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GUM Analysis for TIMS Isotopic Ratios in BEPO Graphite Qualification Samples, Round 2

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PG Heasler

January 2009

Pacific Northwest
NATIONAL LABORATORY

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Pacific Northwest National Laboratory
Richland, Washington 99352

1.0 Sample Receipt and Preparation

In May 2007, one set of three samples from NBL were addressed to Steve Petersen for TIMS analysis, and included BEP0 samples numbered 27008, 30986, and 50846. All cores were trimmed by tooling, and lightly cleaned by CO_2 pellet blasting. Small discs were cut from the second set of samples for SIMS analysis, with the remainder of each used for TIMS preparation.

Three GIRM Phase III QA samples were received from NBL in August 2008, and consisted of UCAR graphite plugs doped with solutions containing uranium and plutonium. The three samples received at PNNL for TIMS analysis were numbered P3-51C, P3-52A, and P3-60C. These were not trimmed or prepared in the manner above, but the as-received samples were immediately ashed, as in step 1 below.

The general sample preparation procedure for TIMS analysis includes the following steps:

1. Samples ashed and ash acid digested, ending up in HCl. A 20% aliquot is kept in reserve for processing or replicates if needed.

2. 40% of ash solution taken for unspiked U separation and TIMS analysis; $^{233}U/^{238}U$ ratios determined by TIMS analysis rather than ICPMS analyses as used earlier.

3. 40% spiked with mixed ^{233}U + ^{244}Pu spike; Pu-244 spike amounts were chosen to be appropriate for the sample based on either the SIMS results for B isotopes or the unspiked U isotope ratios, to minimize spike correction on minor Pu isotopes, and because Pu contents were expected to vary by up to 300-fold. This is based on our accumulated experience with the BEP0 samples, and may be useful in other, future sample studies

4. Portion of separated spiked U fraction aliquotted for Pu TIMS analysis and additional U TIMS analysis based on observed U total contents, 2 ng U usual amount preferred, 1 to 3 pg Pu preferred (more for low burnup samples).

5. Total U contents calculated based on sample and aliquot weights, and spiked and unspiked $^{233}U/^{238}U$ ratios, since many samples contain ^{233}U already. Total Pu contents determined based on measured amount of ^{244}Pu added.

The three NBL BEP0 samples were prepared following these steps, resulting in both spiked and unspiked U fractions analyzed by TIMS. Unfortunately, U from both the spiked and unspiked separations was lost, and determination of U contents was not possible. The reserved 20% fraction for each sample was later processed to obtain more of the U for TIMS analyses.

The three ('non-BEP0') fabricated QA samples were not split following our usual procedure above, and instead 50% of the sample solution was processed and combined with the U and Pu spikes, and 50% used for unspiked separations and analyses. Separations are completed and preliminary results for these samples will be available soon, but are not included in this report.

2.0 TIMS Analysis

Separated uranium fractions for TIMS analysis are prepared by solution loading using a nanopipettor mounted in a micromanipulator onto carburized Re filaments. Separated plutonium fractions are equilibrated with single anion resin beads that are loaded onto carburized Re filaments to make a better point source for thermal ion emission. Data are acquired on the mass spectrometer in peak-switching cycles, with each cycle including a scan up and a scan down the designated range of masses. Counting times for each mass are chosen to improve counting statistics, and are different for U and Pu acquisitions.

For spiked uranium fractions, the chosen counting times are:

Mass	233	234	235	236	238	240	243
Time(sec)	3	12	6	12	3	3	6

For unspiked uranium fractions, the chosen counting times are:

Mass	233	234	235	236	238	240	243
Time(sec)	12	9	6	12	3	3	6

For plutonium fractions, the chosen counting times are:

Mass	239	240	241	242	243	244
Time(sec)	3	6	12	12	5	7

Run data and results generated by the TIMS mass spectrometer data acquisition routine produce a good initial estimate of run quality and analysis precision. In these preliminary run results, uranium isotope ratio measurements are corrected for measurement mass bias based on results obtained for a natural U standard NBS 950a. Plutonium isotope ratio results are not corrected for mass bias.

