PNNL-17036

Pacific Northwest National Laboratory
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PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

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Abstract

This report describes GUM calculations for TIMS and SIMS isotopic ratio measurements of reactor graphite samples. These isotopic ratios are used to estimate reactor burn-up, and currently consist of various ratios of U, Pu, and Boron impurities in the graphite samples. The GUM calculation is a propagation of error methodology that assigns uncertainties (in the form of standard error and confidence bound) to the final estimates.

Contents

Tables

Glossary

CR	A corrected count rate (particles per second). This is corrected for instrument biases.
GCR	A gross count rate (particles per second). This is the measurement the instrument produces.
GR_{M9},GR_{M10},GR_{M11},GR_{M13}	Gross count rates (counts per sec) of various AMUs.
GUM	Guide quantifying Uncertainty in analytic Measurements
NLB	New Brunswick Laboratory
PPM_B, PPM_{Be}	PPM concentration (atomic) of boron and beryllium in the sample. These two quantities are also end-products of the analysis.
R	Identifies an isotopic ratio
$R_{^{10}Be/^{9}Be}$	This is the isotopic ratio of *Be* produced by nuclear reactions as the reactor operates. This quantity is not measured, but calculated with a reactor code and is approximately 1/45.
$R_{^{13}C/C}$	Abundance of ^{13}C in graphite (.012). This is not measured, but obtained from reference.
$R_{B10/B11}$	Ratio (atomic) of ^{10}B to ^{11}B in the sample. This is the central quantity to be estimated for the sample. It is corrected for ^{10}Be contamination.
$RDE_{B10/B11}$	Relative detector efficiency of ^{10}B versus ^{11}B atoms. This correction factor is determined by measurements on Brookhaven standards. And describes mass bias for the detector.
RDF	Relative Detection Efficiency Factor
$R_{M9/M10}$, $R_{M10/M11}$, $R_{M11/M13}$	Ratios of M9/M10, M10/M11, and M11/M13 particles in the sample.
RSF	Relative Sensitivity Factor
$RSF_{B/C}$	Relative sensitivity factor for boron versus carbon. This correction factor is determined by measuring a standard with the instrument.
$RSF_{Be/C}$	Relative sensitivity factor for beryllium versus carbon. This is also determined by measurements on a standard.
SIMS	Secondary Ionization Mass Spectrometry
TIMS	Thermal Ionization Mass Spectrometry

1.0 Overview of GUM

The section provides a brief summary of the GUM methodology with a description of the tables produced. GUM is basically a propagation of error calculation, with a *GUM table* presenting some terms in the POE calculation for diagnostic evaluation.

Let us suppose the vector $x = (x_1, x_2, ..., x_n)^T$ represents the raw input data (and calibration parameters) from a chemical analysis, and $y = (y_1, y_2, ..., y_p)^T$ the final estimates produced by the chemical analysis, using an estimation procedure described by the function F (·). In other words, the estimation procedure is

$$\hat{y} = F(\hat{x}) \tag{1}$$

Most typically, the estimation procedure is derived from a formula that relates the "true values" *x* and *y* to each other (i.e., $y = F(x)$). As an example, for mass spectrograph measurements, the input vector, *x* would include raw counts of various atomic mass units of interest, and *y* would consist of desired isotopic ratios.

From this overview, propagation of errors is easy to explain. The input variable, x̂ is assumed to be a random vector, with uncertainty[(a)] defined by its covariance matrix $Cov(\hat{x})$. The uncertainty of the final estimate, *y*, is described by its covariance, which is approximated by the POE formula

$$Cov(\hat{y}) \approx dF Cov(\hat{x}) dF^T \tag{2}$$

where *dF* represents the differential of F with respect to x. *dF* is a $p \times n$ matrix, with element *ij* representing the derivative dy_i/dx_j. The GUM uncertainty calculation uses this formula to calculate $Cov(\hat{y})$ as the basis for estimate uncertainty.

However, another quantity is also required to describe the uncertainty in *y* for GUM – its degrees of freedom, represented as *dof* (*y*). The degrees of freedom are used to produce approximate confidence intervals on *y*. Thus, in GUM calculations, uncertainty is described by a covariance matrix *and* a degrees of freedom vector. This requires that a degrees of freedom vector, *dof*(*x*), must be supplied for the inputs. Any component in *x* that is the result of replicated measurements will have a dof associated with it (number of replicates minus 1). Generally, $dof(x_i)$ describes how much data was used to determine $\hat{x}_i$ and $Cov(\hat{x}_i)$. The degrees of freedom associated with *y* is calculated with Saiterwait's approximation, and is given by

$$dof(y_k)^{-1} = \sum_{i=1}^{n} \left(\frac{dy_k}{dx_i} \frac{sd(x_i)}{sd(y_k)} \right)^4 dof(x_i)^{-1} \tag{3}$$

The GUM uncertainty calculation, as represented by Eqs. 1, 2, and 3, is organized into a *Gum Uncertainty Table*, as illustrated in Table 1. The top half of the table contains the inputs to the calculation

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(a) When *x* represents a single value, $Cov(x) = Var(x)$.

(i.e., x) and the last line contains the uncertainty associated with the output, yk. The right-hand side of the table contains intermediate values that can be used as diagnostics. Below the table is a description of the table diagnostics;

Table 1. Format of a GUM Uncertainty Table

Variable	Estimate	Standard Error (SE)	DOF	Sensitivity Factor	Uncertainty Contrib.	% Tot. Var. Index
x_1	$\hat{x}_1$	$sd(\hat{x}_1)$	$dof(\hat{x}_1)$	dy_k/dx_1	U_1	I_1
x_2	$\hat{x}_2$	$sd(\hat{x}_2)$	$dof(\hat{x}_2)$	dy_k/dx_2	U_2	I_2
x_3	$\hat{x}_3$	$sd(\hat{x}_3)$	$dof(\hat{x}_3)$	dy_k/dx_3	U_3	I_3
.	.	.	.	.	.	.
.	.	.	.	.	.	.
.	.	.	.	.	.	.
x_n	$\hat{x}_n$	$sd(\hat{x}_n)$	$dof(\hat{x}_n)$	dy_k/dx_n	U_n	I_n
Result y_k	$\hat{y}_k$	$sd(\hat{y}_k)$	$dof(\hat{y}_k)$			

Sensitivity Factor: This is the derivative dy_k/dx_i (also element k, i in the matrix dF) and represents the rate of change of variable y_k to x_i.

Uncertainty Contribution: This is the standard error times the sensitivity factor and represents the standard error we would see in the result if x_i were the only source of uncertainty.

$$U_i = dy/dx_i \cdot sd(x_i) \tag{4}$$

Index: This is the % contribution of variable x_i to the total variance in the result.

$$I_i = 100\left[\frac{U_i}{sd(y)}\right]^2 \tag{5}$$

It is sometimes more useful to replace the *standard error* column in the GUM table with *Relative Error* (RE). Relative error is defined as

$$RE(\hat{x}) = 100\frac{sd(\hat{x})}{\hat{x}} \tag{6}$$

Note that relative error is expressed as a percentage. The GUM tables presented in this report use relative error instead of standard error.

2.0 SIMS Measurements

2.1 Sample Preparation and Storage for SIMS Analysis

Upon arrival at PNNL, the three samples QA-21353, QA-27277, and QA-21361 were removed from the packaging and put into air-tight Teflon containers for storage. After visual inspection, samples QA-27277 and QA-21361 were deemed appropriate for analysis based on having acceptable dimensions for fitting into the SIMS sample holder and having one flat surface. Neither side of sample QA-21353 was deemed to be acceptable for analysis. The best side had saw chatter and a ridge that would have prohibited having a level analysis surface in the sample holder. A razorblade that had been cleaned by sequential sonication in distilled, deionized water, acetone, and methanol was used to remove the ridge so that the sample could fit with the best possible orientation in the sample holder. Despite this modification, sample QA-21353 was less than optimum for SIMS analysis due to the saw chatter and the fact that the surface was not flat over the entire diameter of the sample.

2.2 Contamination Control

The SIMS at PNNL is equipped with a four-aperture, multiple-immersion lens strip. One of these apertures has been dedicated to B analyses for the GIRM project. A single sample holder was used for these samples. The sample holder and forceps used to manipulate the samples were sonicated sequentially in deionized water, acetone, and methanol between samples. To remove airborne contamination, each analysis location was presputtered for two minutes with a stationary, 1 µA beam, defocused to ~250 µm.

2.3 Analyses

For all analyses, an 8 keV O_2^+ primary beam was used. The 150 µm transfer lens was used with an 400 µm contrast diaphragm and 1800 µm field aperture. The exit slit was wide open, the energy slit was centered and closed to an energy width of 10 eV (FWHM). The entrance slit was closed to allow about 50%–70% transmission of secondary ions. For most analyses, 102 data cycles were acquired. The first cycle was discarded and the remaining 101 were automatically interpolated using the Charles Evans software. After the presputter phase, the primary beam was adjusted so that the ^{11}B signal was about 10^4 cts s^{-1}. The count ratio between ^{10}B and ^{11}B varied between samples so that for sample QA-21353, ^{10}B was counted for 4 seconds and ^{11}B was counted for 2 seconds per cycle. For QA-27277, ^{10}B was counted for 6 seconds and ^{11}B for 2 seconds per cycle, and for sample QA-21361, ^{10}B was counted for 8 seconds and ^{11}B for 2 seconds per cycle.

Two types of analyses were performed on the QA samples (QA-21353, QA-27277, and QA-21361). In the first type, the three samples were analyzed three different times each over the course of nearly two months. Since the instrument was used for a wide variety of analyses between analyzing the GIRM QA samples, these analyses not only capture, analysis-to-analysis, spot-to-spot, and day-to-day variability, they also capture variability induced from retuning the instrument, reorienting the sample in the holder, aging of the electronics, etc. In these analyses, a sample was placed into the sample holder with a random orientation. A spot was chosen at X = 0 mm, and Y = –2 mm on the stage axis. The sample was sputtered with an approximately 1 uA stationary beam for two minutes with the beam defocused to be larger than the 150 µm FOV set by the field aperture (~ 250 µm). Three 102-cycle analytical runs were performed on each spot. After the three analyses, the stage was moved 1 mm in the positive Y direction and the analysis cycle was repeated for a total of five spots. These analyses were repeated three times; on June 2–5, June 7–8, and July 24–26.

The second type of analysis was performed on sample QA-21353 and was designed to test day-to-day variation on the same spot as directed by the steering committee. Five spots were chosen at the X,Y coordinates (-1,0), (0,0), (1,0), (0,-1), and (0,1). The RAE imaging detector was employed in order to find the same spot from day to day. This turned out to be advantageous as there was some discrepancy observed in loading the sample holder from day to day when relying solely on the stage position micrometers. Thus, five spots were analyzed using the same protocol as above (except that only 52 cycles were recorded instead of 102) on three separate days. The sample holder was removed from the instrument daily and replaced. The samples were not removed from the sample holder each day and re-inserted, however – this would have caused difficulties in relocating the same spots for analysis. The same analysis spots were located by comparing the ^{11}B ion image with a reference image saved from day 1.

2.4 Standards

Standards VA3, VB3, and VC3 were analyzed six different times over the time period from October 7, 2005, to May 26, 2006. In these analyses conducted over a relatively long period of time, the standards were removed from the sample holder each time, and no attempt was made to relocate the same spots for repeat analyses. Each standard was analyzed with a similar protocol as the QA samples; i.e., an area was presputtered for 1–2 minutes with a 1-uA stationary beam, followed by analyses of five spots per standard with three analytical runs consisting of 102 cycles per spot. For standard VA3, ^{10}B was counted for 4 seconds and ^{11}B was counted for 2 seconds per cycle. For VB3, ^{10}B was counted for 6 seconds and ^{11}B for 2 seconds per cycle, and for standard VC3, ^{10}B was counted for 8 seconds and ^{11}B for 2 seconds per cycle.

2.5 Results

Table 2 reports the results for the SIMS mass calibration standards (VA3, VB3, and VC3) at PNNL. The mass bias estimate based on 270 individual measurements was 0.962 ± 0.011 (95% CI).

Table 3 reports the results for the day-to-day variability study in which the same five spots were revisited on three consecutive days on the GIRM qualification sample QA-21353. Here relative errors on the estimates for the contributions to σ are reported as well as if the contribution to the total uncertainty is significantly different from zero. These data show that the day-to-day variability of sample QA-21353 was not a significant contributor to the error estimate when the same spots were analyzed on consecutive days.

