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TIMS Analysis of GIRM FY2016 Qualification Samples

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April 2016

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Pacific Northwest National Laboratory
Richland, Washington 99352

1.0 Receipt and Processing

GIRM FY 2016 qualification samples 181 (a plug of BEPO irradiated reactor graphite), 080 (a plug of BEPO irradiated reactor graphite) and 17649 (a pressed graphite pellet Qual sample) were received at PNNL on January 22, 2016. While working in a glove box in the 325 Building, the surfaces of the graphite samples were cleaned using CO_2 pellet blasting. On February 9, 2016, a diamond saw was then used to cut a disk with a nominal thickness of 6 mm from the end of each sample to serve as the PNNL SIMS sample. The remainder of each sample became the PNNL TIMS sample. The name extensions "S1" and "T1" were added to the sample numbers for these SIMS and TIMS splits, respectively. These splits were transferred to the respective PNNL lab analyst teams in the 3420 and 3430 buildings on February 12, 2016.

Ashing, chemical processing, and TIMS measurements of the TIMS splits followed established PNNL GIRM procedures. The analytical approach was also unchanged and is outlined below.

Analytical Approach:

a) Ash sample in a high-purity quartz boat under oxygen flow in quartz tube in a tube furnace.
b) Transfer ash from quartz boat to Teflon vial. Include a 20 minute leach of the boat with 8 M HNO_3.
c) Digest the sample ash using 8 M HNO_3 – 0.02 M HF followed by aqua regia and ending in HNO_3.
d) Round 1 of the TIMS analyses consists of spiked U and preliminary spiked Pu determinations.
e) For Round 1, for each sample and blank, prepare a vial pre-spiked with ^{244}Pu and ^{233}U.
f) Mix a 25% sub-split of the dissolved sample with the spikes and equilibrate.
g) Separate Pu and U fractions from the sample matrix for Round 1.
h) Purify Pu and U fractions and release from rad control for TIMS loading and analysis.
i) Load and analyze Round-1 spiked U fraction.
j) Load and analyze Round-1 spiked Pu fraction.
k) Round 2 of the TIMS analyses consists of un-spiked U and final spiked Pu determinations.
l) Based on the Round-1 Pu data, calculate the optimum ^{244}Pu spike level for the Round-2 TIMS determination. The optimum spike level strikes a balance between a) maximizing the precision of the $^{244}Pu/^{239}Pu$ ratio measurement and b) minimizing the spike correction on the minor Pu isotopes, on ^{242}Pu in particular.
m) For Round 2, for each sample, prepare a vial pre-spiked only with ^{244}Pu. Spike vials for process blanks with both ^{233}U and ^{244}Pu.
n) Mix the remaining 75% sub-split of the dissolved sample with the Round-2 spike and equilibrate.
o) Separate Pu and U fractions from the sample matrix for Round 2.
p) Purify Pu and U fractions for Round 2.
q) Calculate activities and determine size of radiologically-releasable fractions. Preferred loading amounts are 2-4 ng of U and 2-20 pg of Pu.
r) Aliquot and release the final fractions for TIMS analysis.
s) Load and analyze Round-2 un-spiked U fraction.
t) Load and analyze Round-2 spiked Pu fraction.
u) Workup TIMS data.
v) Perform GUM analysis of measurement uncertainties and calculate uncertainty budget.
w) Report to database.

2.0 Final TIMS Results with GUM Uncertainty Analysis

We continue to use the simplified GUM approach adopted in 2011. This approach uses the output from our in-house data reduction routine and simply adds uncertainty to the GUM uncertainty budget by including correction factors (CFs) based on results for traceable, certified U and Pu reference standards that are analyzed under the same instrument run conditions as the samples. This approach was adopted because the in-house data reduction routine already accounts for all other sources of uncertainty, including detector background, sample background, contributions from the small amounts of minor isotopes present in the U and Pu tracers added, counting uncertainty, and detector dead time. The CFs for the U and Pu isotope ratios were derived from the standards data presented and discussed in Section 4.0.