3.0 Preliminary TIMS Data Reduction

Resulting or 'raw' mass spec data files are reduced using an in-house routine, which subtracts spike/tracer contributions on other isotopes, and which also generates cycle-by-cycle raw count tables and interpolated count rates. The latter were used in some portions of the GUM analysis. The 2σ uncertainties reported for all isotope ratios below are preliminary in a sense, having been generated by our in-house offline data reduction program, whereas the GUM uncertainty analysis includes a more complete estimate of measurement uncertainty. The tables also include the internal sample log numbers assigned to each sample for record-keeping. The values reported below are not yet corrected for measurement mass bias.

sample	PNNL No.	$^{234}U/^{238}U$	2 sigma	$^{235}U/^{236}U$	2 sigma	$^{236}U/^{238}U$	2 sigma
27008	85238	0.000224	0.000002	0.005062	0.000026	0.000365	0.000004
30986	85239	0.000246	0.000003	0.004803	0.000017	0.000400	0.000004
50846	85240	0.000108	0.000003	0.005799	0.000020	0.000231	0.000003

sample	PNNL No.	$^{240}Pu/^{239}Pu$	2 sigma	$^{241}Pu/^{239}Pu$	2 sigma	$^{242}Pu/^{239}Pu$	2 sigma
27008	85393	0.12505	0.00030	0.002127	0.000020	0.001039	0.000016
30986	85395	0.13741	0.00031	0.002471	0.000021	0.001364	0.000017
50846	85394	0.07334	0.00018	0.000764	0.000012	0.000210	0.000006

4.0 GUM Analyses of TIMS Results

All notations and calculations used in the GUM analyses and in tables below are the same as used in the previous GUM report for BEP0 TIMS results.

Uncertainties for the concentrations and isotope ratios of the U or Pu tracers or 'spikes' were not directly used in GUM uncertainty analyses. No new independent measurements or recalibrations of tracers were performed during the present study. Results of recent or past such measurements can be provided separately upon request, if there is interest. Instead, the amounts of ion counts estimated contributed by the tracer for all isotopes are used in the GUM uncertainty tables for U and Pu results.

The TIMS mass spectrometer which has been continuously used in this project was down for a period of several months finally ending in July 2008. At that time, a number of tests and standard reference materials were run for operational and quality checks. As a result of this effort, new data for Pu reference standard CRM 138 was acquired and was used to estimate mass bias correction factors (CFs) for these sample results. Recent analyses of natural U standard NBS 950a were also used to estimate mass bias correction factors, however, 'CFs' for $^{233}U/^{238}U$ and $^{236}U/^{238}U$ ratios are not available yet, since this particular standard lacks any ^{233}U or ^{236} U. In the future, we plan to acquire depleted U reference standards for routine use and for measurement of mass bias factors for all of the U isotope ratios. The uncertainty contributions for CFs were estimated in the GUM results below using these newer and more recent results on measurement reference standards.

Pu GUM Tables For Sample 85393 (27008)						
$^{240}Pu/^{239}Pu$						
Quantity	Est	%RE	dof	Sensit	Uncert	Index
R.240.239	0.125	0.156	37.6	1.00E+00	1.95E-04	8.80E+01
CF.240.239	1	0.0576	31	1.25E-01	7.20E-05	1.20E+01
b.tot.239	0.658	27.9	Inf	8.80E-07	1.61E-07	6.03E-05
b.tot.240	3.66	5.05	Inf	-2.06E-05	-3.81E-06	3.37E-02
Cor	NA	NA	NA	NA	-1.11E-06	-2.83E-03
Result	0.125	0.166	47.5	NA	NA	NA
$^{241}Pu/^{239}Pu$						
R.241.239	0.00211	0.527	37.2	1.03E+00	1.15E-05	3.39E+01
CF.241.239	1.03	0.715	31	2.11E-03	1.56E-05	6.24E+01
b.tot.239	0.658	27.9	Inf	1.45E-08	2.67E-09	1.83E-06
b.tot.241	0.928	19.8	Inf	-2.06E-05	-3.79E-06	3.69E+00
Cor	NA	NA	NA	NA	-1.42E-07	-5.20E-03
Result	0.00218	0.905	63.9	NA	NA	NA
$^{242}Pu/^{239}Pu$						
R.242.239	0.00103	0.88	37	1.04E+00	9.38E-06	4.35E+01
CF.242.239	1.04	0.938	31	1.03E-03	1.00E-05	4.94E+01
b.tot.239	0.658	27.9	Inf	6.98E-09	1.28E-09	8.10E-07
b.tot.242	6.71	2.74	Inf	-2.06E-05	-3.80E-06	7.12E+00
Cor	NA	NA	NA	NA	-9.84E-08	-4.79E-03
Result	0.00107	1.33	77.1	NA	NA	NA

