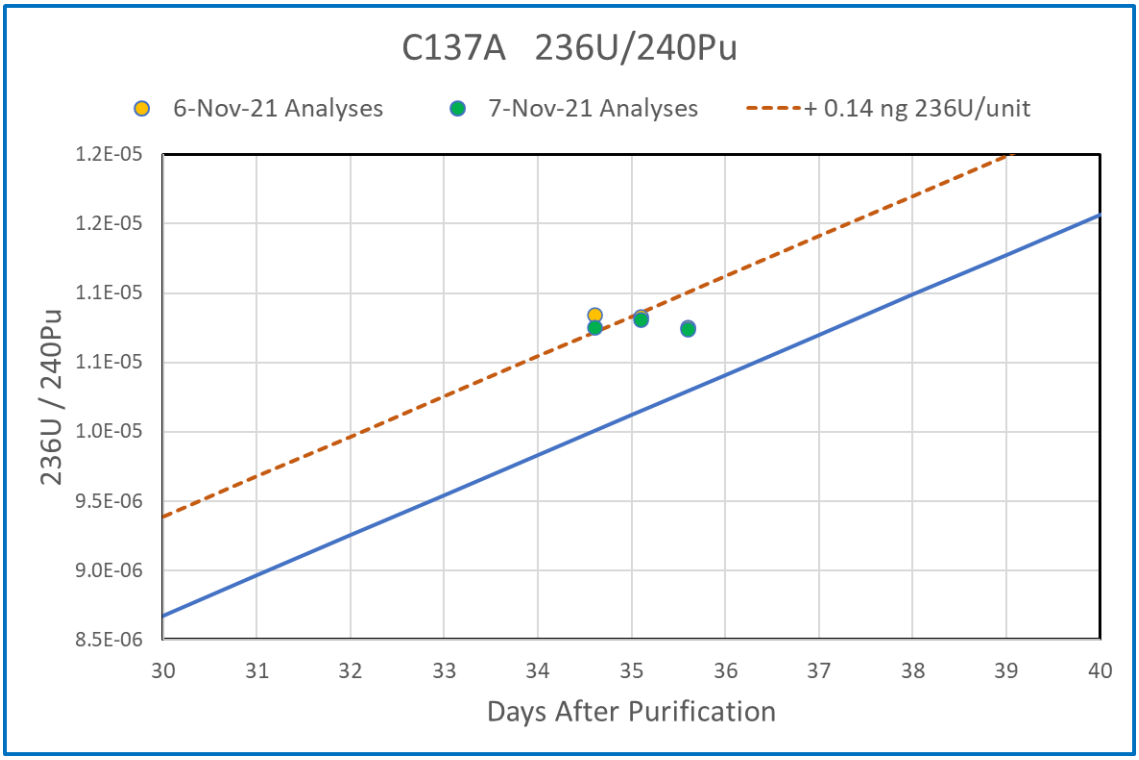

Figure 3. As for ^{234}U, there appears to be excess ^{236}U in these samples, giving a ^{240}Pu-^{236}U model-date approximately three days earlier than the final purification date.