We do not include the $^{233}U/^{238}U$ and $^{244}Pu/^{239}Pu$ ratios in the GUM uncertainty analysis, because those ratios include the U and Pu tracer isotopes, which were added to samples to determine bulk amounts of U and Pu and are of less interest. However, for any irradiated sample, we will continue to determine and report the $^{233}U/^{238}U$ ratio in the sample by performing a TIMS analysis on an un-spiked sub-split of the sample.

Tables 1 and 2 give the reported isotope ratios for U and Pu, respectively, along with the K factors at the 95% confidence level and the expanded uncertainties from the GUM analysis of that data.

Table 1. Corrected Isotope Ratio (Corrected Est.) and GUM Analysis Results for U

Sample	Ratio	Corrected Est.	Standard Error	DoF	K (95%)	Expanded Unc.
181T1	234/238	7.899350e-05	1.036811e-06	39.3	2.022	2.096637e-06
181T1	235/238	6.392266e-03	1.928854e-05	43.5	2.016	3.888612e-05
181T1	236/238	1.327176e-04	1.184340e-06	37.8	2.025	2.397987e-06
080T1	234/238	2.018995e-04	1.263294e-06	48.9	2.010	2.538815e-06
080T1	235/238	5.308914e-03	1.971835e-05	50.8	2.008	3.959003e-05
080T1	236/238	3.105999e-04	1.765587e-06	40.4	2.020	3.567284e-06
17649T1	234/238	4.390065e-05	6.059418e-07	39.0	2.023	1.225633e-06
17649T1	235/238	7.202817e-03	2.242878e-05	44.9	2.014	4.517666e-05
17649T1	236/238	3.279461e-05	7.085655e-07	36.3	2.028	1.436625e-06

Table 2. Corrected Isotope Ratio (Corrected Est.) and GUM Analysis Results for Pu

Sample	Ratio	Corrected Est.	Standard Error	D.o.F.	k (95%)	Expanded Unc.
181T1	240/239	3.627890e-02	1.491272e-04	6.3	2.419	3.607301e-04
181T1	241/239	1.105836e-04	8.695757e-07	61.1	2.000	1.738767e-06
181T1	242/239	2.262960e-05	3.233650e-07	123.0	1.979	6.400813e-07
080T1	240/239	1.037085e-01	4.270966e-04	6.3	2.419	1.033122e-03
080T1	241/239	1.055358e-03	4.885275e-06	10.1	2.225	1.087048e-05
080T1	242/239	6.049585e-04	2.891088e-06	11.4	2.192	6.336107e-06
17649T1	240/239	9.301569e-02	3.818519e-04	6.3	2.419	9.236780e-04
17649T1	241/239	8.965002e-05	7.254267e-07	58.0	2.002	1.452099e-06
17649T1	242/239	2.006717e-04	1.279375e-06	31.6	2.038	2.607296e-06

3.0 GUM Uncertainty Budgets

Tables 3 and 4 give the corresponding uncertainty budgets for the U and Pu TIMS determinations, respectively. As is typically the case, counting statistics often dominates the uncertainties for the low-abundance isotopes (e.g., ^{234}U, ^{236}U, ^{241}Pu, ^{242}Pu, and, to a lesser extent, ^{235}U). Their low count rates cause most of the uncertainty budget to be associated with the calculated ratio (Pct. Estimate). Conversely, the uncertainties for higher-abundance isotopes like ^{240}Pu are often dominated by the uncertainty in the respective standard, as reflected in the uncertainty of the corresponding CF (Pct. Corr. Factor). An exception to these general trends was the Pu data for sample 080T1. Because that sample contained relatively high levels of the minor Pu isotopes, they were measured with higher than average TIMS precision, causing the majority of the uncertainty budget to come from the CF.