Table 4 through Table 6 report the results for GIRM qualification samples QA-21361, QA-21353, and QA-27277. The $^{10}B/^{11}B$ estimate for QA-21363 was 0.07588 ± 0.00077 (95% CI). The $^{10}B/^{11}B$ estimate for QA-21353 was 0.1925 ± 0.0019 (95% CI). The $^{10}B/^{11}B$ estimate for QA-27277 was 0.1125 ± 0.0012 (95% CI).

Table 2. Results for Mass Bias Calibration

Component	DOF	Value	Relative Error (%)
$\bar{X}$	2.84	0.9618	0.340
$\sigma_{standard}$	2	5.18×10^{-3}	54.5
σ_{time}	5	2.38×10^{-3}	58.7
σ_{spot}	72	8.37×10^{-3}	8.0
$\sigma_{residual}$	190	2.39×10^{-3}	5.3
$K_{(0.975,\ 2.84)} = 3.28$, $\bar{X} = 0.962 \pm 0.011$ (95% CI)			

Table 3. Results for Day-to-Day Variability Study

Component	DOF	Value	Relative Error (%)	Significance
σ_{day}	2	2.28×10^{-4}	86.9	No
σ_{spot}	4	4.49×10^{-4}	47.0	No
$\sigma_{day \times dayt}$	8	3.62×10^{-4}	36.7	Yes
$\sigma_{residual}$	29	3.91×10^{-4}	15.9	

Table 4. Results for Sample QA-21361

Quantity	Nominal Value	Relative Error (%)	Effective DOF	Uncertainty Contribution	Index (%)
$^{10}B/^{11}B$	0.0789	0.242	45.00	1.83×10^{-4}	57.9
Mass Bias	0.9618	0.340	2.84	2.58×10^{-4}	81.5
Result	0.0759	0.417	6.34		
$K_{(0.975,\ 6.34)} = 2.42$, $\bar{X} = 0.07588 \pm 0.00077$ (95% CI)					

Table 5. Results for Sample QA-21353

Quantity	Nominal Value	Relative Error (%)	Effective DOF	Uncertainty Contribution	Index (%)
$^{10}B/^{11}B$	0.2001	0.233	49.60	4.49×10^{-4}	56.6
Mass Bias	0.9618	0.340	2.84	6.54×10^{-4}	82.4
Result	0.1925	0.412	6.08		
$K_{(0.975,\ 6.08)} = 2.44$, $\bar{X} = 0.1925 \pm 0.0019$ (95% CI)					

Table 6. Results for Sample QA-27277

Quantity	Nominal Value	Relative Error (%)	Effective DOF	Uncertainty Contribution	Index (%)
$^{10}B/^{11}B$	0.1170	0.136	39.90	1.53×10^{-4}	37.1
Mass Bias	0.9618	0.340	2.84	3.83×10^{-4}	92.8
Result	0.1125	0.366	3.82		
$K_{(0.975,\ 3.82)} = 2.83$, $\bar{X} = 0.1125 \pm 0.0012$ (95% CI)					

For estimation of the Boron isotopic ratio in graphite, the SIMS instrument is set up to use a cycle that measures AMU_9, AMU_{10}, AMU_{11}, and AMU_{13} particles (corresponding to chiefly ^{9}Be, ^{10}B, ^{11}B, and ^{13}C isotopes). The time the instrument accumulates counts on each atomic mass is determined by a 1% limit on Poisson counting error for the Boron and ^{9}Be isotopes. The ^{13}C isotope, being relatively abundant, is only accumulated for 1 second. For typical reactor-grade graphite, one might expect to see counting times of 1 sec for AMU_9, 8 sec for AMU_{10}, 2 sec for AMU_{11}, and finally 1 sec for AMU_{13}, resulting in a measurement cycle of 12 seconds.

At least three spots (a spot diameter is approximately 150 microns) are chosen for analysis on a sample, and a time-series of measurements is taken at each spot. At each spot, measurements are taken until the $^{10}B/^{11}B$ ratio shows that surface contamination has been "burned off." Because of surface contamination, the $^{10}B/^{11}B$ time series might start off near the natural boron ratio (i.e., 0.23) and decrease to an asymptote, which is assumed to represent the "true" boron ratio in the sample. When this asymptote is reached, a time series of 100 measurements is averaged together and is used to produce an estimate of the desired ratio.

The variability in the measurements is quantified by ANOVA, and a "best" estimate is calculated for the desired $^{10}B/^{11}B$ ratio as well as boron and beryllium concentrations. The uncertainties associated with the three estimates are produced by plugging the ANOVA results into the propagation of error formulas as proscribed by the GUM procedure.

A summary of the important features of the SIMS measurement process is given below:

Measurement Cycle: The measurement cycle measures four atomic masses AMU_9, AMU_{10}, AMU_{11}, and AMU_{13}.

Calibration Factors: Standards are used to calculate *relative sensitivity factors* (RSF) for beryllium/carbon, and boron/carbon. Standards are also used to calculate the *mass bias* for ^{10}B verses ^{11}B.

Sample Measurement: A graphite sample is placed in the instrument, a suitable "spot" is chosen for measurement, and a time series of measurements is taken. Measurements are taken until the boron ratio stabilizes indicating that surface contamination has been burned away. After the ratio has stabilized, the cycle replicates are recorded and used to produce the desired estimates.

This measurement sequence is repeated at several spots on the sample. Measurement of more than one spot allows one to calculate spot variability for the error analysis.

Calculation of Estimates: The sample measurements are combined to estimate the desired quantities and the associated standard errors using the formulas described in this report.

2.6 Estimation Procedure

For purposes of description, we have organized the estimation procedure into three steps:

- **Step 1**: Correct gross measurements for dead times and cycle bias.
- **Step 2**: Estimate ratios and their variability with ANOVA.
- **Step 3**: Calculate final estimates.

2.6.1 Step 1: Gross Measurement Corrections

Gross count rates, GR, are corrected for dead time and then interpolated. The dead-time correction uses the standard formula

$$\mathbf{GR}_{dtc} = \mathbf{GR}_{exp}(\tau\mathbf{GR}) \tag{7}$$

where τ represents the instrument dead time. The error associated with this correction depends on the uncertainty in the dead time. Given the count-rates used for these measurements, this uncertainty is insignificant (with a RSD less than 10^{-4}) and is considered to be zero in the uncertainty calculations.

The instrument measurements produce 4 gross count time series ($\mathbf{CR}_{M9}$, $\mathbf{CR}_{M10}$, $\mathbf{CR}_{M11}$, and $\mathbf{CR}_{M13}$), which are then used to form isotopic ratios. Since the measurements occur at slightly different times in the measurement cycle, they need to be interpolated to place the gross counts all at a consistent time before the ratios are calculated. The time series are corrected using the interpolation procedure described in (Coakley et al. 2005).

Dead-time corrected and interpolated count rates are then used to produce the five desired isotopic ratios: $\mathbf{R}_{M9/M10}$, $\mathbf{R}_{M10/M11}$, $\mathbf{R}_{M9/M13}$, $\mathbf{R}_{M10/M13}$, and $\mathbf{R}_{M11/M13}$.

2.6.2 Step 2: ANOVA Analysis

A set of replicate runs is taken on each sample so important components of measurement uncertainty can be determined. For a single sample, at least three spots are chosen and three replicate measurement series are run at each spot. A measurement series consists of at least 100 cycles that are averaged together. With these measurements, the uncertainty associated with a particular ratio, such as $\mathbf{R}_{M10/M11}$, can be calculated in three ways.

First, the Poisson count error can be propagated through the measurements to produce a standard error for the ratio. (This propagation of errors is built into the SIMS analysis software.) Second, a standard deviation from the time-series of measurements can be computed and used to compute a standard error for the ratio. Third, the ANOVA analysis of the replicate measurements can determine the standard error of the ratio. Of the three methods, ANOVA should give the most authoritative standard error; the ANOVA analysis includes more sources of variability than the other methods of calculation. In particular, ANOVA quantifies spot-to-spot variability and replicate variability.

One would expect to see an ordering between the three standard errors with the Poisson count standard error the smallest, the time series standard error intermediate, and the ANOVA standard error the largest of all.

The ANOVA model for the SIMS ratio data is given by:

$$R_{ij} = \mu + S_i + e_{ij} \tag{8}$$

where R_{ij} represents the ratio measurement taken at spot i during replicate run j. The terms S_i and e_{ij} represent the spot-to-spot and replicate variations, respectively. This model is a simpler version of the ANOVA model presented in (Simons 2004). The term, μ, represents the "best estimate" for the ratio. The most important results from the ANOVA analysis are the best estimate, $\hat{\mu}$, and its standard error, $sd\left(\hat{\mu}\right)$. Estimates of the spot-to-spot and replicate variability are also produced by the ANOVA.

Since four ratios are simultaneously produced by SIMS, and correlations exist between the four, the ratio data should actually be considered to be the vector;

$$R_{ij} = \begin{bmatrix} \mathbf{R}_{M9/M10} \\ \mathbf{R}_{M10/M11} \\ \mathbf{R}_{M9/M13} \\ \mathbf{R}_{M10/M13} \\ \mathbf{R}_{M11/M13} \end{bmatrix} \tag{9}$$

so that correlations between the ratio can be calculated in a *multivariate* ANOVA (MANOVA) analysis.

Results from the ANOVA analysis of SIMS data are illustrated in Table 7 and Table 8. The uncertainties produced by the ANOVA are expressed in terms of *Percent Relative Standard Deviation*, which is the standard deviation of the quantity divided by the estimate. From these results, one can see that the critical ratio for boron (i.e., $\mathbf{R}_{M10/M11}$) seems to be estimated with high accuracy (with a relative standard deviation of only 0.26%). Also present in the table are the relative standard deviations of an individual measurement, *Rij*, calculated using the (1) time-series and (2) Poisson Count statistics. These relative standard deviations should be compared to *RSD(Repl)*, which should be measuring the same variability. As one can see, the ANOVA-based relative standard deviation is larger, indicating that the data contains sources of variability that are not captured by the other two calculations.

Table 7. Results from ANOVA Analysis of SIMS Data

Ratio	ANOVA Results				%RSD from Time-Series	Other Calc. Poisson Cnt
	$\hat{\mu}$	$\%RSD(\hat{\mu})$	%RSD(Spot)	%RSD(Repl)		
$\mathbf{R}_{M9/M10}$	1.750000	4.400	8.65e+00	3.62	0.285	0.1670
$\mathbf{R}_{M10/M11}$	0.073400	0.266	2.26e-01	1.08	0.196	0.1970
$\mathbf{R}_{M9/M13}$	0.000352	6.630	1.28e-05	28.90	0.476	0.1670
$\mathbf{R}_{M10/M13}$	0.000203	6.940	4.90e-10	30.30	0.504	0.1730
$\mathbf{R}_{M11/M13}$	0.002770	6.950	9.04e-06	30.30	0.490	0.0939
Note: $\%RSD(x) = 100 \cdot sd(x) / \hat{\mu}$						

Also note that the correlation between $\mathbf{R}_{M9/M10}$ and $\mathbf{R}_{M10/M11}$ (see Table 8) is negative, as one would expect from their mathematical form, but that it is relatively small. Since both of these ratios are used to estimate boron, this correlation will influence the uncertainty associated with the boron estimate.

Table 8. Correlations from ANOVA Analysis of SIMS Data

	$\mathbf{R}_{M10/M11}$	$\mathbf{R}_{M9/M13}$	$\mathbf{R}_{M10/M13}$	$\mathbf{R}_{M11/M13}$
$\mathbf{R}_{M9/M10}$	–0.072	–0.019	–0.045	–0.048
$\mathbf{R}_{M10/M11}$	—	–0.034	–0.020	–0.049
$\mathbf{R}_{M9/M13}$	—	—	0.955	0.956
$\mathbf{R}_{M10/M13}$	—	—	—	1.000

2.6.3 Step 3: Final Estimates

In its most general terms, an estimation procedure can be represented as a mathematical function, $F(\cdot)$, that transforms the raw measurements, as represented by a vector X into the desired quantities, as represented by Y. So the estimate for a particular sample is produced by the evaluation of

$$Y = F(X) \tag{10}$$

For this problem, Y represents three quantities – the boron $^{10}B/^{11}B$ ratio, the boron concentration, and the beryllium concentration. The inputs are the ratios produced by the SIMS instrument and all constants and correction factors described in the previous sections. While the process of estimation may seem simple at this level, the actual formulas that define $F(\cdot)$ can be quite complex.

Once $F(\cdot)$ is defined, the calculation of the uncertainty of the estimates, as represented by Y follows in a straightforward manner. The covariance of the estimates is given by the matrix formula

$$Cov(Y) = \left[\frac{dF}{dX}\right] Cov(X) \left[\frac{dF}{dX}\right]^T \tag{11}$$

This is the propagation of error formula used by GUM.