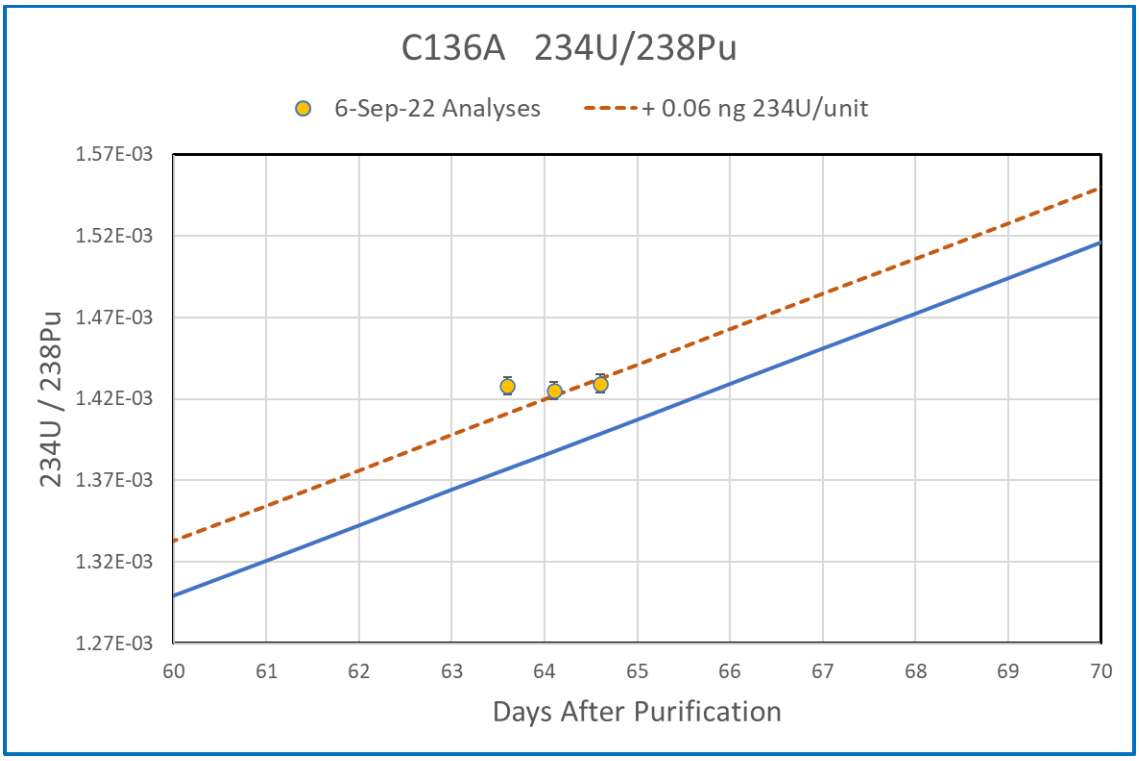

Figure 4. Similar to C137A, the ^{238}Pu-^{234}U model-date for C136A appears to be a few days before the Pu purification date of 29-Jun-2022.

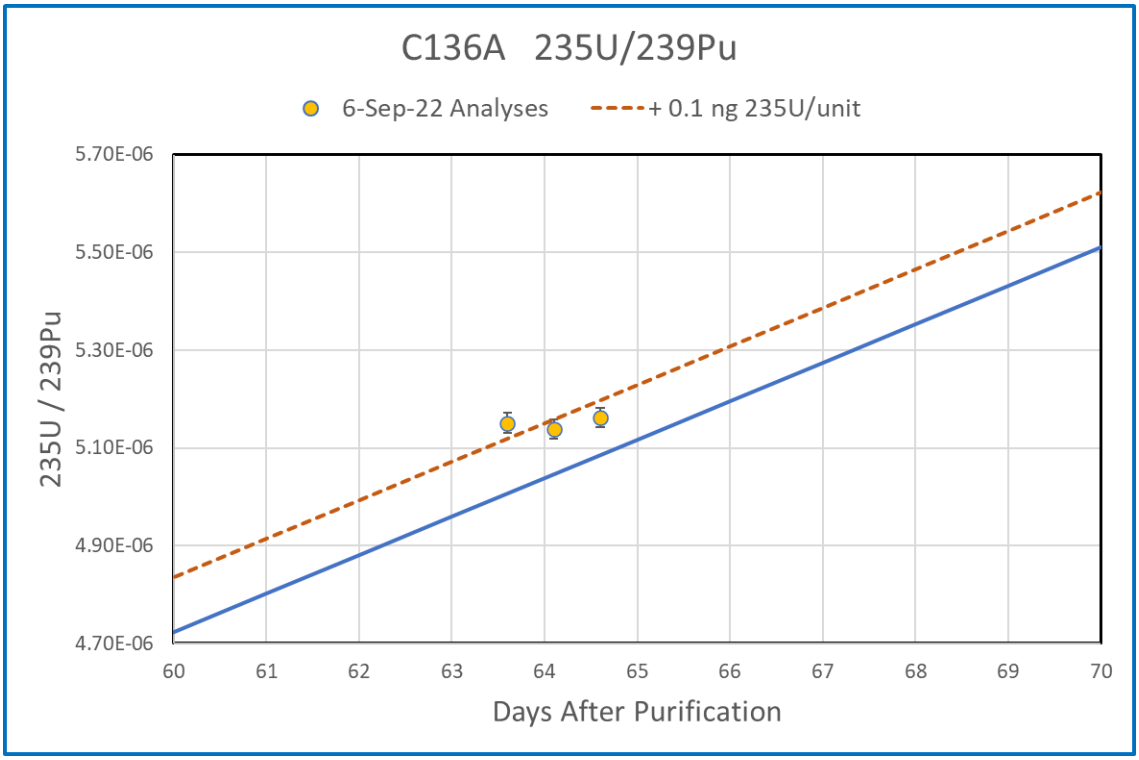

Figure 5. The off-set of approximately two days is also seen in the ^{239}Pu-^{235}U model-date.