Table 3. GUM Uncertainty Budgets for U Measurements.

		Uncertainty Budget	
Sample	Ratio	Pct. Estimate	Pct. Corr. Factor
181T1	234/238	95.5%	4.5%
181T1	235/238	51.7%	48.3%
181T1	236/238	97.5%	2.5%
080T1	234/238	80.0%	20.0%
080T1	235/238	68.1%	31.9%
080T1	236/238	93.9%	6.1%
17649T1	234/238	95.9%	4.1%
17649T1	235/238	54.6%	45.4%
17649T1	236/238	99.6%	0.4%

Table 4. GUM Uncertainty Budget for Pu Measurements.

		Uncertainty Budget	
Sample	Ratio	Pct. Estimate	Pct. Corr. Factor
181T1	240/239	2.4%	97.6%
181T1	241/239	73.3%	26.7%
181T1	242/239	91.9%	8.1%
080T1	240/239	2.7%	97.3%
080T1	241/239	23.0%	77.0%
080T1	242/239	27.8%	72.2%
17649T1	240/239	2.1%	97.9%
17649T1	241/239	74.8%	25.2%
17649T1	242/239	59.4%	40.6%

4.0 U and Pu Isotopic Standards

Tables 5 and 6 give the results for the U and Pu isotope ratio standards that were analyzed in conjunction with the GIRM FY2016 qualification samples.

Per standard practice, the mean $^{235}U/^{238}U$ ratio observed for a number of 2 ng loads of the certified Nat. U isotopic standard CRM 129A was used to calculate the CF for the $^{235}U/^{238}U$ ratio. The CFs for the $^{233}U/^{238}U$, $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios were in turn calculated from the CF for the $^{235}U/^{238}U$ ratio using a power law relationship. In this case, the certified $^{235}U/^{238}U$ ratio for CRM 129A of 0.0072614 was divided by the mean $^{235}U/^{238}U$ ratio of 0.007292 that was observed for the 15 trials listed in Table 5 to yield a $^{235}U/^{238}U$ CF of 0.9958 ± 0.0021 (1 standard deviation). The cube root of that ratio, 0.99860 ± 0.00070, is the CF per unit mass difference. That factor is taken to the power of the mass difference between the two isotopes in a given ratio pair to give the CF for that ratio.

Table 5. Results for CRM 129A Standard Used to Determine Correction Factors for U Isotope Ratios.

Analysis	Analysis	$^{235}U/^{238}U$	
Number	Date	Mean Ratio	2σ Uncertainty
U-89859A	2/8/2016	0.007279	0.000013
U-89859B	2/8/2016	0.007300	0.000018
U-89859C	2/9/2016	0.007294	0.000018
U-89859D	2/9/2016	0.007266	0.000014
U-89859E	2/9/2016	0.007285	0.000018
U-89859F	2/11/2016	0.007294	0.000014
U-89871A	2/11/2016	0.007320	0.000016
U-89871B	2/16/2016	0.007279	0.000012
U-89871C	2/16/2016	0.007310	0.000014
U-89871D	2/29/2016	0.007301	0.000017
U-89871E	2/29/2016	0.007306	0.000018
U-89901A	3/4/2016	0.007282	0.000016
U-89901B	3/4/2016	0.007302	0.000015
U-89901C	3/30/2016	0.007275	0.000021
U-89901D	4/7/2016	0.007286	0.000015
	Mean	0.007292	
	Standard Deviation	0.000015	
	RSD	0.20%	