The estimation function $Y = F(X)$ is defined by the following three formulas. Y_1, the *Boron isotopic ratio*, $\mathbf{R}_{^{10}B/^{11}B}$, is calculated from the formula

$$\mathbf{R}_{^{10}B/^{11}B} = \mathbf{RDE}_{^{10}B/^{11}B} \cdot \mathbf{R}_{M10/M11} \cdot \left[1 - \mathbf{R}_{^{10}Be/^{11}Be} \cdot \mathbf{R}_{M9/M10}\right] \tag{12}$$

Note that the values $\mathbf{R}_{M10/M11}$ and $\mathbf{R}_{M9/M10}$ originate from Step 2, while the other ratio $\mathbf{R}_{^{10}Be/^{9}Be}$ is a constant calculated from reactor codes. Finally $\mathbf{RDE}_{^{10}B/^{11}B}$ is a calibration constant produced by evaluation of New Brunswick standards. The formula contains a correction for beryllium produced during reactor operation.

Y_2, the boron concentration, $\mathbf{PPM}_B$, is calculated using the formula

$$\mathbf{PPM}_B = 10^6 \cdot \mathbf{RSF}_{B/C} \cdot \left(\mathbf{R}_{M10/M13} + \mathbf{R}_{M11/M13}\right) \cdot \mathbf{R}_{^{13}C/C} \tag{13}$$

And, finally, Y_3, the *beryllium concentration*, $\mathbf{PPM}_{\mathrm{Be}}$, is calculated using the formula

$$\mathbf{PPM}_{Be} = 10^6 \cdot \mathbf{RSF}_{Be/C} \cdot \mathbf{R}_{M9/M13} \cdot \left[1 + \mathbf{R}_{^{10}Be/^{9}Be}\right] \cdot \mathbf{R}_{^{13}C/C} \tag{14}$$

2.7 Results from BEPO Test Samples

This section contains the results from the analysis of three BEPO test samples sent out by New Brunswick Laboratory. The three BEPO samples (Sample IDs 28402, 37796, and 44746) include graphite experiencing both low and high burn-up conditions. Table 9 through Table 11 describe the uncertainty calculations for each sample, while Table 12 describes the ANOVA results.

The estimate of most importance is the boron 10/11 ratio, and the results are

Sample ID	**$^{10}B/^{11}B$ Ratio**	**RSD**
28402	0.0679	0.736%
37796	0.2250	0.675%
44746	0.0344	0.982%

The uncertainty seems to be limited to below 1%, even for the high burn-up sample. For all three of these samples, the dominant source of error is due to a calibration factor, the relative detector efficiency (RDE). This calibration factor was determined from an experiment performed on three New Brunswick standards; a more extensive calibration experiment could lower the uncertainty associated with this input variable.

At high burn-ups (see Table 11), uncertainty in the M9/M10 ratio becomes important. However, at moderate to low burn-ups, this ratio does not contribute to significant error in the final estimate.

Table 9. GUM Results for BEPO Sample 28402

Quantity	Estimate	RE (%)	DOF	Sensitivity Coefficient	Uncertainty Contribution	Index	K value
X	$\mu(X)$	SD/μ		dF/dX	SD(X) • dF/dX	%	
Results for Boron $^{10}B/^{11}B$							
$\mathbf{R}_{M9/M10}$	1.75070	4.402	4.28	-0.002	-1.208E-04	14.2496	
$\mathbf{R}_{M10/M11}$	0.07339	0.266	23.97	0.924	1.806E-04	31.8794	
$\mathbf{RDE}_{10B/11B}$	0.96182	0.340	2.84	0.071	2.307E-04	51.9830	
$\mathbf{R}_{9Be/10Be}$	0.02220	1.000	1000.00	-0.124	-2.744E-05	0.7354	
$\mathbf{R}_{10B/11B}$	0.06785	0.472	9.61				2.240
Results for Boron Concentration (ppm)							
$\mathbf{R}_{M10/M13}$	0.00020	6.940	22.16	156.000	2.202E-03	0.1506	
$\mathbf{R}_{M11/M13}$	0.00277	6.952	22.16	156.000	3.008E-02	28.0978	
RSF*B/C*	0.01300	10.000	1000.00	35.718	4.643E-02	66.9693	
$\mathbf{R}_{13C/C}$	0.01200	1.000	1000.00	38.695	4.643E-03	0.6697	
PPM(*B*)	0.46434	12.220	280.69				1.968
Results for Beryllium Concentration (ppm)							
$\mathbf{R}_{M9/M13}$	0.00035	6.632	22.16	34.346	8.012E-04	56.6516	
RSF*Be/C*	0.00280	5.714	1000.00	4.315	6.903E-04	42.0597	
$\mathbf{R}_{9Be/10Be}$	0.02220	1.000	1000.00	0.012	2.624E-06	0.0006	
$\mathbf{R}_{13C/C}$	0.01200	1.000	1000.00	1.007	1.208E-04	1.2881	
PPM(*Be*)	0.01208	8.811	69.05				1.995
Note: Input variables that make no contribution are deleted.							

Table 10. GUM Results for BEPO Sample 37796

Quantity	**Estimate**	**RE (%)**	**DOF**	**Sensitivity Coefficient**	**Uncertainty Contribution**	**Index**	**K value**
X	*μ*(*X*)	*SD*/*μ*		*dF*/*dX*	SD(X) • *dF*/*dX*	%	
Results for Boron $^{10}B/^{11}B$							
$\mathbf{R}_{M9/M10}$	0.01739	28.281	8.73	-0.005	-2.449E-05	0.0875	
$\mathbf{R}_{M10/M11}$	0.23323	0.143	18.00	0.961	3.196E-04	14.8920	
$\mathbf{RDE}_{10B/11B}$	0.96182	0.340	2.84	0.233	7.624E-04	84.7379	
$\mathbf{R}_{9Be/10Be}$	0.02220	1.000	1000.00	-0.004	-8.660E-07	0.0001	
$\mathbf{R}_{10B/11B}$	0.22424	0.369	3.94				2.793
Results for Boron Concentration (ppm)							
$\mathbf{R}_{M10/M13}$	0.00084	17.054	7.37	156.000	2.226E-02	2.6250	
$\mathbf{R}_{M11/M13}$	0.00359	17.189	7.29	156.000	9.632E-02	49.1316	
RSF*B/C*	0.01300	10.000	1000.00	53.145	6.909E-02	25.2788	
$\mathbf{R}_{13C/C}$	0.01200	1.000	1000.00	57.573	6.909E-03	0.2528	
PPM(*B*)	0.69088	19.889	30.10				2.042
Results for Beryllium Concentration (ppm)							
$\mathbf{R}_{M9/M13}$	0.00001	16.432	18.00	34.346	7.063E-05	88.9180	
RSF*Be/C*	0.00280	5.714	1000.00	0.153	2.456E-05	10.7525	
$\mathbf{R}_{9Be/10Be}$	0.02220	1.000	1000.00	0.000	9.334E-08	0.0002	
$\mathbf{R}_{13C/C}$	0.01200	1.000	1000.00	0.036	4.298E-06	0.3293	
PPM(*Be*)	0.00043	17.426	22.77				2.070
Note: Input variables that make no contribution are deleted.							

Table 11. GUM Results for BEPO Sample 44746

Quantity	**Estimate**	**RE (%)**	**DOF**	**Sensitivity Coefficient**	**Uncertainty Contribution**	**Index**	**K value**
X	*μ*(*X*)	*SD*/*μ*		*dF*/*dX*	SD(X) • *dF*/*dX*	%	
Results for Boron $^{10}B/^{11}B$							
$\mathbf{R}_{M9/M10}$	4.43666	5.043	7.69	-0.001	-1.891E-04	47.0791	
$\mathbf{R}_{M10/M11}$	0.03957	0.459	23.99	0.867	1.575E-04	32.6536	
$\mathbf{RDE}_{10B/11B}$	0.96182	0.340	2.84	0.036	1.167E-04	17.9263	
$\mathbf{R}_{9Be/10Be}$	0.02220	1.000	1000.00	-0.169	-3.749E-05	1.8512	
$\mathbf{R}_{10B/11B}$	0.03431	0.803	22.44				2.071
Results for Boron Concentration (ppm)							
$\mathbf{R}_{M10/M13}$	0.00009	11.825	10.44	156.000	1.726E-03	0.0854	
$\mathbf{R}_{M11/M13}$	0.00237	11.629	11.14	156.000	4.297E-02	52.9439	
RSF*B/C*	0.01300	10.000	1000.00	29.544	3.841E-02	42.3055	
$\mathbf{R}_{13C/C}$	0.01200	1.000	1000.00	32.006	3.841E-03	0.4231	
PPM(*B*)	0.38408	15.375	39.75				2.021
Results for Beryllium Concentration (ppm)							
$\mathbf{R}_{M9/M13}$	0.00040	8.132	16.37	34.346	1.115E-03	66.2738	
RSF*Be/C*	0.00280	5.714	1000.00	4.897	7.834E-04	32.7235	
$\mathbf{R}_{9Be/10Be}$	0.02220	1.000	1000.00	0.013	2.978E-06	0.0005	
$\mathbf{R}_{13C/C}$	0.01200	1.000	1000.00	1.143	1.371E-04	1.0022	
PPM(*Be*)	0.01371	9.989	37.27				2.026
Note: Input variables that make no contribution are deleted.							

Table 12. ANOVA Results from BEPO Samples

Ratio	ANOVA Results				%RE from Other Calc.	
	$\hat{\mu}$	%RE $\hat{\mu}$	%RE(Spot)	%RE(Repl)	Time-Series	Poisson Cnt
Sample 28402						
$\mathbf{R}_{M9/M10}$	1.750000	4.400	8.65e+00	3.62	0.285	0.1670
$\mathbf{R}_{M10/M11}$	0.073400	0.266	2.26e-01	1.08	0.196	0.1970
$\mathbf{R}_{M9/M13}$	0.000352	6.630	1.28e-05	28.90	0.476	0.1670
$\mathbf{R}_{M10/M13}$	0.000203	6.940	4.90e-10	30.30	0.504	0.1730
$\mathbf{R}_{M11/M13}$	0.002770	6.950	9.04e-06	30.30	0.490	0.0939
Sample 37796						
$\mathbf{R}_{M9/M10}$	1.74e-02	28.300	5.46e+01	59.000	8.700	0.6610
$\mathbf{R}_{M10/M11}$	2.33e-01	0.143	9.01e-10	0.605	0.117	0.121
$\mathbf{R}_{M9/M13}$	1.25e-05	16.400	7.18e-06	69.700	8.320	0.6530
$\mathbf{R}_{M10/M13}$	8.37e-04	17.100	3.45e+01	29.900	1.270	0.1060
$\mathbf{R}_{M11/M13}$	3.59e-03	17.200	3.49e+01	29.700	1.260	0.0725
Sample 44746						
$\mathbf{R}_{M9/M10}$	4.44e+00	5.040	11.600	9.45	0.416	0.242
$\mathbf{R}_{M10/M11}$	3.96e-02	0.459	0.738	1.89	0.250	0.234
$\mathbf{R}_{M9/M13}$	3.99e-04	8.130	15.100	28.40	0.908	0.271
$\mathbf{R}_{M10/M13}$	9.35e-05	11.800	25.100	31.70	1.010	0.237
$\mathbf{R}_{M11/M13}$	2.37e-03	11.600	24.200	32.80	1.060	0.116

The boron and beryllium concentrations seem to be consistent with what is known about the samples; the boron concentration is approximately 0.5 ppm for all three samples. For the samples with the highest burn-up (i.e., 28402 and 44746), the beryllium concentration is about 0.01 ppm, while the lowest burn-up sample has a very much lower beryllium concentration (0.0004 ppm).

The ANOVA results presented in Table 12 merit a few comments. First note that the spot-to-spot variability for the most important ratio $\mathbf{R}_{M10/M11}$ is near zero for all three samples. (It is, in fact, not significantly different from zero.) Since spot-to-spot variability should include variability due to contamination, this is an indication that the SIMS measurement protocol has successfully dealt with contamination. Also note that RSD(repl) is approximately a factor of 5 greater that RSD (time-series), an indication that the ANOVA analysis gives a much more realistic estimate of measurement uncertainty than the standard deviation calculated from the time-series.