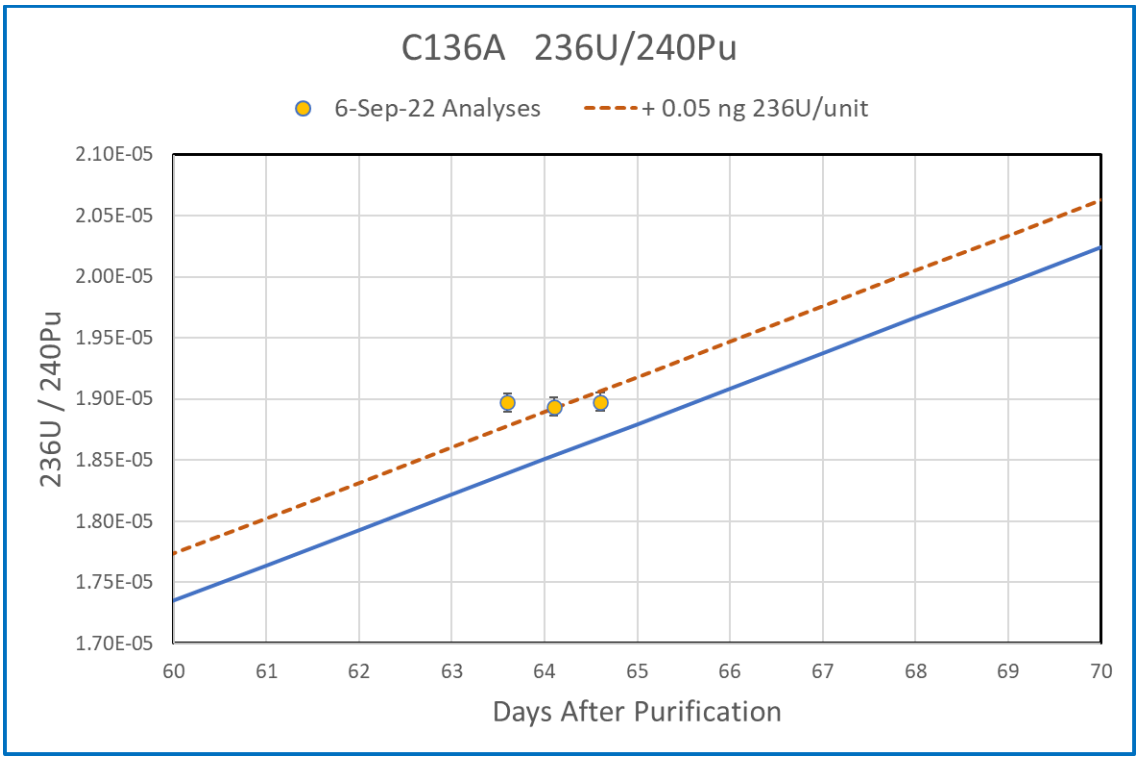

Figure 6. There is a similar offset in the model-date for the ^{240}Pu-^{236}U chronometer.

Discussion of the Uranium Results

The results presented in Figures 1-6 generally indicate that the two-step anion exchange purification of Pu for production of the new units did not remove all of the uranium. The U-progeny had been increasing in the original units of C137 and C136 for approximately 51 and 52 years, respectively. Dates used are from the report titled *A Documentary History of the United States's First Plutonium Reference Materials*, by P. Mason, U. Narayanan, New Brunswick Laboratory [5]. Also, it is probable that some initial U was present in the original Pu CRM units. Table 11 gives the ingrown U-isotope content of the new units if there was no separation of U prior to preparation.

	Ingrown U-isotopes (atoms/unit)	
	C137A	**C136A**
234U	2.74E+15	2.35E+15
235U	3.06E+15	3.44E+15
236U	2.71E+15	1.83E+15

Table 11. The minimum U-isotope content of the starting materials prior to purification.

Tables 12 and 13 give the excess U-isotopes present in the new units at the time of final purification, and the apparent separation factors for each CRM are calculated, assuming the original units had no excess U at the time of preparation and behaved as closed systems until they were purified in this work. These excess values are used to construct the dashed lines in Figures 1-6.

	Approximate Excess on Purification Date	
C137A	atoms/unit	Separation Factor
234U	3.60E+11	7605
235U	7.69E+10	39808
236U	3.57E+11	7585

Table 12. The excess initial U-isotope content of the C137A units.

	Approximate Excess on Purification Date	
C136A	atoms/unit	Separation Factor
234U	1.54E+11	15212
235U	2.56E+11	13438
236U	1.28E+11	14347

Table 13. The excess initial U-isotope content of the C136A units.

Uranium has a smaller (but non-zero) sorption coefficient on anion exchange resin in 8 M HNO_3 than Pu. While our earlier work on small-scale columns[6] showed that a separation factor of 1660 could be expected, greater purification factors were likely achieved in the scaled-up chemistry. If 99% of the uranium was removed in each column pass, this would be a separation factor of 10000. It appears that Pu/U separation factor for C136A was better than this, and that for C137A was slightly worse.

The anomaly in this scenario is that the ^{235}U content of the C137A units is consistent with essentially complete purification from Pu at the final preparation date/time. One possible explanation for this is that the U-content of the original units was not zero, and that the initial U contaminant had an isotopic composition with excess ^{234}U and ^{236}U relative to ^{235}U. Another possibility is that the C137A UID analyses were affected by some unidentified isobaric interferences at mass 234 and 236. However, this does not seem to be the case for C136A, and the anomalous U-isotopic composition of C137A remains a mystery.