Also per standard practice, the mean $^{240}Pu/^{239}Pu$ from multiple runs of 0.8 ng loads of the certified Pu isotopic standard CRM 138 was used to calculate the CF for the $^{240}Pu/^{239}Pu$ ratio. Because the Pu TIMS runs are performed in total evaporation mode, mass fractionation bias, which is usually the dominant source of measurement bias in TIMS runs, averages out to zero and a CF of unity is expected. Furthermore, since the correction factors for the minor Pu isotopes cannot be measured with much precision, they are taken as being equivalent to the CF for the $^{240}Pu/^{239}Pu$ ratio. In this case, the 6 runs of CRM 138 gave a mean $^{240}Pu/^{239}Pu$ ratio of 0.08595 ± 0.00035 (1 standard deviation) and a mean $^{240}Pu/^{239}Pu$ ratio CF of 1.0028 ± 0.0041 (1 standard deviation) relative to the certified $^{240}Pu/^{239}Pu$ ratio of 0.08619 ± 0.00011. Since that CF is not statistically distinguishable from unity, it was taken as unity. As a result, a CF of unity with an uncertainty of 0.41% was applied to all measured Pu isotope ratios.

Table 6. Results for CRM 138 Standard Used to Determine Correction Factors for Pu Isotope Ratios.

Analysis	Analysis	$^{240}Pu/^{239}Pu$	
Number	Date	Mean Ratio	2σ Uncertainty
89889	3-Mar-16	0.08578	±0.00047
89890	4-Mar-16	0.08538	±0.00050
89891	4-Mar-16	0.08602	±0.00059
89892	24-Mar-16	0.08632	±0.00049
89893	24-Mar-16	0.08628	±0.00044
89894	25-Mar-16	0.08590	±0.00044
	Mean	0.08595	
	Standard Deviation	0.00035	
	RSD	0.41%	

5.0 Process Blanks

Tables 7 – 12 give the results for the process blanks that accompanied the GIRM FY2016 qualification samples throughout their processing.

Tables 7 and 8 list the quantities of ^{238}U in the sub-splits of the samples and process blanks that were analyzed for Rounds 1 and 2, respectively, as well as the U atom ratios observed during the respective round of analyses. The concentration of ^{238}U in the graphite, which is calculated using data from both the spiked and un-spiked U TIMS runs is also listed. The process blanks started at Step a) of the analytical approach outlined in Section 1.0, whereas the chemistry blanks started at Step c). The quantities of U in the blanks are lower on average than the levels that were observed during the 2013 qualification exercise. While the U in the blanks is slightly enriched, as was also the case in 2013, it is less perturbed than it was in 2013. The ^{238}U quantity data suggest that the blanks are insignificant relative to the samples. However, the significance of the blanks can be more rigorously evaluated by comparing their levels to those of the samples on an isotope by isotope basis (see Tables 9 and 10).

Table 7. Uranium Atom Ratios and ^{238}U Quantities and Concentrations from Round-1 Analyses.

TIMS Analysis Number	Customer Number or Identification	Sample Size (g)	^{238}U Quantity ± U and Concentration ± U (k = 2) (ng analyzed)	(ng/g graphite)	U Atom Ratio ± 2σ Uncertainty $^{234}U/^{238}U$	$^{235}U/^{238}U$	$^{236}U/^{238}U$
89875U	181T1	2.7734 ±.0007	8.69 0.15	12.36 0.22	0.0000787 ±.0000016	0.006403 ±.000033	0.0001298 ±.0000026
89876U	080T1	2.6339 ±.0007	3.604 0.063	5.524 0.097	0.0002033 ±.0000031	0.005334 ±.000029	0.0003119 ±.0000038
89877U	17649T1	3.1021 ±.0007	15.99 0.27	20.81 0.35	0.0000434 ±.0000011	0.007214 ±.000036	0.00003215 ±.00000098
89878U	PNNL Blank (Process)	---	0.00952 0.00016	---	0.000070 ±.000016	0.00760 ±.00014	---
89879U	PNNL Blank (Chemistry 1)	---	0.00897 0.00015	---	0.000059 ±.000019	0.00757 ±.00014	---
89880U	PNNL Blank (Chemistry 2)	---	0.00944 0.00016	---	0.000053 ±.000014	0.00810 ±.00015	---

Table 8. Uranium Atom Ratios and ^{238}U Quantities and Concentrations from Round-2 Analyses.