2.8 August 2006 Qualification Sample Results

Here are the results for the August 2006 qualification samples:

Calibration Standard Anova:
Estimate and Standard Error

	Est	%RE	N-levels	DOF
RDE	0.961800	0.340	NA	2.844
block	0.005181	54.470	3	2.000
month	0.002384	58.660	6	5.000
spot %in% (block + month)	0.008367	8.022	90	72.000
Residuals	0.002388	5.298	270	190.000

Call:
varcomp(formula = "rde ~ (block+month)/spot", data = cal.std, method = "reml")

Variance Estimates:

	Variance
block	2.684078e-05
month	5.683441e-06
spot %in% (block + month)	7.000312e-05
Residuals	5.703625e-06

Method: reml
Approximate Covariance Matrix of Variance Estimates:

	block	month spot	%in% (block + month)
block	8.550333e-10	2.80200e-13	–4.203400e-12
month	2.802000e-13	4.44648e-11	–8.406800e-12
spot %in% (block + month)	–4.203400e-12	–8.40680e-12	1.261423e-10
Residuals	0.000000e+00	0.00000e+00	–1.217000e-13

	Residuals
block	0.000e+00
month	0.000e+00
spot %in% (block + month)	–1.217e-13
Residuals	3.652e-13

Coefficients:
(Intercept)
0.9618235

Approximate Covariance Matrix of Coefficients:
[1] 1.06931e-05

2.8.1 Results for Sample QA-21353 Anova Results

Replicate X Spot Design Matrix

```
  1 2 3 4 5
1 3 3 3 3 3
2 3 3 3 3 3
3 3 3 3 3 3
```

MANOVA Estimates and Variance Components (in terms of percent relative error)

	est	RE.est	RE.spot	RE.rep	RE.cycle	RE.pois
M10.11	0.20000	0.233	0.142000	1.51	1.22e-01	0.11

Error Propagation and Estimates

	Est	RE	dof	Sensit	Uncert	Index
r.m10.m11	0.2000	0.233	49.60	0.96200	0.000449	56.6
rde.b10.b11	0.9620	0.340	2.84	0.20000	0.000654	82.4
Result	0.1920	0.412	6.08	NA	NA	NA

K-value: qt(.975,6.08)=2.44

2.8.2 Results for Sample QA-21361, ANOVA Results

Replicate X Spot Design Matrix

```
  1 2 3 4 5
1 3 3 3 3 3
2 3 3 3 3 3
3 3 3 3 3 3
```

MANOVA Estimates and Variance Components (in terms of percent relative error)

	est	RE.est	RE.spot	RE.rep	RE.cycle	RE.pois
M10.11	0.0789	0.242	3.40e-07	1.62	0.12	0.108

Error Propagation and Estimates

	Est	RE	dof	Sensit	Uncert	Index
r.m10.m11	0.0789	0.242	45.00	0.96200	0.000183	57.9
rde.b10.b11	0.9620	0.340	2.84	0.07890	0.000258	81.5
Result	0.0759	0.417	6.34	NA	NA	NA

K-value: qt(.975,6.34)=2.42

2.8.3 Results for Sample QA-27277, Anova Results

Replicate X Spot Design Matrix

```
  1 2 3 4 5
1 3 3 3 3 3
2 3 3 3 3 3
3 3 3 3 3 3
```

MANOVA Estimates and Variance Components (in terms of percent relative error)

	est	RE.est	RE.spot	RE.rep	RE.cycle	RE.pois
M10.11	0.1170	0.136	1.52e-01	0.79	0.123	0.109

Error Propagation and Estimates

	Est	RE	dof	Sensit	Uncert	Index
r.m10.m11	0.1170	0.136	39.90	0.96200	0.000153	37.1
rde.b10.b11	0.9620	0.340	2.84	0.1170	0.000383	9.28
Result	0.1130	0.366	3.82	NA	NA	NA

K-value: qt(.975,3.82) = 2.83

2.8.4 Day-to-Day Variability Study

Anova model is
    Y.ijk = U + load.i + spot.ij + E.ijk

Call:
varcomp(formula = "M10.ll ˜ load/spot", data = qual2.dat, method = "reml")

Variance Estimates

	Variance	Sd(Var)	
load	1.597735e-08	9.85-08	Not significant
spot %in% load	3.337117e-07	1.58-07	Significant
Residuals	1.514183e-07		

Method: reml

Approximate Covariance Matrix of Variance Estimates

	load	spot %in% load	Residuals
load	9.69886e-15	–4.895350e-15	–2.09600e-17
spot %in% load	–4.89535e-15	2.483763e-14	–7.25000e-16
Residuals	–2.09600e-17	–7.250000e-16	2.28818e-15

Coefficients:
 (Intercept)
   0.1986207
Approximate Covariance Matrix of Coefficients:
[1] 3.104391e-08

2.8.5 GUM Tables for Qualification samples

Since the qualification samples were not irradiated, the samples were not expected to contain ^{9}Be and ^{10}Be. Thus, Be isotopes and ^{13}C were not included in analyses, as for the NBL BEPO samples, and the GUM uncertainty budget for the NBL QA samples below is simpler.

Table 13. GUM Table for Qualification Sample 21353 SIMS Results

Quantity	Estimate	RE (%)	DOF	Sensitivity Coefficient	Uncertainty Contribution	Index	K value
X	*μ*(*X*)	*SD*/*μ*		*dF*/*dX*	SD(X) • *dF*/*dX*	%	
$\mathbf{R}_{M9/M10}$	n.d	n.d	n.d				
$\mathbf{R}_{M10/M11}$	0.20009	0.233	49.61	0.962	4.492E-04	32.0339	
$\mathbf{RDE}_{10B/11B}$	0.96182	0.340	2.84	0.200	6.543E-04	67.9661	
$\mathbf{R}_{10B/11B}$	0.19245	0.412	6.08				2.439
Note: Input variables that make no contribution are deleted.							

Table 14. GUM Table for Qualification Sample 21361 SIMS Results

Quantity	**Estimate**	**RE (%)**	**DOF**	**Sensitivity Coefficient**	**Uncertainty Contribution**	**Index**	**K value**
X	*μ*(*X*)	*SD*/*μ*		*dF*/*dX*	SD(X) • *dF*/*dX*	%	
$\mathbf{R}_{M9/M10}$	n.d	n.d	n.d				
$\mathbf{R}_{M10/M11}$	0.07889	0.242	45.00	0.962	1.833E-04	33.5498	
$\mathbf{RDE}_{10B/11B}$	0.96182	0.340	2.84	0.079	2.580E-04	66.4502	
$\mathbf{R}_{10B/11B}$	0.07588	0.417	6.34				2.416
Note: Input variables that make no contribution are deleted.							

Table 15. GUM Table for Qualification Sample 27277 SIMS Results

Quantity	**Estimate**	**RE (%)**	**DOF**	**Sensitivity Coefficient**	**Uncertainty Contribution**	**Index**	**K value**
X	*μ*(*X*)	*SD*/*μ*		*dF*/*dX*	SD(X) • *dF*/*dX*	%	
$\mathbf{R}_{M9/M10}$	n.d	n.d	n.d				
$\mathbf{R}_{M10/M11}$	0.11701	0.136	39.95	0.962	1.530E-04	13.7915	
$\mathbf{RDE}_{10B/11B}$	0.96182	0.340	2.84	0.117	3.826E-04	86.2085	
$\mathbf{R}_{10B/11B}$	0.11254	0.366	3.82				2.829
Note: Input variables that make no contribution are deleted.							

3.0 TIMS Measurements

3.1 Samples for TIMS Analyses, Preparation and Processing

In Fall 2005, one set of three samples from New Brunswick Laboratory (NBL) were addressed to Steve Petersen for TIMS analysis, and included BEPO samples numbered 10431, 16819, and 27727, and three blanks numbered B-17, B-27, and B-58. A second set of three samples from NBL was addressed to David Gerlach for SIMS analysis, and these included BEPO samples 28402, 37796, and 44746, and three blanks numbered B-49, B-64, and B-77. All cores were trimmed by tooling, and lightly cleaned by CO2 pellet blasting. Small discs were cut from the second set of samples for SIMS analysis, with the remainder of each used for TIMS preparation.

The GIRM Phase II QA samples were received from NBL in May 2006, and consisted of UCAR graphite plugs doped with solutions containing uranium and plutonium. The three samples received at PNNL for TIMS analysis were numbered UCAR 25-B, UCAR 41-B, and UCAR 57-B. These were not trimmed or prepared in the manner above, but the as-received samples were 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.

2. 10% of ash solution taken for unspiked U separation and TIMS analysis; 233U/238U ratios determined by TIMS analysis rather than ICPMS analyses as used earlier.

3. Remaining 90% spiked with mixed U-233 + Pu-244 spike; Pu-244 spike amount chosen to be appropriate for sample based on 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.

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 233U/238U ratios, since many samples contain U-233 already. Total Pu contents determined based on measured amount of Pu-244 added.

The six NBL BEPO samples were prepared following these steps, resulting in both spiked and unspiked U fractions analyzed by TIMS. Based on instructions from NBL, the three QA samples were not split following our usual procedure as outline above, and instead, the entire sample was processed and combined with the U and Pu spikes.

Uranium samples for TIMS analysis are prepared by solution loading onto carburized Re filaments. 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. 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.

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 portion of the GUM analysis. The 2σ uncertainties reported for all isotope ratio analyses in Table 16 through Table 19 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.

Uncertainties for the concentrations and isotope ratios of the Pu tracer or ‘spike’ were not directly used in GUM uncertainty analysis. 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 as contributed by the Pu tracer are used in the GUM uncertainty tables.

Table 16. Uranium TIMS Results for NBL BEPO Samples

NBL BEPO Sample	PNNL Sample Log #	U 233/238*	33/38 2sig	U 234/238	34/38 2 sig	U235/238	35/38 2sig	U236/238	36/38 2sig	Total U, ng/g
16819	U83599	2.251E-03	1.156E-05	6.126E-05	1.160E-05	7.243E-03	1.928E-05	7.150E-06	4.000E-07	2.34
10431	U83600	1.377E-02	3.310E-05	2.459E-04	2.180E-06	4.919E-03	1.728E-05	3.742E-04	2.680E-06	1.58
27727	U83601	4.970E-03	2.412E-05	7.156E-05	1.180E-05	6.649E-03	2.420E-05	8.439E-05	1.280E-06	11.75
28402	U28402	8.025E-03	2.838E-05	1.229E-04	1.480E-06	5.839E-03	1.472E-05	2.347E-04	2.060E-06	20.38
37796	U37796	9.105E-04	7.460E-06	6.071E-05	1.180E-06	7.057E-03	2.170E-05	2.823E-05	9.800E-07	62.59
44746	U44746	1.418E-02	6.610E-05	2.774E-04	3.100E-06	5.450E-03	2.936E-05	3.045E-04	3.440E-06	0.37
*233U/238U ratios measured in sample aliquots without added 233U spike/tracer										

Table 17. Plutonium TIMS Results for NBL BEPO Samples

NBL BEPO Sample	PNNL Sample Log #	Pu 240/239	40/39 2sig	Pu 241/239	41/39 2sig	Pu 242/239	42/39 2sig	Total Pu, pg/g
16819	P83599	7.924E-03	8.200E-05	8.450E-05	7.400E-06	5.870E-05	6.600E-06	0.47
10431	P83600	1.303E-01	3.042E-04	2.645E-03	3.318E-05	1.152E-03	2.172E-05	82.81
27727	P83601	2.176E-02	5.266E-05	4.907E-05	1.820E-06	8.000E-06	3.160E-06	6.07
28402	P83673	7.424E-02	2.335E-04	8.734E-04	4.240E-05	2.154E-04	7.540E-06	50.62
37796	P83749	8.973E-03	1.520E-04	3.600E-05	2.000E-05	3.110E-05	1.660E-05	0.77
44746	P83674.1	1.153E-01	1.700E-04	2.082E-03	2.000E-05	8.084E-04	8.800E-06	12.28
	P83674.2	1.150E-01	1.250E-04	2.068E-03	1.360E-05	8.121E-04	5.000E-06	

Table 18. Uranium TIMS Results for NBL QA Samples

NBL QA Sample	PNNL Sample Log #	U 233/238*	33/38 2sig	U 234/238	34/38 2 sig	U235/238	35/38 2sig	U236/238	36/38 2sig	Total U, ng/g
UCAR 25-B	U84104	4.395E-04	4.600E-06	3.380E-05	1.090E-06	5.746E-03	2.200E-05	2.999E-05	8.200E-07	62.2
	**	4.428E-04	1.170E-05	3.360E-05	2.600E-06	5.821E-03	5.400E-05	2.960E-05	2.900E-06	
UCAR 41-B	U84105	4.138E-04	7.500E-06	3.997E-05	9.700E-07	6.221E-03	3.000E-05	1.951E-05	9.100E-07	66.4
	**	4.219E-04	7.900E-06	4.081E-05	1.190E-06	6.277E-03	5.800E-05	1.918E-05	9.200E-07	
UCAR 57-B	U84106	3.893E-04	5.400E-06	4.694E-05	1.160E-06	6.747E-03	2.900E-05	8.770E-06	5.600E-07	70.4
	**	3.883E-04	7.200E-06	4.538E-05	2.030E-06	6.793E-03	2.900E-05	7.300E-06	3.100E-06	

*233U/238U ratios measured include added 233U spike/tracer, total U contents determined using measured 233U/238U value.
**replicate analyses from same separated fraction, not used in subsequent GUM analyses.