The ^{241}Am Analyses

The Am contents in CRM 136A and 137A were characterized by isotope dilution (AmID). This involved weighing aliquots of the X, Y and Z primary solutions into Savillex vials and spiking with the high-purity Nuclear Forensic Reference Material (NFRM) ^{243}Am spike. This ^{243}Am is from the high-purity stock obtained from the UK National Physical Laboratory (NPL) and was calibrated primarily by IDMS crosses with a NIST ^{241}Am radioactivity standard. The LLNL spike (NPL Am-243 NFRM) was calibrated at LLNL in collaboration with Richard Essex for the Department of Homeland Security and contains 8.4964E+12 ^{243}Am atoms/g with a relative standard uncertainty of 0.45%.

Figures 7 and 8 for the ^{241}Pu-^{241}Am chronometer follow the same conventions used for the earlier figures. Similarly, the purification of americium was performed by loading and washing Am through anion exchange resin in 8 M HNO_3. Because the sorption of Am from this media is essentially zero, the Am fraction can be collected in the first few mL of acid passed through the column, which decreases the amount of Pu that bleeds through. A second purification column was performed the following day to

remove any residual Pu. The date/time of Am/Pu separation is easier to constrain than for uranium. Hence, the X, Y and Z $^{241}Am/^{241}Pu$ ratios are plotted at 2 hour intervals, instead of the 12-hour interval used in the U plots.

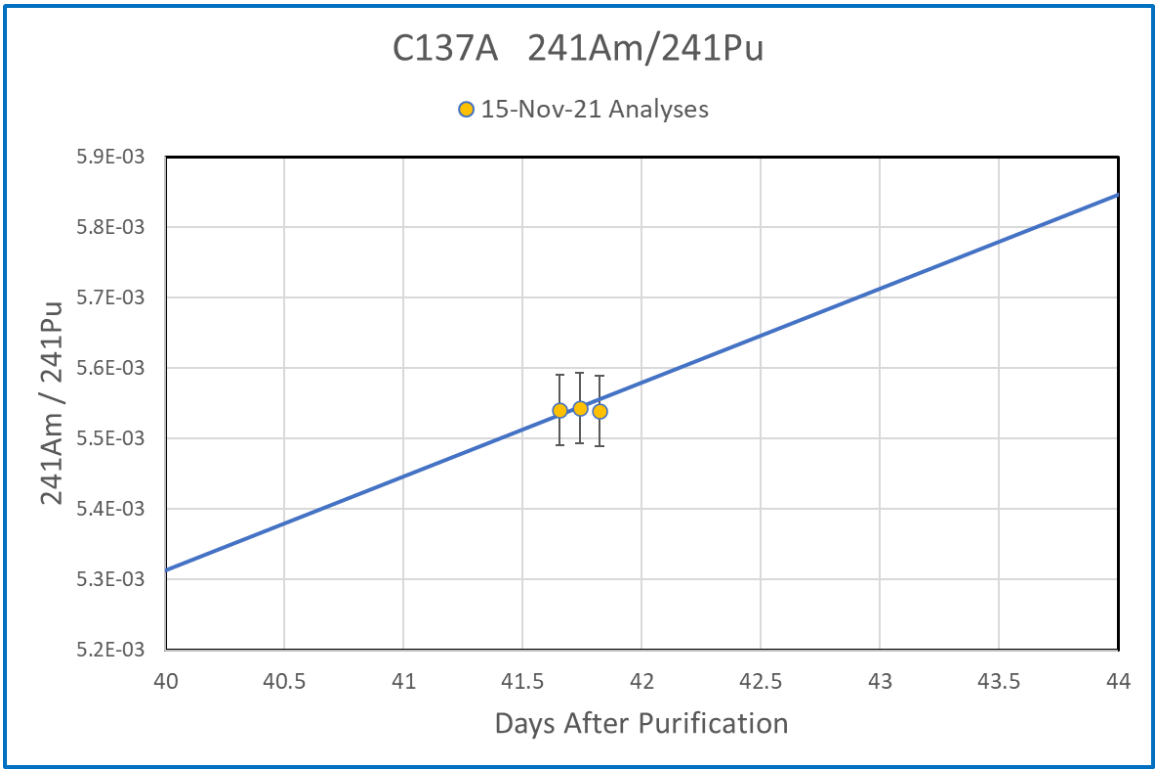

Figure 7. $^{241}Am/^{241}Pu$ measured in units X, Y, and Z are exactly as expected for complete removal of ^{241}Am at purification. The ^{241}Am purification date/time for C137A was 9-Nov-2021 13:45.