TIMS Analysis Number	Customer Number or Identification	Sample Size (g)	^{238}U Quantity ± U and Concentration ± U (k = 2) (ng analyzed)	(ng/g graphite)	U Atom Ratio ± 2σ Uncertainty $^{234}U/^{238}U$	$^{235}U/^{238}U$	$^{236}U/^{238}U$	$^{233}U/^{238}U$
			(Estimates Based on Round 1)					
89881U	181T1	2.7734 ±.0007	26.08 0.46	12.36 0.22	0.0000790 ±.0000021	0.006392 ±.000039	0.0001327 ±.0000024	0.003589 ±.000036
89882U	080T1	2.6339 ±.0007	10.81 0.19	5.524 0.097	0.0002019 ±.0000025	0.005309 ±.000040	0.0003106 ±.0000036	0.009810 ±.000073
89883U	17649T1	3.1021 ±.0007	47.97 0.80	20.81 0.35	0.0000439 ±.0000012	0.007203 ±.000045	0.0000328 ±.0000014	---
89884U	PNNL Blank (Process)	---	0.01890 ±.00031	---	0.000045 ±.000015	0.00778 ±.00010	---	---
89885U	PNNL Blank (Chemistry 1)	---	0.00835 ±.00014	---	0.000070 ±.000021	0.00781 ±.00014	---	---
89886U	PNNL Blank (Chemistry 2)	---	0.007609 ±.000064	---	0.000082 ±.000019	0.00789 ±.00027	---	---

Tables 9 and 10 list the quantities of each U isotope in the sub-splits of the samples and process blanks that were analyzed for Rounds 1 and 2, respectively. Those tables also include the estimated contribution of the process blank to the three samples both in units of percent and of expanded uncertainty U. For Round 1, the worst case contribution of the process blank is 0.38% (0.20U) to sample 080T1. For Round 2, the worst case contribution of the process blank is 0.26% (0.13U) to sample 080T1. Any perturbations of sample results that may be caused by the process blank should therefore be covered by the reported uncertainties.

Table 9. Uranium Atom Quantities from Round-1 Analyses.

TIMS Analysis Number	TIMS Analysis Date	Customer Sample Number or Identification	Atoms in Fraction Analyzed ± U (k = 2) (Bias Corrected w.r.t. CRM 129A) ^{234}U	^{235}U	^{236}U	^{238}U
89875U	30Mar16	181T1	1.737E+09 5.6E+07	1.406E+11 2.6E+09	2.918E+09 7.4E+07	2.199E+13 3.9E+11
89876U	30Mar16	080T1	1.841E+09 4.0E+07	4.841E+10 9.2E+08	2.832E+09 5.9E+07	9.12E+12 1.6E+11
89877U	30Mar16	17649T1	1.776E+09 5.8E+07	2.913E+11 5.2E+09	1.326E+09 6.2E+07	4.045E+13 6.7E+11
89878U	30Mar16	PNNL Blank (PSF Process)	1.69E+06 3.9E+05	1.831E+08 4.5E+06	<8E+05	2.408E+10 4.0E+08
89879U	30Mar16	PNNL Blank (Chemistry - 1)	1.35E+06 4.3E+05	1.717E+08 4.1E+06	<1E+06	2.268E+10 3.8E+08
89880U	30Mar16	PNNL Blank (Chemistry - 2)	1.26E+06 3.4E+05	1.935E+08 4.6E+06	<1E+06	2.387E+10 4.0E+08
		Estimated Contribution of Process Blank 89878 to Sample in Units of %				
		181T1	0.10%	0.13%	<0.03%	0.11%
		080T1	0.09%	0.38%	<0.03%	0.26%
		17649T1	0.10%	0.06%	<0.06%	0.06%
		Estimated Contribution of Process Blank 89878 to Sample in Units of U				
		181T1	0.030	0.069	<0.011	0.061
		080T1	0.043	0.199	<0.013	0.151
		17649T1	0.029	0.035	<0.013	0.036

Table 10. Uranium Atom Quantities from Round-2 Analyses.