Pu GUM Tables For Sample 85395 (50846)						
$^{240}Pu/^{239}Pu$						
Quantity	Est	%RE	dof	Sensit	Uncert	Index
R.240.239	0.0734	0.173	36.9	1.00E+00	1.27E-04	8.99E+01
CF.240.239	1	0.0576	31	7.34E-02	4.23E-05	1.00E+01
b.tot.239	0.697	28.3	Inf	4.02E-07	7.94E-08	3.52E-05
b.tot.240	4.18	4.76	Inf	-1.62E-05	-3.23E-06	5.83E-02
Cor	NA	NA	NA	NA	-7.13E-07	-2.84E-03
Result	0.0735	0.182	44.9	NA	NA	NA
$^{241}Pu/^{239}Pu$						
R.241.239	0.000764	0.642	36.8	1.03E+00	5.05E-06	3.78E+01
CF.241.239	1.03	0.715	31	7.64E-04	5.63E-06	4.70E+01
b.tot.239	0.697	28.3	Inf	4.13E-09	8.15E-10	9.84E-07
b.tot.241	1.01	19.5	Inf	-1.62E-05	-3.20E-06	1.52E+01
Cor	NA	NA	NA	NA	-7.23E-08	-7.73E-03
Result	0.000787	1.04	90.8	NA	NA	NA
$^{242}Pu/^{239}Pu$						
R.242.239	0.00021	1.46	35.2	1.04E+00	3.18E-06	4.11E+01
CF.242.239	1.04	0.938	31	2.10E-04	2.04E-06	1.69E+01
b.tot.239	0.697	28.3	Inf	1.11E-09	2.19E-10	1.95E-07
b.tot.242	7.71	2.56	Inf	-1.62E-05	-3.21E-06	4.20E+01
Cor	NA	NA	NA	NA	-3.74E-08	-5.70E-03
Result	0.000218	2.28	175	NA	NA	NA

Pu GUM Tables For Sample 85394 (30986)						
$^{240}Pu/^{239}Pu$						
Quantity	Est	%RE	dof	Sensit	Uncert	Index
R.240.239	0.137	0.172	44	1.00E+00	2.36E-04	8.99E+01
CF.240.239	1	0.0576	31	1.37E-01	7.90E-05	1.01E+01
b.tot.239	0.603	29.3	Inf	1.43E-06	2.52E-07	1.02E-04
b.tot.240	2.69	6.58	Inf	-3.09E-05	-5.46E-06	4.81E-02
Cor	NA	NA	NA	NA	-1.66E-06	-4.42E-03
Result	0.137	0.182	53.5	NA	NA	NA
$^{241}Pu/^{239}Pu$						
R.241.239	0.00245	0.593	44.1	1.03E+00	1.50E-05	3.86E+01
CF.241.239	1.03	0.715	31	2.45E-03	1.81E-05	5.63E+01
b.tot.239	0.603	29.3	Inf	2.53E-08	4.46E-09	3.41E-06
b.tot.241	0.791	22.3	Inf	-3.09E-05	-5.44E-06	5.09E+00
Cor	NA	NA	NA	NA	-2.20E-07	-8.34E-03
Result	0.00253	0.953	73.5	NA	NA	NA
$^{242}Pu/^{239}Pu$						
R.242.239	0.00136	0.93	43.4	1.04E+00	1.31E-05	4.57E+01
CF.242.239	1.04	0.938	31	1.36E-03	1.32E-05	4.64E+01
b.tot.239	0.603	29.3	Inf	1.39E-08	2.45E-09	1.60E-06
b.tot.242	4.81	3.67	Inf	-3.09E-05	-5.45E-06	7.91E+00
Cor	NA	NA	NA	NA	-1.63E-07	-7.10E-03
Result	0.00141	1.38	85	NA	NA	NA

Summary Table For Pu					
$^{240}Pu/^{239}Pu$					
Sample	Est	%RE	dof	K.factor	95% CB
85393	0.125	0.1662	47.49	2.011	0.0004179
85395	0.07348	0.1821	44.93	2.014	0.0002695
85394	0.1373	0.1815	53.49	2.005	0.0004996
$^{241}Pu/^{239}Pu$					
85393	0.002175	0.9053	63.88	1.998	3.93E-05
85395	0.0007875	1.043	90.8	1.986	1.63E-05
85394	0.00253	0.9533	73.51	1.993	4.81E-05
$^{242}Pu/^{239}Pu$					
85393	0.001066	1.334	77.06	1.991	2.83E-05
85395	0.0002175	2.279	175.1	1.974	9.78E-06
85394	0.001408	1.376	85.02	1.988	3.85E-05