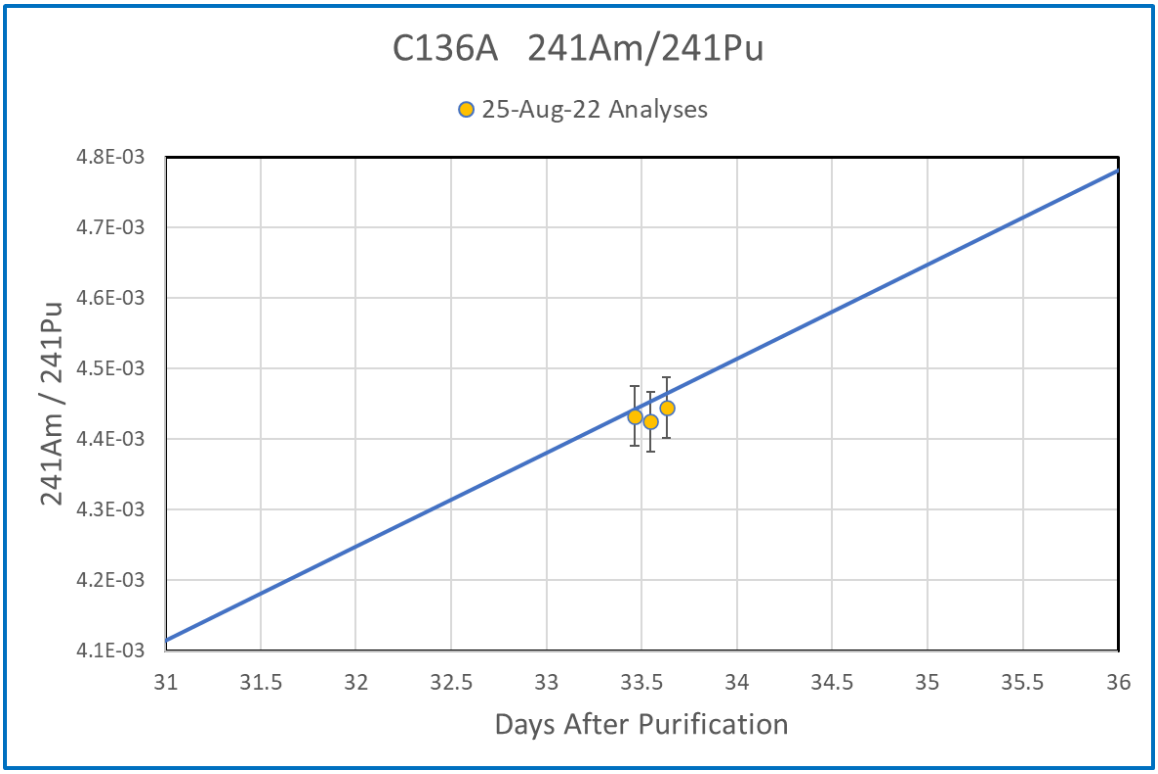

Figure 8. ^{241}Am/^{241}Pu measured in units X, Y, and Z are exactly as expected for complete removal of ^{241}Am at purification. The ^{241}Am purification date/time for C136A was 2-Aug-2022 10:33

Within the expanded uncertainty of approximately 4 hours, the ^{241}Pu-^{241}Am model-dates for both CRMs are coincident with the purification date/times of those materials. As expected from earlier tests, Am was completely eliminated from both CRMs at that time.

The ^{237}Np Analyses

The analyses of trace ^{237}Np in Pu is the most difficult of the trace actinide analyses for two reasons. First, because an IDMS spike (i.e. ^{236}Np) is not available at LLNL, and second, because Np and Pu share common valence states and complexation in acidic aqueous solutions which can result in poor and unreliable separations. To date, the best separation factors have been achieved using an anion exhange method from a nitric acid-methanol-hydroxylamine hydrochloride solution. The LLNL method is given in Williams *et al.* [7] The purification method is based on Patil *et al*.[8] The Np recovery is measured by gamma spectrometry using a ^{239}Np tracer milked from ^{243}Am, and the ^{237}Np concentration is measured by ICPMS using a standard calibration curve method. The art of this Pu/Np separation method lies in establishing Np(IV) and Pu(III) in the mixed media column load solution. For the analyses of C137A and C136A presented in Figures 9-10, the Np recoveries varied from 35 to 67%.

During the development phase of this project we found that the CRM preparation method did not quantitatively remove Np from the Pu[6] so the results of the ^{237}Np analysis are not unexpected.

Both CRMs contained residual ^{237}Np at the time of preparation. C137A has approximately 11.7 ng/unit and C136A has 0.04 ng/unit.