Table 19. Plutonium TIMS Results for NBL QA Samples

NBL QA Sample	PNNL Sample Log #	Pu 240/239	40/39 2sig	Pu 241/239	41/39 2sig	Pu 242/239	42/39 2sig	Total Pu, pg/g
UCAR 25-B	P84104	1.021E-01	5.103E-04	5.893E-04	3.800E-06	1.023E-04	2.300E-06	17.6
UCAR 41-B	P84178	7.299E-03	1.900E-04	4.120E-05	2.600E-06	8.800E-06	2.900E-06	21.1
UCAR 57-B	P84106	4.410E-02	2.205E-04	2.534E-04	2.100E-06	4.380E-05	1.400E-06	20.6

The contents of U and Pu determined by adding spikes or tracers as outlined above are calculated separately in a spreadsheet which includes initial (unprocessed) sample weights, weights of the spiked and unspiked aliquots (for uranium), and measured isotope ratios corrected for spike/tracer contributions on all isotopes. The U and Pu contents determined in the qualification samples compared very favorably with the amounts estimated that were added, as stated in the shipping memo for the samples. The U and Pu contents in the 6 BEPO cores sent from NBL vary a bit, but we have seen a similar range of variation in samples taken from the 19 BEPO cores studied at PNNL, and in some cases, even in intra-block variability over relatively small areas.

As outlined in subsequent sections, GUM analyses of Pu results included uncertainty due to subtraction of minor amounts of isotope present in the spike or tracer added. Results of U TIMS analyses on unspiked aliquots were used for GUM analysis of U data for the six NBL BEPO cores. Since the three NBL QA core solutions prepared were not split before adding U spike, the GUM analyses for these three samples were performed without correction of minor isotopes present in the U spike, at this time.

3.2 TIMS Blanks

In the current study, two types of ‘blanks’ were prepared and analyzed. Uranium and plutonium tracers were added to each to precisely determine U and Pu contents. One type consisted of high-purity UCAR graphite powder, pressed into plugs, provided by New Brunswick Laboratory. Two additional samples of very high-purity graphite from PNNL archives were also processed for blank Pu contents for comparison. These graphite ‘blanks’ were ashed and dissolved as in other types of samples, and the tracers usually added to 80% of the sample digestion. For two of the graphite blanks, B17 and B58, tracers were added to 10% of the sample solution for an initial determination, and tracers were later added to 80% of the sample solution for a replicate determination. The NBL blank graphite samples ranged in U contents from 0.4 to 2 ng/g, and were also found to contain small amounts of Pu (Table 20 and Table 21). The Pu contents in the blank graphite samples ranged from 3 fg to 18 fg, and were similar in amounts to sample processing blanks.

The other type of TIMS blank includes sample processing blanks where an empty quartz glass boat is heated in the furnace, washed with acid as for an ash removal step and U and Pu tracers added to the solution, followed by the same U and Pu separation procedures. Sample processing blanks are usually prepared along with samples, and the various blanks in Table 20 and Table 21 accompanied sets of NBL BEPO or qualification samples. Blank levels of U ranged from <1 pg to 42 pg (Table 20) and most resembled natural U or were slightly enriched in ^{235}U. Sample processing blanks for Pu ranged from 2 to 37 fg, except for one catastrophic blank of 417 fg, which was clearly a case of cross contamination from the sample adjacent during processing, due to similarities in the Pu isotope ratios.

Table 20. Uranium Contents and Isotope Ratios in Blank Graphite and Sample Processing Blanks

PNNL Sample Log Number	**NBL Sample Number**	**$^{234}U/^{238}U$, ±2 σ**	**$^{235}U/^{238}U$, ±2 σ**	**U, ng/g**
'Blank' Graphite Samples				
83596	B17	0.000043 0.000038	0.00757 0.00069	1.14
83597	B58	0.0000519 0.0000118	0.007145 0.000164	0.934
83602	B17	0.0000564 0.0000016	0.007125 0.000034	1.12
83603	B58	0.0000614 0.000096	0.007291 0.000032	0.939
83746	B64	0.000056 0.0000024	0.007257 0.000034	2.02
83747	B49	0.00005415 0.0000017	0.007327 0.000032	0.421
Sample Processing Blanks				**Total ng**
83598		0.000032 0.000042	0.00608 0.00025	0.0125
83615		0.000115 0.0000064	0.006848 0.000098	0.0037
83676		0.0001038 0.0000025	0.006401 0.00003	0.0317
83748		0.0000635 0.0000032	0.007397 0.000042	0.0203
83819		0.000158 0.0000067	0.00794 0.000054	0.0423
83825		0.0001415 0.0000109	0.007585 0.000086	0.0187
84059		0.0000857 0.0000041	0.008448 0.000072	0.019
84107		0.000117 0.000048	0.00753 0.00031	0.0038
84203		0.00024 0.00032	0.0237 0.0117	0.0008

Table 21. Plutonium Contents and Isotope Ratios in Blank Graphite and Sample Processing Blanks

PNNL Sample Log Number	NBL Sample Number	$^{240}Pu/^{239}Pu$, ±2 σ	$^{241}Pu/^{239}Pu$, ±2 σ	$^{242}Pu/^{239}Pu$, ±2 σ	Pu, pg/g
'Blank' Graphite Samples					
83598	B17	0.10685 0.00087	0.002389 0.000084	0.0001285 0.000061	0.0147
83597	B58	0.11571 0.00082	0.002461 0.000077	0.001324 0.000056	0.0178
83602	B17	0.1072 0.0043	0.00258 0.00026	0.00127 0.00035	0.0143
83603	B58	0.1159 0.00195	0.00247 0.00037	0.00132 0.0002	0.017
83897	B17	0.1244 0.003	0.00252 0.0006	0.00265 0.00042	unsp
83898	B58	0.1285 0.0027	0.00263 0.00042	0.00188 0.0003	unsp
83746	B64	0.1006 0.0034	0.00655 0.00068	0.00391 0.00159	0.0033
83747	B49	0.0908 0.0051	0.00201 0.00101	0.00204 0.00063	0.0023
83745 SGBF graphite		0.1231 0.0022	0.01193 0.00075	0.0234 0.0015	0.0111
83753 TSX graphite		0.088 0.002	0.00217 0.00021	0.00046 0.00046	0.0154
Sample Processing Blanks					**Pu, pg**
83604		0.0888 0.0074	0.0018 0.0023	0.0031 0.0022	0.0063
83676		0.074 0.00018	0.000884 0.000013	0.000244 0.000007	0.417
83748		0.1101 0.0017	0.00638 0.00048	0.0066 0.0003	0.0121
83754		0.09128 0.00087	0.00134 0.00011	0.0006 0.00011	0.0291
83919		0.1013 0.00091	0.00169 0.000063	0.00065 0.00007	0.037
84059		0.1208 0.0065	0.00211 0.00056	0.01116 0.0016	0.002

3.3 Uranium Reference Standard Results

Until recently, over the last two years, uranium and plutonium certified reference standards were not routinely analyzed. Other types of particulate uranium standards were run instead, to estimate measurement mass bias on the TIMS mass spectrometer. Uranium standards prepared by solution loading onto the Re filaments were not routinely done. Plutonium standards prepared for TIMS analyses using the bead equilibration and loading methods were also not routinely done, due to concerns about having relatively large quantities of even diluted Pu reference standards in the clean laboratories. As a result, the instrument mass bias for both U and Pu TIMS measurements, and the correlation coefficient for an uncertainty budget in GUM estimates, is arbitrarily set at unity, for now.

In the future, we will devise ways of running Pu reference standards, either as solution loads on a new mass spectrometer, after tests of detection efficiencies, or using the proven successful bead-loading methods. As a start at assessing mass bias correlation coefficients in U TIMS analyses based on results for a U reference standard, results for a natural U isotope standard, NBS 950a, are tabulated in Table 22. These results cover part of the time period of TIMS sample analyses presented in this report, however, Table 22 includes results for different types of TIMS filament solution loading methods, such as use of 0.3-mm O.D. gel loader pipet tips, and other methods still under development, such as use of pulled glass capillaries (O.D. to < 0.05 mm) mounted and controlled with a high-resolution micromanipulator. The results in Table 22 do not appear to vary with the particular loading method, and when further NBS 950a results are available, correlation coefficients will be calculated for uncertainty contributions of $^{234}U/^{238}U$ and $^{235}U/^{238}U$ TIMS measurements in the near future.

Table 22. Compilation of Results for NBS 950s Natural U Standard

PNNL Analysis Number	Analysis Date	$^{234}U/^{238}U$	± 2 sigma	$^{235}U/^{238}U$	± 2 sigma
84064	6/15/2006	0.00005412	0.00000119	0.007209	0.000021
84065	6/15/2006	0.00005274	0.00000129	0.007251	0.000028
84066	6/15/2006	0.00005253	0.00000184	0.007194	0.000022
84067	6/18/2006	0.00005337	0.00000073	0.0072568	0.0000083
84068	6/18/2006	0.00005303	0.00000065	0.0072333	0.0000096
84069	6/18/2006	0.00005258	0.00000073	0.007237	0.000012
84148	7/25/2006	0.00005054	0.00000176	0.007018	0.000033
84149	7/25/2006	0.00005358	0.0000012	0.007196	0.000026
84160A	8/7/2006	0.00005437	0.00000076	0.007293	0.000015
84160B	8/7/2006	0.00005386	0.00000061	0.007283	0.00001
84160C	8/7/2006	0.00005442	0.00000071	0.007261	0.000013
84161A	8/7/2006	0.0000545	0.000001	0.007291	0.000013
84161B	8/7/2006	0.00005398	0.00000072	0.007234	0.000014
84161C	8/7/2006	0.00005455	0.0000009	0.007206	0.000011
84197	8/17/2006	0.00005473	0.00000179	0.007272	0.000027
84201	8/29/2006	0.00005393	0.00000151	0.007248	0.000024

PNNL Analysis Number	Analysis Date	$^{234}U/^{238}U$	± 2 sigma	$^{235}U/^{238}U$	± 2 sigma
84202	8/29/2006	0.00005505	0.00000157	0.007275	0.000021
84425A	10/20/2006	0.00005477	0.00000184	0.007277	0.000024
84425B	10/20/2006	0.00005299	0.00000126	0.0072473	0.0000191
84425C	10/27/2006	0.00005525	0.00000125	0.0072654	0.0000187
84550A	1/4/2007	0.0000549	0.0000021	0.007256	0.00005
84550B	1/4/2007	0.00005414	0.00000166	0.007241	0.000021
84597	2/9/2007	0.00005574	0.00000142	0.007286	0.000028
84599	2/9/2007	0.00005587	0.00000157	0.007259	0.000056
84600	2/9/2007	0.00005413	0.00000192	0.007241	0.000035
84601	2/9/2007	0.00005441	0.00000168	0.007243	0.000028
84602	2/9/2007	0.00005596	0.00000162	0.007272	0.000023
84615	2/23/2007	0.00005363	0.00000189	0.007222	0.000055
84616	2/23/2007	0.0000523	0.0000021	0.007134	0.000034
84617	2/23/2007	0.00005433	0.00000148	0.007237	0.000047
84618	2/23/2007	0.0000561	0.0000034	0.007342	0.000043
84619	2/23/2007	0.00005461	0.0000019	0.00732	0.000024
84620	2/23/2007	0.0000546	0.0000023	0.0073356	0.000025
84621	2/26/2007	0.0000551	0.0000016	0.007245	0.000034
84622	2/26/2007	0.00005376	0.00000159	0.007202	0.000024
84623	2/26/2007	0.0000541	0.0000026	0.007265	0.000046
84624	2/26/2007	0.00005551	0.0000015	0.007245	0.000018
84625	2/26/2007	0.0000544	0.000002	0.007223	0.000049
84626	2/26/2007	0.00005436	0.00000141	0.007212	0.000033
84670	3/16/2006	0.00005371	0.00000193	0.007212	0.000026
84671	3/16/2006	0.000054	0.00000158	0.007235	0.000022
84672	3/16/2006	0.00005322	0.00000132	0.007248	0.000023
Mean ratio or 41 measurements		5.41374E-05		0.007243414	
Sample standard deviation		1.08619E-06		5.24712E-05	
Sample RSD		2.01%		0.72%	
Average measurement uncertainty		2.81%		0.37%	

3.4 TIMS Estimation Procedure

For purposes of description, we have organized the estimation procedure into four steps. These steps are performed by an in-hour data reduction software package using raw data files from the mass spectrometer. Table 20 through Table 22 present TIMS results with 2-sigma uncertainties calculated by the program, although these will be slightly lower than GUM uncertainty estimates as shown later.