U GUM Tables For Sample 85238 (27008)						
$^{236}U/^{238}U$						
Quantity	Est	%RE	dof	Sensit	Uncert	Index
R.236.238	0.000364	0.566	34.6	1.00E+00	2.06E-06	4.05E+01
CF.236.238	1	0.5	Inf	3.64E-04	1.82E-06	3.16E+01
b.tot.238	0.722	48.8	Inf	4.42E-10	1.56E-10	2.31E-07
b.tot.236	0.722	48.8	Inf	-4.86E-06	-1.71E-06	2.79E+01
Cor	NA	NA	NA	NA	-2.31E-08	-5.08E-03
Result	0.000364	0.89	211	NA	NA	NA
$^{235}U/^{236}U$						
R.235.238	0.00505	0.286	34.8	9.96E-01	1.44E-05	9.17E+01
CF.235.238	0.996	0.079	8	5.05E-03	3.97E-06	7.02E+00
b.tot.238	0.722	48.8	Inf	6.13E-09	2.16E-09	2.07E-06
b.tot.235	0.722	48.8	Inf	-4.86E-06	-1.71E-06	1.30E+00
Cor	NA	NA	NA	NA	-8.60E-08	-3.29E-03
Result	0.00503	0.298	40.4	NA	NA	NA
$^{234}U/^{238}U$						
R.234.238	0.000223	0.543	34.6	9.85E-01	1.19E-06	2.93E+01
CF.234.238	0.985	0.326	8	2.23E-04	7.17E-07	1.05E+01
b.tot.238	0.722	48.8	Inf	2.71E-10	9.56E-11	1.87E-07
b.tot.234	0.722	48.8	Inf	-4.86E-06	-1.71E-06	6.02E+01
Cor	NA	NA	NA	NA	-1.81E-08	-6.72E-03
Result	0.00022	1	259	NA	NA	NA

U GUM Tables For Sample 85239 (30986)						
$^{236}U/^{238}U$						
Quantity	Est	%RE	dof	Sensit	Uncert	Index
R.236.238	0.0004	0.488	34.6	1.00E+00	1.95E-06	4.86E+01
CF.236.238	1	0.5	Inf	4.00E-04	2.00E-06	5.10E+01
b.tot.238	0.407	9.18	Inf	4.96E-10	1.86E-11	4.38E-09
b.tot.236	0.407	9.18	Inf	-4.96E-06	-1.86E-07	4.38E-01
Cor	NA	NA	NA	NA	-2.62E-09	-8.76E-05
Result	0.0004	0.7	146	NA	NA	NA
$^{235}U/^{236}U$						
R.235.238	0.0048	0.234	34.6	9.96E-01	1.12E-05	8.98E+01
CF.235.238	0.996	0.079	8	4.80E-03	3.78E-06	1.02E+01
b.tot.238	0.407	9.18	Inf	5.96E-09	2.23E-10	3.55E-08
b.tot.235	0.407	9.18	Inf	-4.96E-06	-1.86E-07	2.46E-02
Cor	NA	NA	NA	NA	-9.09E-09	-5.91E-05
Result	0.00479	0.247	40.7	NA	NA	NA
$^{234}U/^{238}U$						
R.234.238	0.000246	0.69	34.6	9.85E-01	1.67E-06	8.10E+01
CF.234.238	0.985	0.326	8	2.46E-04	7.89E-07	1.80E+01
b.tot.238	0.407	9.18	Inf	3.05E-10	1.14E-11	3.76E-09
b.tot.234	0.407	9.18	Inf	-4.96E-06	-1.86E-07	9.98E-01
Cor	NA	NA	NA	NA	-2.06E-09	-1.23E-04
Result	0.000242	0.767	43.5	NA	NA	NA