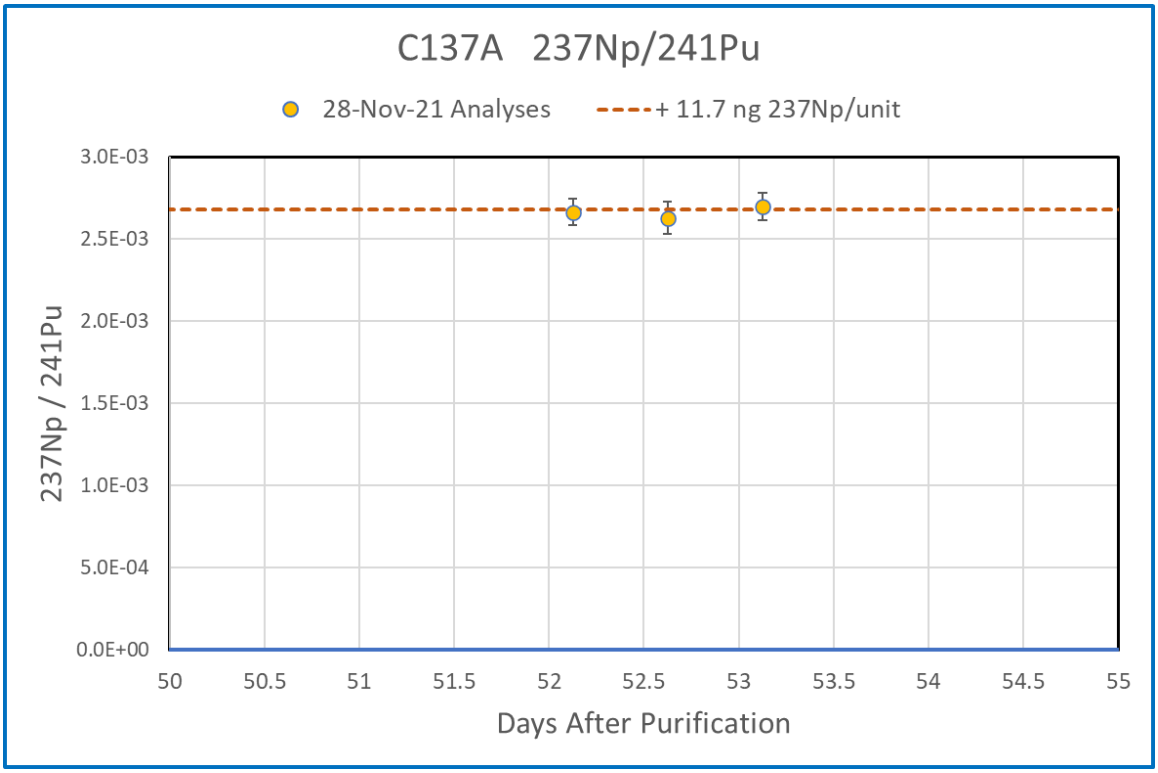

Figure 9. The measured $^{237}Np/^{241}Pu$ in units X, Y, and Z indicate an initial 11.7 ng ^{237}Np per unit C137A. The purification date/time for these ^{237}Np analyses was 20-Nov-2021 11:00.