- Step 1: Calculate corrected count rates.
- Step 2: Calculate atomic ratios for each acquisition.
- Step 3: Calculate mean atomic ratios (i.e., final estimates).
- Step 4: Calculate corrected ratios.

3.4.1 Step 1: Calculate Corrected Count Rates

The gross counts, c_x,*i*, are corrected for dead time, interpolated, and corrected for background, to produce a corrected count rate, $r_{x,i}$. The index *x* identifies the AMU being measured, while *i* identifies the acquisition time (i.e., duty cycle) that the count is associated with. The formula describing these operations is:

$$r_{x,i} = \frac{c_{x,i}}{t_x - \tau c_{x,i}} - b_{tot,x,i} \tag{15}$$

where

τ	=	is the instrument dead time
t_x	=	acquisition counting time for mass *x*
$b_{tot,x,i}$	=	Total background count rate. This is composed of three components that are due to the detector, mass spectral, and tracer impurity.

$$b_{tot,x,i}=b_{det}+b_{mspec,x,i}+b_{tracer,x,i} \tag{16}$$

b_{det}	=	Detector dark noise, the same for each mass and acquisition
$b_{mspec,x,i} = f_{x.tracer}(r_{tracer,i} - b_{det})$	=	This is correction for M243 (r_{243} uncorrected for background)
$b_{tracer,x,i} = F_{x.tracer} \bullet r_{tracer,i}$	=	This is correction for impurities in the tracer. $F_{x.tracer}$ estimated from analysis of tracer.
$f_{x.tracer}$	=	Mass spec correction factor to AMU *x* for tracer 243
$F_{x.tracer}$	=	Impurity corection factor for tracer.

3.4.2 Step 2: Calculate Atomic Ratios

$$R_{xy,i} = \frac{r_{x,i}}{r_{y,i}} \tag{17}$$

3.4.3 Step 3: Calculate Means

The estimate for isotopic ratio *x/y* is calculated by

$$\bar{R}_{xy} = \frac{1}{W_+}\sum_{i=1}^{N} W_i R_{xy,i} \tag{18}$$

with the weights $W_i = 1/se(R_{xy,i})^2$, and $W_+ = \Sigma W_i$.

The standard error can be calculated with either of two formulas; first, via propagation of error (POE):

$$se\left(\bar{R}_{xy}\right)^2 = W_+^{-1} \tag{19}$$

or, empirically, from the replicate measurements, $R_{xy,i}$:

$$se\left(\bar{R}_{xy}\right)^2 = \frac{1}{N}\sum_{i=1}^{N}\frac{W_i}{W_+}\left(R_{xy,i} - \bar{R}_{xy}\right)^2 \tag{20}$$

It should be noted that either calculation of standard error does not include systematic background correction errors, such as those produced by b_{det}, for example.

3.4.4 Step 4: Correct Means for Bias

$$R_{xy.final} = CF_{xy} \cdot \bar{R}_{xy} \tag{21}$$

where CF_{xy} is the correction due to mass and instrument bias. CF_{xy} should be determined from a calibration experiment using NBL standards, but this experiment hasn't been run. We assume:

- $CF_{xy} = 1$
- $RE(CF_{xy}) = 0.5\%$

3.5 GUM Version of Estimation Procedure for TIMS data

The systematic effects of background correction are dealt with using the approximation

$$\bar{R}_{xy}\left(b_{tot}\right) = \bar{R}_{xy} - \frac{1}{N}\sum_i \frac{1}{r_{y.i}}\left(b_{tot.x} - b_{tot.x.i}\right) + \frac{1}{N}\sum_i \frac{r_{x.i}}{r_{y.x}^2}\left(b_{tot.y}\right) \tag{22}$$

Uncertainty Calculation Details:

- Empirical SE of $\bar{R}$ is used. This includes uncertainty due to Poisson count variability, interpolation, and other (possibly unknown) sources.

- Uncertainties in background calibration factors (i.e., $f_{x.243}$ and F_{tracer}) are propagated to final estimate.

- Uncertainties in calibration factors $C\,F_{xy}$ propagated to final estimate.

Table 23. Typical Uncertainties for Pu Estimates of BEPO Sample Ratios Pu240/Pu239, Pu241/Pu239, and Pu242/Pu239

Source	RE
$\bar{R}_{xy}$	0.5–1.5%
$C\,F_{xy}$	0.5%
$f_{x.243}$	100%
$F_{x.tracer}$	0.2%

Table 24. Correlation Table for Pu Ratios

	240/239	241/239	242/239
240/239	1.00	0.00	0.00
241/239	0.00	1.00	0.51
242/239	0.00	0.51	1.00
Bet. Sample	0.92	0.59	0.72

Table 25. Empirical vs. POE RE

	Rel. Err. %	
	Empirical	POE
$\bar{R}_{240/239}$	0.148	0.110
$\bar{R}_{241/239}$	0.699	0.694
$\bar{R}_{242/239}$	1.830	1.585

3.6 August 2006 Qualification Sample Results

The GUM analysis for TIMS results is a propagation of errors calculation with a few intermediate results displayed in a table. The in-house data reduction procedures described earlier also do propagation-of-errors, but these do not occur for possible correlations caused by the background corrections. The

GUM approach here then is really as an added-on component performing an additional correction to the in-house data reduction results.

As an example of this, let us consider Sample 84104. Required inputs to the calculation include calibration parameters used in TIMS estimation, and corrected count-rates and associated uncertainties. The calibration parameter table lists the calibration parameter (as "est"), its uncertainty (sd), and its degrees of freedom (dof). The calibration parameter table for Sample 84104 is shown in Table 26:

In Table 26, the parameter names identify quantities appearing in the basic in-house data reduction estimation formulas as outlined earlier, to be used in subsequent GUM tables. For example,

b.det = background correction for dark detector noise
b.mspec = background correction counted at mass 243
b.tracer, 239 = background contributed by small amounts in added tracer

The only significant difference between quantities in Table 26 and those appearing in Steve's formulas is that some GUM table quantities represent averages. For example, b.mspec above is the average of Steve's b.mspec.i values (with i representing accumulation time). Other required inputs inlcude corrected count rates (and associated POE standard deviation) for each atomic mass unit used in the calculation. Here is an example for Sample 84104:

Table 26. Calibration Parameter Table for Sample 84104

Parameter	Est.	sd	dof
b.det	0.156667	0.016744	28
b.mspec	0.4113	0	Inf
f.243	1	1	Inf
b.tracer.239	2.82E-01	0	Inf
b.tracer.240	5.64E+00	0	Inf
b.tracer.241	7.64E-01	0	Inf
b.tracer.242	1.11E+01	0	Inf
F.tracer.239	3.45E-04	1.00E-06	100
F.tracer.240	6.90E-03	5.00E-05	100
F.tracer.241	9.35E-04	2.00E-06	100
F.tracer.242	1.36E-02	3.00E-05	100
CF.xy	1	0.005	Inf

Table 27. Example of Corrected Count-Rate Table for Sample 84104, Based on Interpolated Count Rates Supplied by PNNL TIMS Data Reduction Program

amu.239	sd.239	amu.240	sd.240	amu.241	sd.241	amu.242	sd.242
471200.80	588.23	48930.62	128.02	279.64	7.07	45.29	3.91
409165.35	534.26	41842.03	118.35	250.92	7.14	43.31	5.01
393071.95	518.75	39915.86	115.57	220.14	6.17	30.29	2.96
.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.
6767.12	63.05	685.69	15.12	3.79	0.81	1.04	0.55
5768.89	58.77	594.56	14.08	3.15	0.74	0.27	0.33
2035.04	34.30	207.14	8.33	0.25	0.58	–0.15	0.55

The values in this table are supposed to represent the corrected count rates as calculated by the in-house data reduction described earlier, as represented by the notation, r.x.i and se(r.x.i); the count rate for amu “x” at acquisition time “i”.

The Gum table that is calculated from this input data should contain all the calibration factors present in the above table. However, to simplify the table, we instead use an intermediate result into the GUM table, b.tot, which is defined by

$$b.tot.x = b.det + b.mspec + b.tracer.x$$

Below is an intermediate GUM table provided as an example that describes the relationship between b.tot.239 and the above inputs.

Table 28. GUM Relationship between Total Ion Counts for Mass 239 and Preceding Data Inputs (Table 26 and Table 27).

	Est	RE	dof	Sensit	Uncert	Index
b.det	1.57e-01	10.700	2.80e+01	0.00e+00	0.000000	0.000
b.mspec	5.68e-01	0.000	Inf	1.00e+00	0.000000	0.000
f.243	1.00e+00	100.000	Inf	4.11e-01	0.411000	100.000
b.tracer.239	8.17e+02	0.000	Inf	3.45e-04	0.000000	0.000
b.tracer.240	8.17e+02	0.000	Inf	0.00e+00	0.000000	0.000
b.tracer.241	8.17e+02	0.000	Inf	0.00e+00	0.000000	0.000
b.tracer.242	8.16e+02	0.000	Inf	0.00e+00	0.000000	0.000
F.tracer.239	3.45e-04	0.290	1.00e+02	8.17e+02	0.000817	0.199
F.tracer.240	6.90e-03	0.725	1.00e+02	0.00e+00	0.000000	0.000
F.tracer.241	9.35e-04	0.214	1.00e+02	0.00e+00	0.000000	0.000
F.tracer.242	1.36e-02	0.221	1.00e+02	0.00e+00	0.000000	0.000
Result	8.50e-01	48.400	6.41e+12	NA	NA	NA

So b.tot.239 = .85 with a relative error (RSD) of 48%. You might note that the big error in the background parameters is associated with "f.243". The preceding tables mainly serve to illustrate the relationship between the input values supplied by the data reduction routine and the values appearing in the GUM. Table 29 presents an example of GUM uncertainties for the desired Pu isotopic ratios measured in sample UCAR-25B (PNNL # 84104), with "b.tot.239" appearing in each table for each result or isotope ratio.

The first parameter appearing in the GUM table (for example R.242.239) represents the mean ratio, calculated using weights (or alternatively, a straight average). The weights are calculated from the se(r.x.i) values present in the second input table appearing above. The Relative Error associated with R.242.239 can be calculated by two methods, either POE or empirical. The POE method should conform to the in-hour data reduction methodology for calculating uncertainty on the R.242.239 isotopic ratio. The "empirical" method uses the replicate measurements in the second input table to calculate a relative error, and is currently used to calculate RE in the GUM tables.

However, using the POE method, the Est and RE associated with R.242.239 should correspond exactly to the estimate and relative error produced by our in-house data reduction routine calculations. Note also that the resulting estimate is equal to the estimate associated with R.242.239, but the relative errors are not. The GUM analysis is adding on extra uncertainty due to calibration parameters.

GUM tables for all U and Pu TIMS analyses in the NBL BEPO samples and the qualification samples are presented in the Appendix.

Table 29. Pu GUM Tables for Sample 84104

Quantity	Estimate	Relative Error (%)	DOF	Sensitivity Coefficient	Uncertainty Contribution	Index	K value
Isotopic Ratio R.240.239							
R.240.239	0.102141205	0.0858348	36.56269995	1	8.76727E-05	2.862237729	
CF.240.239	1	0.5	1000	0.102141205	0.000510706	97.12228932	
b.tot.239	0.849967	48.39020953	1000	5.48343E-07	2.25534E-07	1.89409E-05	
b.tot.240	6.207967	6.657985639	1000	-1.61386E-05	-6.67051E-06	0.016568931	
Result	0.102141205	0.507353369	44629.99666				1.96001714
Isotopic Ratio R.241.239							
R.241.239	0.000584171	0.730406644	36.42968672	1	4.26682E-06	25.72104334	
CF.241.239	1	0.5	1000	0.000584171	2.92085E-06	12.05311109	
b.tot.239	0.849967	48.39020953	1000	3.08938E-09	1.27066E-09	2.28109E-06	
b.tot.241	1.331967	30.87938715	1000	-1.61386E-05	-6.63787E-06	62.24967555	
Result	0.000584171	1.440192101	550.6533354				1.964281411
Isotopic Ratio R.242.239							
R.242.239	0.000101524	2.385971462	34.57936055	1	2.42233E-06	11.65632452	
CF.242.239	1	0.5	1000	0.000101524	5.0762E-07	0.511883522	
b.tot.239	0.849967	48.39020953	1000	5.36702E-10	2.20746E-10	9.68008E-08	
b.tot.242	11.667967	3.531276513	1000	-1.61386E-05	-6.64957E-06	87.83761343	
Result	0.000101524	6.988507406	2545.03464				1.960896538
Note: Input variables that make no contribution are deleted.							