U GUM Tables For Sample 85240 (50846)						
$^{236}U/^{238}U$						
Quantity	Est	%RE	dof	Sensit	Uncert	Index
R.236.238	0.000231	0.728	34.1	1.00E+00	1.68E-06	6.20E+01
CF.236.238	1	0.5	Inf	2.31E-04	1.16E-06	2.92E+01
b.tot.238	0.481	23.2	Inf	3.28E-10	3.66E-11	2.93E-08
b.tot.236	0.481	23.2	Inf	-5.68E-06	-6.33E-07	8.77E+00
Cor	NA	NA	NA	NA	-6.81E-09	-1.01E-03
Result	0.000231	0.925	88.8	NA	NA	NA
$^{235}U/^{236}U$						
R.235.238	0.00582	0.204	34.2	9.96E-01	1.18E-05	8.67E+01
CF.235.238	0.996	0.079	8	5.82E-03	4.58E-06	1.30E+01
b.tot.238	0.481	23.2	Inf	8.27E-09	9.23E-10	5.27E-07
b.tot.235	0.481	23.2	Inf	-5.68E-06	-6.33E-07	2.48E-01
Cor	NA	NA	NA	NA	-3.42E-08	-7.24E-04
Result	0.0058	0.219	41.5	NA	NA	NA
$^{234}U/^{238}U$						
R.234.238	0.000109	0.968	33.9	9.85E-01	1.04E-06	6.74E+01
CF.234.238	0.985	0.326	8	1.09E-04	3.51E-07	7.65E+00
b.tot.238	0.481	23.2	Inf	1.55E-10	1.73E-11	1.86E-08
b.tot.234	0.481	23.2	Inf	-5.68E-06	-6.33E-07	2.49E+01
Cor	NA	NA	NA	NA	-4.68E-09	-1.36E-03
Result	0.000108	1.18	70.6	NA	NA	NA

Summary Table For U					
$^{236}U/^{238}U$					
Sample	Est	%RE	dof	K.factor	95% CB
85238	0.0003641	0.8899	210.8	1.971	6.39E-06
85239	0.0004004	0.7004	146.4	1.976	5.54E-06
85240	0.0002312	0.9249	88.76	1.987	4.25E-06
$^{235}U/^{236}U$					
85238	0.005029	0.2982	40.36	2.021	3.03E-05
85239	0.004786	0.2472	40.7	2.02	2.39E-05
85240	0.005802	0.219	41.46	2.019	2.57E-05
$^{234}U/^{238}U$					
85238	0.00022	1.003	258.9	1.969	4.35E-06
85239	0.0002421	0.767	43.5	2.016	3.74E-06
85240	0.0001077	1.178	70.6	1.994	2.53E-06

5.0 Summary

Most U and Pu ratio estimates determined in the GUM analyses compare very well, within analytical uncertainty, with ratios determined by the in-house data reduction program. Comparisons are summarized in the table below. Data values with 2 sigma are corrected for mass bias and are from the in-house data reduction routine, and values with 'RE' (relative error) are estimates of 95% confidence intervals from GUM uncertainty analysis which are also corrected for measurement mass bias. The in-house routine may underestimate uncertainty and error, and the 'RE' determined by the GUM analysis is typically slightly higher than the 2-sigma values reported for some ratios.

sample	PNNL No.	$^{234}U/^{238}U$	2 sigma	$^{235}U/^{236}U$	2 sigma	$^{236}U/^{238}U$	2 sigma
27008	85238	0.000221	0.000002	0.005042	0.000026	0.000365	0.000004
30986	85239	0.000242	0.000003	0.004784	0.000017	0.000400	0.000004
50846	85240	0.000107	0.000003	0.005776	0.000020	0.000231	0.000003
			RE		RE		RE
27008	85238	0.00022	0.000004	0.00503	0.000030	0.000364	0.000006
30986	85239	0.00024	0.000004	0.00479	0.000024	0.000400	0.000006
50846	85240	0.000108	0.000003	0.0058	0.000026	0.000231	0.000004
1		$^{240}Pu/^{239}Pu$	2 sigma	$^{241}Pu/^{239}Pu$	2 sigma	$^{242}Pu/^{239}Pu$	2 sigma
27008	85393	0.12505	0.00030	0.002190	0.000020	0.001081	0.000016
30986	85395	0.13741	0.00031	0.002545	0.000021	0.001419	0.000017
50846	85394	0.07334	0.00018	0.000787	0.000012	0.000218	0.000006
2			RE		RE		RE
27008	85393	0.12500	0.00042	0.002180	0.000042	0.001030	0.000028
30986	85395	0.13700	0.00050	0.002530	0.000048	0.001410	0.000038
50846	85394	0.07350	0.00026	0.000787	0.000016	0.000218	0.000010

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