TIMS Analysis Number	TIMS Analysis Date	Customer Sample Number or Identification	Atoms in Fraction Analyzed ± U (k = 2) (Bias Corrected w.r.t. CRM 129A) ^{234}U	^{235}U	^{236}U	^{238}U
			(For samples, taken as 3 times the Round-1 values)			
89881U	08Apr16	181T1	5.21E+09	4.217E+11	8.76E+09	6.60E+13
			1.7E+08	7.9E+09	2.2E+08	1.2E+12
89882U	08Apr16	080T1	5.52E+09	1.452E+11	8.50E+09	2.735E+13
			1.2E+08	2.8E+09	1.8E+08	4.8E+11
89883U	08Apr16	17649T1	5.33E+09	8.74E+11	3.98E+09	1.213E+14
			1.7E+08	1.6E+10	1.9E+08	2.0E+12
89884U	08Apr16	PNNL Blank (PSF Process)	2.17E+06	3.718E+08	<2E+06	4.782E+10
			7.1E+05	7.8E+06		7.9E+08
89885U	08Apr16	PNNL Blank (Chemistry - 1)	1.49E+06	1.649E+08	<8E+05	2.112E+10
			4.5E+05	4.0E+06		3.5E+08
89886U	08Apr16	PNNL Blank (Chemistry - 2)	1.59E+06	1.518E+08	<1E+06	1.925E+10
			3.6E+05	5.6E+06		3.3E+08
		Estimated Contribution of Process Blank 89878 to Sample in Units of %				
		181T1	0.04%	0.09%	<0.02%	0.07%
		080T1	0.04%	0.26%	<0.02%	0.17%
		17649T1	0.04%	0.04%	<0.05%	0.04%
		Estimated Contribution of Process Blank 89878 to Sample in Units of U				
		181T1	0.013	0.047	<0.009	0.041
		080T1	0.018	0.134	<0.011	0.100
		17649T1	0.013	0.024	<0.011	0.024

Note that standard practice, which was followed here, is to report the U isotope ratios from Round 2 of the analyses, since they are less likely to be perturbed by the corresponding process blank (because the relative contribution of the process blank to these 75% sub-splits should be smaller than for the 25% sub-splits used for Round 1), and since unlike the Round 1 results they cannot be perturbed by the U isotopic impurities that are present in the ^{233} U tracer. So, although the Round-1 U isotope ratios agree well with the Round-2 results, and in some cases have smaller uncertainties than the Round-2 results, they did not contribute to the reported U isotope ratios.

Also note that the reported U results for the samples are not corrected for the process blank, because the U quantities in the process blanks have not been found to be reproducible.

Table 11 lists the quantities of ^{239}Pu in the sub-splits of the samples and process blanks that were analyzed for Round 2. The concentration of ^{239}Pu in the graphite and the Pu atom ratios observed during that round of analyses are also listed. The quantities of Pu in the blanks are about twice that observed during the 2013 qualification exercise. While the ^{239}Pu quantity data suggest that the blanks are insignificant relative to the samples, the significance of the blanks can again be more rigorously evaluated by comparing their levels to those of the samples on an isotope by isotope basis (see Table 12).

Table 11. Plutonium Atom Ratios and ^{239}Pu Quantities and Concentrations from Round-2 Analyses.