However, using the POE method, the Est and RE associated with R.242.239 should correspond exactly to the estimate and relative error produced by our in-house data reduction routine calculations. Note also that the resulting estimate is equal to the estimate associated with R.242.239, but the relative errors are not. The GUM analysis is adding on extra uncertainty due to calibration parameters.

GUM tables for all TIMS analyses in the NBL BEPO samples and the qualification samples are presented in the Appendix.

4.0 References

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Appendix A

GUM Tables for All TIMS Analyses of NBL BEPO Sample and NBL Qualification Samples

Appendix A

GUM Tables for All TIMS Analyses of NBL BEPO Sample and NBL Qualification Samples

PNNL Sample Number	NBL Sample Number	Quantity	Estimate	Relative Error (%)	DOF	Sensitivity Coefficient	Uncertainty Contribution	Index	K value
P83599	16819	R.240.239	7.903E-03	0.56	37.33	1.000E+00	4.395E-05	4.150E+01	
		CF.240.239	1.000E+00	0.50	1000.00	7.903E-03	3.952E-05	3.355E+01	
		b.tot.239	6.186E-01	77.58	1000.00	2.004E-07	9.616E-08	1.987E-04	
		b.tot.240	1.070E+00	44.86	1000.00	-7.121E-05	-3.417E-05	2.509E+01	
		Result	7.903E-03	0.86	216.80				1.971
		R.241.239	8.379E-05	3.55	27.56	1.000E+00	2.976E-06	7.528E-01	
		CF.241.239	1.000E+00	0.50	1000.00	8.379E-05	4.189E-07	1.492E-02	
		b.tot.239	6.186E-01	77.58	1000.00	2.017E-09	9.681E-10	7.965E-08	
		b.tot.241	6.592E-01	72.80	1000.00	-7.121E-05	-3.417E-05	9.924E+01	
		Result	8.379E-05	40.94	486260.63				1.960
		R.242.239	5.901E-05	5.28	26.51	1.000E+00	3.115E-06	8.241E-01	
		CF.242.239	1.000E+00	0.50	1000.00	5.901E-05	2.951E-07	7.394E-03	
		b.tot.239	6.186E-01	77.58	1000.00	1.385E-09	6.647E-10	3.753E-08	
		b.tot.242	1.527E+00	31.43	1000.00	-7.121E-05	-3.417E-05	9.917E+01	
		Result	5.901E-05	58.15	390404.88				1.960
P83600	10431	R.240.239	1.303E-01	0.16	24.54	1.000E+00	2.056E-04	9.059E+00	
		CF.240.239	1.000E+00	0.50	1000.00	1.303E-01	6.515E-04	9.092E+01	
		b.tot.239	5.365E-01	69.69	1000.00	1.186E-06	4.433E-07	4.210E-05	
		b.tot.240	1.441E+00	25.95	1000.00	-2.683E-05	-1.003E-05	2.156E-02	
		Result	1.303E-01	0.52	2989.67				1.961

PNNL Sample Number	NBL Sample Number	Quantity	Estimate	Relative Error (%)	DOF	Sensitivity Coefficient	Uncertainty Contribution	Index	K value
		R.241.239	2.630E-03	0.77	23.44	1.000E+00	2.029E-05	6.010E+01	
		CF.241.239	1.000E+00	0.50	1000.00	2.630E-03	1.315E-05	2.524E+01	
		b.tot.239	5.365E-01	69.69	1000.00	2.371E-08	8.866E-09	1.148E-05	
		b.tot.241	6.179E-01	60.51	1000.00	-2.683E-05	-1.003E-05	1.469E+01	
		Result	2.630E-03	1.00	64.90				1.997
		R.242.239	1.147E-03	1.26	23.10	1.000E+00	1.444E-05	6.100E+01	
		CF.242.239	1.000E+00	0.50	1000.00	1.147E-03	5.733E-06	9.609E+00	
		b.tot.239	5.365E-01	69.69	1000.00	1.026E-08	3.835E-09	4.300E-06	
		b.tot.242	2.359E+00	15.85	1000.00	-2.683E-05	-1.003E-05	2.942E+01	
		Result	1.147E-03	1.61	62.09				1.999
P83601	27727	R.240.239	2.177E-02	0.12	34.91	1.000E+00	2.701E-05	5.798E+00	
		CF.240.239	1.000E+00	0.50	1000.00	2.177E-02	1.088E-04	9.416E+01	
		b.tot.239	2.295E+00	5.23	1000.00	5.615E-08	6.735E-09	3.605E-07	
		b.tot.240	4.153E+01	0.78	134.62	-7.485E-06	-2.413E-06	4.627E-02	
		Result	2.177E-02	0.52	10384.42				1.960
		R.241.239	3.929E-05	1.89	33.49	1.000E+00	7.417E-07	3.927E+01	
		CF.241.239	1.000E+00	0.50	1000.00	3.929E-05	1.965E-07	2.755E+00	
		b.tot.239	2.295E+00	5.23	1000.00	9.745E-11	1.169E-11	9.753E-09	
		b.tot.241	5.835E+00	2.06	1000.00	-7.485E-06	-9.012E-07	5.798E+01	
		Result	3.929E-05	3.01	217.17				1.971
		R.242.239	7.711E-06	26.15	33.87	1.000E+00	2.017E-06	6.101E+01	
		CF.242.239	1.000E+00	0.50	1000.00	7.711E-06	3.856E-08	2.230E-02	
		b.tot.239	2.295E+00	5.23	1000.00	1.844E-11	2.212E-12	7.339E-11	
		b.tot.242	8.133E+01	0.26	209.80	-7.485E-06	-1.612E-06	3.897E+01	
		Result	7.711E-06	33.48	85.37				1.988

PNNL Sample Number	NBL Sample Number	Quantity	Estimate	Relative Error (%)	DOF	Sensitivity Coefficient	Uncertainty Contribution	Index	K value
P83673	28402	R.240.239	7.433E-02	0.14	45.19	1.000E+00	1.072E-04	7.669E+00	
		CF.240.239	1.000E+00	0.50	1000.00	7.433E-02	3.716E-04	9.211E+01	
		b.tot.239	6.246E-01	71.02	1000.00	1.022E-06	4.533E-07	1.370E-04	
		b.tot.240	1.907E+00	23.27	1000.00	-4.166E-05	-1.848E-05	2.279E-01	
		Result	7.433E-02	0.52	7684.05				1.960
		R.241.239	7.760E-04	4.86	25.44	1.000E+00	3.772E-05	7.997E+01	
		CF.241.239	1.000E+00	0.50	1000.00	7.760E-04	3.880E-06	8.461E-01	
		b.tot.239	6.246E-01	71.02	1000.00	1.056E-08	4.684E-09	1.233E-06	
		b.tot.241	7.409E-01	59.87	1000.00	-4.166E-05	-1.848E-05	1.919E+01	
		Result	7.760E-04	5.44	39.78				2.021
		R.242.239	2.160E-04	1.83	44.13	1.000E+00	3.953E-06	4.361E+00	
		CF.242.239	1.000E+00	0.50	1000.00	2.160E-04	1.080E-06	3.254E-01	
		b.tot.239	6.246E-01	71.02	1000.00	2.960E-09	1.313E-09	4.813E-07	
		b.tot.242	3.217E+00	13.79	1000.00	-4.166E-05	-1.848E-05	9.533E+01	
		Result	2.160E-04	8.76	23201.22				1.960
P83674.1	44746	R.240.239	1.155E-01	0.40	31.83	1.000E+00	4.564E-04	3.833E+01	
		CF.240.239	1.000E+00	0.50	1000.00	1.155E-01	5.773E-04	6.134E+01	
		b.tot.239	3.027E-01	53.08	1000.00	1.039E-05	1.669E-06	5.127E-04	
		b.tot.240	8.480E-01	18.96	1000.00	-2.740E-04	-4.405E-05	3.571E-01	
		Result	1.155E-01	0.64	216.67				1.971

PNNL Sample Number	NBL Sample Number	Quantity	Estimate	Relative Error (%)	DOF	Sensitivity Coefficient	Uncertainty Contribution	Index	K value
		R.241.239	2.067E-03	1.34	32.88	1.000E+00	2.772E-05	2.733E+01	
		CF.241.239	1.000E+00	0.50	1000.00	2.067E-03	1.034E-05	3.800E+00	
		b.tot.239	3.027E-01	53.08	1000.00	1.889E-07	3.035E-08	3.277E-05	
		b.tot.241	3.518E-01	45.68	1000.00	-2.740E-04	-4.403E-05	6.896E+01	
		Result	2.067E-03	2.57	440.13				1.965
		R.242.239	7.566E-04	3.95	31.38	1.000E+00	2.989E-05	3.139E+01	
		CF.242.239	1.000E+00	0.50	1000.00	7.566E-04	3.783E-06	5.028E-01	
		b.tot.239	3.027E-01	53.08	1000.00	7.030E-08	1.130E-08	4.483E-06	
		b.tot.242	1.404E+00	11.45	1000.00	-2.740E-04	-4.404E-05	6.814E+01	
		Result	7.566E-04	7.05	318.34				1.967
P83674.2	44746	R.240.239	1.150E-01	0.15	58.95	1.000E+00	1.678E-04	7.853E+00	
		CF.240.239	1.000E+00	0.50	1000.00	1.150E-01	5.748E-04	9.215E+01	
		b.tot.239	1.936E+00	4.26	1000.00	2.179E-07	1.799E-08	9.023E-08	
		b.tot.240	3.491E+01	0.76	122.63	-5.531E-06	-1.463E-06	5.973E-04	
		Result	1.150E-01	0.52	9559.32				1.960
		R.241.239	2.057E-03	0.30	56.94	1.000E+00	6.131E-06	2.618E+01	
		CF.241.239	1.000E+00	0.50	1000.00	2.057E-03	1.028E-05	7.367E+01	
		b.tot.239	1.936E+00	4.26	1000.00	3.777E-09	3.118E-10	6.770E-08	
		b.tot.241	4.906E+00	1.69	1000.00	-5.531E-06	-4.591E-07	1.468E-01	
		Result	2.057E-03	0.58	830.69				1.963
		R.242.239	8.080E-04	0.54	56.49	1.000E+00	4.358E-06	5.245E+01	
		CF.242.239	1.000E+00	0.50	1000.00	8.080E-04	4.040E-06	4.507E+01	
		b.tot.239	1.936E+00	4.26	1000.00	1.470E-09	1.214E-10	4.068E-08	
		b.tot.242	6.831E+01	0.25	169.23	-5.531E-06	-9.476E-07	2.479E+00	
		Result	8.080E-04	0.74	205.18				1.972

PNNL Sample Number	NBL Sample Number	Quantity	Estimate	Relative Error (%)	DOF	Sensitivity Coefficient	Uncertainty Contribution	Index	K value
P83749	37796	R.240.239	8.975E-03	0.70	43.33	1.000E+00	6.258E-05	3.773E+01	
		CF.240.239	1.000E+00	0.50	1000.00	8.975E-03	4.488E-05	1.940E+01	
		b.tot.239	4.434E-01	62.40	1000.00	7.165E-07	1.983E-07	3.787E-04	
		b.tot.240	1.267E+00	21.84	1000.00	-2.417E-04	-6.691E-05	4.312E+01	
		Result	8.975E-03	1.14	304.38				1.968
		R.241.239	2.920E-05	17.29	18.51	1.000E+00	5.049E-06	5.666E-01	
		CF.241.239	1.000E+00	0.50	1000.00	2.920E-05	1.460E-07	4.736E-04	
		b.tot.239	4.434E-01	62.40	1000.00	2.159E-09	5.973E-10	7.929E-09	
		b.tot.241	5.170E-01	53.52	1000.00	-2.417E-04	-6.689E-05	9.943E+01	
		Result	2.920E-05	229.76	576778.58				1.960
		R.242.239	3.013E-05	27.21	35.37	1.000E+00	8.199E-06	1.480E+00	
		CF.242.239	1.000E+00	0.50	1000.00	3.013E-05	1.507E-07	4.998E-04	
		b.tot.239	4.434E-01	62.40	1000.00	1.472E-09	4.073E-10	3.652E-09	
		b.tot.242	2.100E+00	13.18	1000.00	-2.417E-04	-6.690E-05	9.852E+01	
		Result	3.013E-05	223.65	161496.88				1.960
P84104	UCAR 25-B	R.240.239	1.021E-01	0.09	36.56	1.000E+00	8.767E-05	2.862E+00	
		CF.240.239	1.000E+00	0.50	1000.00	1.021E-01	5.107E-04	9.712E+01	
		b.tot.239	8.500E-01	48.39	1000.00	5.483E-07	2.255E-07	1.894E-05	
		b.tot.240	6.208E+00	6.66	1000.00	-1.614E-05	-6.671E-06	1.657E-02	
		Result	1.021E-01	0.51	44630.00				1.960