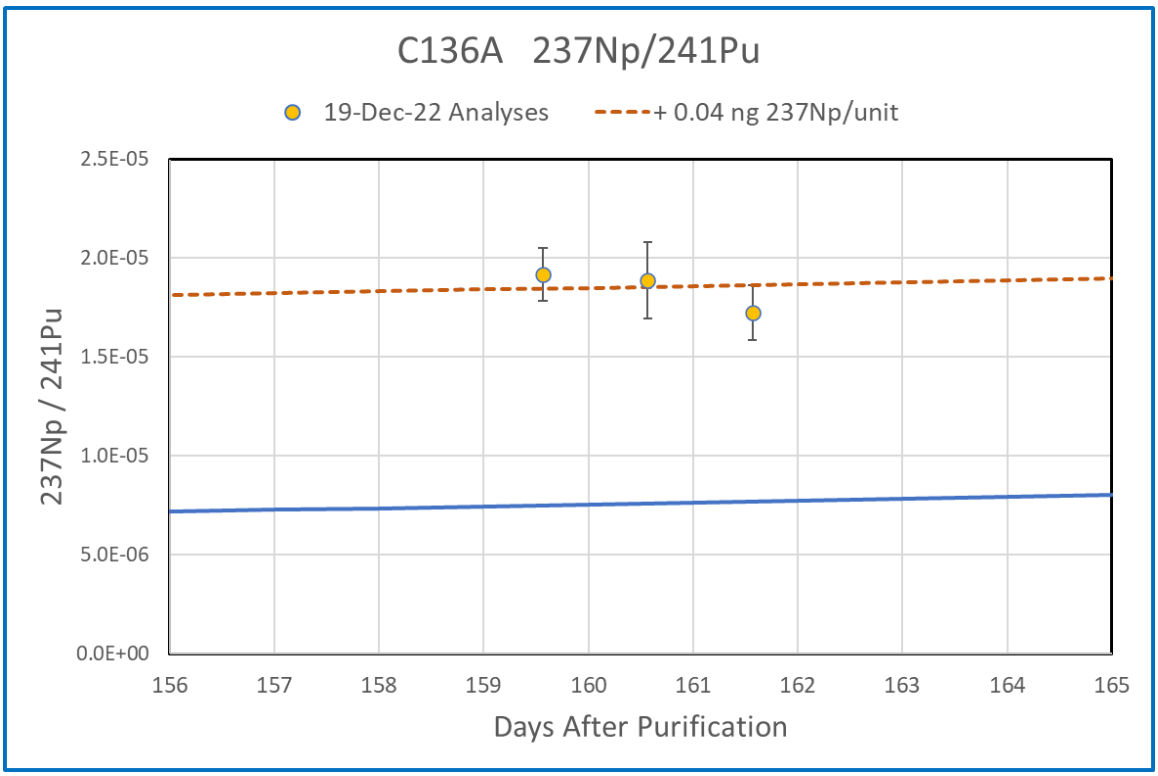

Figure 10. The measured $^{237}Np/^{241}Pu$ in units X, Y, and Z indicate an initial 0.04 ng ^{237}Np per unit C136A. The purification date/time for these ^{237}Np analyses was 6-Dec-2022 11:00.

Radiochronometry Calculations

The full expression for calculating the Model Age (t) for radiochronometry of a parent-progeny pair is

$$t = \frac{1}{(\lambda_1 - \lambda_2)} ln\left[1 + \frac{R(\lambda_1 - \lambda_2)}{\lambda_1}\right]$$

where R is the progeny/parent atomic ratio, and λ_1 and λ_2 are the parent and progeny decay constants, respectively.

Because the decay progeny of the Pu isotopes all have half-lives that are significantly longer than their parents (*i.e.*, have decay constants that are much smaller; effectively zero for these time-frames), the age-dating equation can be simplified as follows

$$t = \frac{1}{\lambda_1} ln[1 + R]$$

Un-simplified, the sensitivity coefficients for calculating the uncertainty on the age are

$$\frac{\partial t}{\partial \lambda_1} = \left(\frac{1}{\lambda_1 - \lambda_2}\right)\left(\frac{1}{1 + \frac{R(\lambda_1 - \lambda_2)}{\lambda_1}}\right)\left(\frac{\lambda_2 R}{{\lambda_1}^2}\right) - \frac{1}{(\lambda_1 - \lambda_2)^2} ln\left(1 + \frac{R(\lambda_1 - \lambda_2)}{\lambda_1}\right)$$

and

$$\frac{\partial t}{\partial R} = \frac{1}{\lambda_1 + R(\lambda_1 - \lambda_2)}$$

These expressions and a more complete discussion can be found in Williams *et al.* [9].

The decay constants used for the calculations are given in Table 14.

	Decay constant (per day)	**U (k=2)**
238Pu	2.16394E-05	7.4E-09
239Pu	7.8713E-08	3.6E-11
240Pu	2.8916E-07	3.1E-10
241Pu	1.32480E-04	5.5E-08

Table 14. Decay constants used in calculations.

Tables 15 and 16 give the IDMS results for the progeny isotopes and the parent isotope concentrations in atoms/unit, and the Model Age (t) in days. The Model Dates are obtained by subtracting the Model Ages from the date/times when the progeny were separated from their parents for analysis.

Sample	234U	U (K=2)	238Pu	U (K=2)	Model Age (days)	U (K=2)	Model Date
C137A -Unit X	4.4785E+12	8.4E+09	5.51369E+15	1.9E+12	37.52	0.07	9/25/21 22:15
C137A -Unit Y	4.4997E+12	8.3E+09	5.51369E+15	1.9E+12	37.70	0.07	9/25/21 17:59
C137A -Unit Z	4.4769E+12	8.3E+09	5.51369E+15	1.9E+12	37.51	0.07	9/25/21 22:34
Sample	**235U**	**U (K=2)**	**239Pu**	**U (K=2)**			
C137A -Unit X	5.7126E+12	1.2E+10	2.08379E+18	5.9E+14	34.83	0.08	9/28/21 14:52
C137A -Unit Y	5.7279E+12	1.2E+10	2.08379E+18	5.9E+14	34.92	0.08	9/28/21 12:38
C137A -Unit Z	5.6837E+12	1.2E+10	2.08379E+18	5.9E+14	34.65	0.08	9/28/21 19:06
Sample	**236U**	**U (K=2)**	**240Pu**	**U (K=2)**			
C137A -Unit X	5.3909E+12	1.1E+10	5.01279E+17	1.4E+14	37.19	0.09	9/26/21 6:10
C137A -Unit Y	5.4189E+12	1.1E+10	5.01279E+17	1.4E+14	37.38	0.09	9/26/21 1:31
C137A -Unit Z	5.3847E+12	1.1E+10	5.01279E+17	1.4E+14	37.15	0.09	9/26/21 7:11

Table 14. UID results for C137A. U was separated from Pu on 2-Nov-2021 10:45 AM. Final purification for unit prep on 9/28/2021 8:00:00 PM.