TIMS Analysis Number	Customer Sample Number or Identification	Sample Size (g)	^{239}Pu Quantity ± U and Concentration ± U (k = 2) (pg analyzed)	(pg/g graphite)	Plutonium Atom Ratio ± U (k = 2) ^{240}Pu/^{239}Pu	^{241}Pu/^{239}Pu	^{242}Pu/^{239}Pu
89881P	181T1	2.7734 ±.0007	44.96 ±.86	21.71 ±.42	0.03628 ±.00036	0.0001106 ±.0000017	0.00002263 ±.00000064
89882P	080T1	2.6339 ±.0007	69.21 ±1.40	34.94 ±.71	0.1037 ±.0010	0.001055 ±.000011	0.0006050 ±.0000063
89883P	17649T1	3.1021 ±.0007	26.90 ±0.52	11.60 ±0.22	0.09302 ±.00092	0.0000897 ±.0000015	0.0002007 ±.0000026
89884P	PNNL Blank (PSF Process)	---	<0.0002	---	---	---	---
89885P	PNNL Blank (Chemistry - 1)	---	<0.0002	---	---	---	---
89886P	PNNL Blank (Chemistry - 2)	---	<0.0002	---	---	---	---

Table 12 lists the quantities of each Pu isotope in the sub-splits of the samples and process blanks that were analyzed for Round 2, along with the estimated upper-limit contribution of the process blank to the three samples both in units of percent and of expanded uncertainty U. The estimated upper-limit contribution of the process blank to the ^{239}Pu and ^{240}Pu observed in the samples is insignificant. The estimated upper-limit contribution of the process blank to the ^{241}Pu and ^{242}Pu observed in sample 080T1 is insignificant. While the estimated upper-limit contribution of the process blank to the ^{241}Pu and ^{242}Pu observed in samples 180T1 and 17649T1 could be significant, the upper-limit of that estimated contribution only exceeds 1U for ^{242}Pu in sample 181T1 and for ^{241}Pu in sample 17649T1.

Table 12. Plutonium Atom Quantities from Round-2 Analyses.

TIMS Analysis Number	TIMS Analysis Date	Customer Sample Number or Identification	Atoms in Fraction Analyzed ± U (k = 2) ^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
89881P	24Mar16	181T1	1.133E+11 2.2E+09	4.109E+09 8.9E+07	1.252E+07 3.1E+05	2.563E+06 8.8E+04
89882P	24Mar16	080T1	1.743E+11 3.5E+09	1.808E+10 4.1E+08	1.840E+08 4.2E+06	1.055E+08 2.4E+06
89883P	24Mar16	17649T1	6.78E+10 1.3E+09	6.30E+09 1.4E+08	6.07E+06 1.5E+05	1.360E+07 3.2E+05
89884P	24Mar16	PNNL Blank (PSF Process)	<4E+05	<2E+05	<2E+05	<2E+05
89885P	24Mar16	PNNL Blank (Chemistry - 1)	<3E+05	<2E+05	<2E+05	<2E+05
89886P	24Mar16	PNNL Blank (Chemistry - 2)	<3E+05	<2E+05	<2E+05	<2E+05
			Fractional Contribution of Blank 89884 to Sample			
		181T1	<0.0004%	<0.0049%	<1.60%	<7.80%
		080T1	<0.0002%	<0.0011%	<0.11%	<0.19%
		17649T1	<0.0006%	<0.0032%	<3.29%	<1.47%
			Fractional Contribution of Blank 89884 to Sample			
		181T1	<0.0002	<0.0023	<0.644	<2.284
		080T1	<0.0001	<0.0005	<0.048	<0.083
		17649T1	<0.0003	<0.0015	<1.310	<0.634

6.0 Problems

Apparent ion transmission issues with the TIMS instrument that was used for the Pu determinations may have caused negative biases in the measured $^{240}Pu/^{239}Pu$ ratios of about 0.5%. However, any such bias should be covered by the reported uncertainties, which at the 95% confidence level were about 1.0%. For future GIRM work, Pu measurements may be moved to the commercial Triton TIMS instrument, which is already in use for the U measurements, because it provides a more stable instrument platform that has been optimized for measurement accuracy.

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