Sample	234U	U (K=2)	238Pu	U (K=2)	Model Age (days)	U (K=2)	Model Date
C136A -Unit X	6.5441E+12	1.2E+10	4.58893E+15	1.6E+13	65.85	0.26	6/27/22 16:09
C136A -Unit Y	6.5307E+12	1.2E+10	4.58893E+15	1.6E+13	65.72	0.26	6/27/22 19:23
C136A -Unit Z	6.5507E+12	1.2E+10	4.58893E+15	1.6E+13	65.92	0.26	6/27/22 14:33
Sample	**235U**	**U (K=2)**	**239Pu**	**U (K=2)**			
C136A -Unit X	1.1789E+13	2.3E+10	2.28858E+18	7.6E+15	65.44	0.26	6/28/22 2:05
C136A -Unit Y	1.1761E+13	2.3E+10	2.28858E+18	7.6E+15	65.29	0.25	6/28/22 5:45
C136A -Unit Z	1.1815E+13	2.3E+10	2.28858E+18	7.6E+15	65.59	0.26	6/27/22 22:34
Sample	**236U**	**U (K=2)**	**240Pu**	**U (K=2)**			
C136A -Unit X	6.2699E+12	1.2E+10	3.30483E+17	1.1E+15	65.61	0.26	6/27/22 22:02
C136A -Unit Y	6.2581E+12	1.2E+10	3.30483E+17	1.1E+15	65.49	0.26	6/28/22 1:01
C136A -Unit Z	6.2716E+12	1.2E+10	3.30483E+17	1.1E+15	65.63	0.26	6/27/22 21:37

Table 15. UID results for C136A. U was separated from Pu on 1-Sep-2022 12:40 PM. Final purification for unit prep on 6/29/2022 9:25:00 PM.

Sample	241Am	U (K=2)	241Pu	U (K=2)	Model Age (days)	U (K=2)	Model Date
C137A -Unit X	6.1541E+13	5.5E+11	1.11073E+16	3.5E+12	41.71	0.37	9/28/21 20:47
C137A -Unit Y	6.1574E+13	5.5E+11	1.11073E+16	3.5E+12	41.73	0.37	9/28/21 20:15
C137A -Unit Z	6.1526E+13	5.5E+11	1.11073E+16	3.5E+12	41.70	0.37	9/28/21 21:01
Sample	**241Am**	**U (K=2)**	**241Pu**	**U (K=2)**			
C136A -Unit X	4.1774E+13	3.7E+11	9.42405E+15	3.2E+13	33.39	0.32	6/30/22 1:17
C136A -Unit Y	4.1701E+13	3.7E+11	9.42405E+15	3.2E+13	33.33	0.32	6/30/22 2:41
C136A -Unit Z	4.1888E+13	3.8E+11	9.42405E+15	3.2E+13	33.48	0.32	6/29/22 23:07

Table 16. AmID results for C137A and C136A. Am was separated from Pu on 11/9/2021 1:45:00 PM and 8/2/2022 10:33:00 AM, respectively.

In Table 16, the ^{241}Pu atoms/unit are calculated at the separation time for the AmID samples. These values differ slightly from those in Table 10 which were calculated for the CRM unit preparation time.

Conclusions

Trace actinide progeny measurements of triplicate units of C136A and C137A produced results consistent with our expectations based on earlier small-scale testing of the chemistry. ^{241}Am was quantitatively removed from Pu by the double anion exchange procedure, while a very small fraction of U and larger fraction of ^{237}Np carried through with the Pu. Most importantly, the results amongst triplicate units were consistent, showing that the purified Pu solution from which they were dispensed was homogenous and no elemental fractionation was associated with the dispensing process. This indicates that the initial quantities of progeny nuclides relative to Pu parent isotopes should be consistent across the entire set of units produced for NBL PO, making them appropriate as working reference materials for radio chronometry in nuclear forensics. Discordance of model ages measured via different radio chronometers is common in nuclear forensics due to differences in daughter element behavior during the chemical and/or physical processes that produce nuclear materials. In these materials the measured ^{241}Pu-^{241}Am model age is representative of the Pu chemical purification time, while ^{238}Pu-^{234}U and ^{240}Pu-^{236}U model ages are approximately 2 and 3 days earlier for C136A and C137A respectively. The slight discordance amongst Pu-U chronometers observed in C137A may be explained by the unknown isotopic composition of U contaminants present when the parent NBS 947 material was produced. As the C136A and C137A units age, the initial sub-ng amounts of uranium isotopes will become a smaller fraction of the total U, and only high-precision analytical techniques will be able to measure the discordance. Production of the weapons-grade Pu isotopic standard C138A will commence in 2023, and similar informational values for trace actinides will be provided in the C138A production report.

Disclaimer

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