PNNL Sample Number	NBL Sample Number	Quantity	Estimate	Relative Error (%)	DOF	Sensitivity Coefficient	Uncertainty Contribution	Index	K value
		R.241.239	5.842E-04	0.73	36.43	1.000E+00	4.267E-06	2.572E+01	
		CF.241.239	1.000E+00	0.50	1000.00	5.842E-04	2.921E-06	1.205E+01	
		b.tot.239	8.500E-01	48.39	1000.00	3.089E-09	1.271E-09	2.281E-06	
		b.tot.241	1.332E+00	30.88	1000.00	-1.614E-05	-6.638E-06	6.225E+01	
		Result	5.842E-04	1.44	550.65				1.964
		R.242.239	1.015E-04	2.39	34.58	1.000E+00	2.422E-06	1.166E+01	
		CF.242.239	1.000E+00	0.50	1000.00	1.015E-04	5.076E-07	5.119E-01	
		b.tot.239	8.500E-01	48.39	1000.00	5.367E-10	2.207E-10	9.680E-08	
		b.tot.242	1.167E+01	3.53	1000.00	-1.614E-05	-6.650E-06	8.784E+01	
		Result	1.015E-04	6.99	2545.03				1.961
P84106	UCAR 57-B	R.240.239	4.411E-02	0.12	37.07	1.000E+00	5.282E-05	5.424E+00	
		CF.240.239	1.000E+00	0.50	1000.00	4.411E-02	2.206E-04	9.456E+01	
		b.tot.239	7.451E-01	35.76	1000.00	1.772E-07	4.720E-08	4.330E-06	
		b.tot.240	6.863E+00	3.94	1000.00	-1.216E-05	-3.288E-06	2.102E-02	
		Result	4.411E-02	0.51	12601.93				1.960
		R.241.239	2.501E-04	0.86	38.87	1.000E+00	2.161E-06	2.793E+01	
		CF.241.239	1.000E+00	0.50	1000.00	2.501E-04	1.250E-06	9.351E+00	
		b.tot.239	7.451E-01	35.76	1000.00	1.011E-09	2.694E-10	4.340E-07	
		b.tot.241	1.296E+00	20.55	1000.00	-1.216E-05	-3.239E-06	6.273E+01	
		Result	2.501E-04	1.64	498.25				1.965
		R.242.239	4.366E-05	2.92	38.02	1.000E+00	1.273E-06	1.321E+01	
		CF.242.239	1.000E+00	0.50	1000.00	4.366E-05	2.183E-07	3.883E-01	
		b.tot.239	7.451E-01	35.76	1000.00	1.823E-10	4.857E-11	1.922E-08	
		b.tot.242	1.312E+01	2.04	1000.00	-1.216E-05	-3.257E-06	8.641E+01	
		Result	4.366E-05	8.02	2179.27				1.961

PNNL Sample Number	NBL Sample Number	Quantity	Estimate	Relative Error (%)	DOF	Sensitivity Coefficient	Uncertainty Contribution	Index	K value
P84178	UCAR 41-B	R.240.239	7.287E-03	0.25	53.19	1.000E+00	1.804E-05	1.941E+01	
		CF.240.239	1.000E+00	0.50	1000.00	7.287E-03	3.643E-05	7.916E+01	
		b.tot.239	6.346E-01	42.22	1000.00	4.555E-08	1.220E-08	8.881E-06	
		b.tot.240	4.635E+00	5.82	1000.00	-1.823E-05	-4.915E-06	1.441E+00	
		Result	7.287E-03	0.56	1412.39				1.962
		R.241.239	3.842E-05	2.56	48.50	1.000E+00	9.855E-07	3.908E+00	
		CF.241.239	1.000E+00	0.50	1000.00	3.842E-05	1.921E-07	1.485E-01	
		b.tot.239	6.346E-01	42.22	1000.00	2.286E-10	6.125E-11	1.510E-08	
		b.tot.241	9.946E-01	26.94	65535.00	-1.823E-05	-4.883E-06	9.595E+01	
		Result	3.842E-05	12.98	31766.31				1.960
		R.242.239	8.763E-06	15.11	49.70	1.000E+00	1.324E-06	6.819E+00	
		CF.242.239	1.000E+00	0.50	1000.00	8.763E-06	4.382E-08	7.468E-03	
		b.tot.239	6.346E-01	42.22	1000.00	4.782E-11	1.281E-11	6.383E-10	
		b.tot.242	8.685E+00	3.09	1000.00	-1.823E-05	-4.894E-06	9.317E+01	
		Result	8.763E-06	57.86	10688.37				1.960
U28402	28402	R.236.238	2.356E-04	0.58	34.90	1.000E+00	1.366E-06	5.597E+01	
		CF.236.238	1.000E+00	0.50	1000.00	2.356E-04	1.178E-06	4.163E+01	
		b.tot.238	1.852E-01	39.70	1000.00	2.266E-10	1.666E-11	8.325E-09	
		b.tot.236	1.852E-01	39.70	1000.00	-3.848E-06	-2.828E-07	2.400E+00	
		Result	2.356E-04	0.77	111.41				1.981

PNNL Sample Number	NBL Sample Number	Quantity	Estimate	Relative Error (%)	DOF	Sensitivity Coefficient	Uncertainty Contribution	Index	K value
		R.235.238	5.873E-03	0.12	34.97	1.000E+00	6.893E-06	5.222E+00	
		CF.235.238	1.000E+00	0.50	1000.00	5.873E-03	2.936E-05	9.477E+01	
		b.tot.238	1.852E-01	39.70	1000.00	5.650E-09	4.153E-10	1.895E-08	
		b.tot.235	1.852E-01	39.70	1000.00	-3.848E-06	-2.828E-07	8.793E-03	
		Result	5.873E-03	0.51	12820.59				1.960
		R.234.238	1.238E-04	0.68	34.89	1.000E+00	8.382E-07	6.025E+01	
		CF.234.238	1.000E+00	0.50	1000.00	1.238E-04	6.192E-07	3.289E+01	
		b.tot.238	1.852E-01	39.70	1000.00	1.192E-10	8.758E-12	6.578E-09	
		b.tot.234	1.852E-01	39.70	1000.00	-3.848E-06	-2.828E-07	6.861E+00	
		Result	1.238E-04	0.87	96.09				1.985
		R.233.238	8.103E-03	0.17	34.96	1.000E+00	1.365E-05	1.019E+01	
		CF.233.238	1.000E+00	0.50	1000.00	8.103E-03	4.051E-05	8.981E+01	
		b.tot.238	1.852E-01	39.70	1000.00	7.795E-09	5.729E-10	1.796E-08	
		b.tot.233	1.852E-01	39.70	1000.00	-3.848E-06	-2.828E-07	4.377E-03	
		Result	8.103E-03	0.53	3368.40				1.961
U37796	37796	R.236.238	2.834E-05	1.83	34.01	1.000E+00	5.174E-07	8.493E+01	
		CF.236.238	1.000E+00	0.50	1000.00	2.834E-05	1.417E-07	6.371E+00	
		b.tot.238	1.482E-01	24.64	1000.00	3.215E-11	1.173E-12	4.367E-10	
		b.tot.236	1.482E-01	24.64	1000.00	-4.536E-06	-1.656E-07	8.697E+00	
		Result	2.834E-05	1.98	47.15				2.012
		R.235.238	7.095E-03	0.30	34.41	1.000E+00	2.143E-05	2.673E+01	
		CF.235.238	1.000E+00	0.50	1000.00	7.095E-03	3.548E-05	7.327E+01	
		b.tot.238	1.482E-01	24.64	1000.00	8.036E-09	2.933E-10	5.008E-09	
		b.tot.235	1.482E-01	24.64	1000.00	-4.536E-06	-1.656E-07	1.596E-03	
		Result	7.095E-03	0.58	481.61				1.965

PNNL Sample Number	NBL Sample Number	Quantity	Estimate	Relative Error (%)	DOF	Sensitivity Coefficient	Uncertainty Contribution	Index	K value
		R.234.238	6.118E-05	0.99	34.33	1.000E+00	6.064E-07	7.525E+01	
		CF.234.238	1.000E+00	0.50	1000.00	6.118E-05	3.059E-07	1.915E+01	
		b.tot.238	1.482E-01	24.64	1000.00	6.930E-11	2.529E-12	1.309E-09	
		b.tot.234	1.482E-01	24.64	1000.00	-4.536E-06	-1.656E-07	5.609E+00	
		Result	6.118E-05	1.14	60.63				2.000
		R.233.238	9.190E-04	0.37	34.38	1.000E+00	3.365E-06	3.488E+01	
		CF.233.238	1.000E+00	0.50	1000.00	9.190E-04	4.595E-06	6.503E+01	
		b.tot.238	1.482E-01	24.64	1000.00	1.040E-09	3.797E-11	4.441E-09	
		b.tot.233	1.482E-01	24.64	1000.00	-4.536E-06	-1.656E-07	8.444E-02	
		Result	9.190E-04	0.62	282.54				1.968
U44746	44746	R.236.238	3.055E-04	1.06	22.43	1.000E+00	3.252E-06	8.181E+01	
		CF.236.238	1.000E+00	0.50	1000.00	3.055E-04	1.527E-06	1.805E+01	
		b.tot.238	1.389E-01	19.59	1000.00	3.817E-10	1.038E-11	8.340E-10	
		b.tot.236	1.389E-01	19.59	1000.00	-5.005E-06	-1.361E-07	1.434E-01	
		Result	3.055E-04	1.18	33.52				2.033
		R.235.238	5.481E-03	0.55	22.42	1.000E+00	3.035E-05	5.508E+01	
		CF.235.238	1.000E+00	0.50	1000.00	5.481E-03	2.741E-05	4.492E+01	
		b.tot.238	1.389E-01	19.59	1000.00	6.853E-09	1.864E-10	2.078E-09	
		b.tot.235	1.389E-01	19.59	1000.00	-5.005E-06	-1.361E-07	1.108E-03	
		Result	5.481E-03	0.75	73.89				1.993
		R.234.238	2.796E-04	0.66	22.46	1.000E+00	1.856E-06	6.359E+01	
		CF.234.238	1.000E+00	0.50	1000.00	2.796E-04	1.398E-06	3.607E+01	
		b.tot.238	1.389E-01	19.59	1000.00	3.495E-10	9.505E-12	1.667E-09	
		b.tot.234	1.389E-01	19.59	1000.00	-5.005E-06	-1.361E-07	3.420E-01	
		Result	2.796E-04	0.83	55.56				2.004

PNNL Sample Number	NBL Sample Number	Quantity	Estimate	Relative Error (%)	DOF	Sensitivity Coefficient	Uncertainty Contribution	Index	K value
		R.233.238	1.432E-02	0.28	22.40	1.000E+00	4.001E-05	2.380E+01	
		CF.233.238	1.000E+00	0.50	1000.00	1.432E-02	7.160E-05	7.620E+01	
		b.tot.238	1.389E-01	19.59	1000.00	1.790E-08	4.870E-10	3.525E-09	
		b.tot.233	1.389E-01	19.59	1000.00	-5.005E-06	-1.361E-07	2.755E-04	
		Result	1.432E-02	0.57	395.56				1.966
U83599	16819	R.236.238	7.224E-06	2.68	32.52	1.000E+00	1.939E-07	1.490E+01	
		CF.236.238	1.000E+00	0.50	1000.00	7.224E-06	3.612E-08	5.168E-01	
		b.tot.238	2.222E-01	48.24	1000.00	7.787E-12	8.347E-13	2.760E-10	
		b.tot.236	2.222E-01	48.24	1000.00	-4.311E-06	-4.621E-07	8.459E+01	
		Result	7.224E-06	6.96	1465.73				1.962
		R.235.238	7.285E-03	0.16	34.71	1.000E+00	1.172E-05	9.387E+00	
		CF.235.238	1.000E+00	0.50	1000.00	7.285E-03	3.642E-05	9.060E+01	
		b.tot.238	2.222E-01	48.24	1000.00	7.843E-09	8.408E-10	4.827E-08	
		b.tot.235	2.222E-01	48.24	1000.00	-4.311E-06	-4.621E-07	1.458E-02	
		Result	7.285E-03	0.53	3938.58				1.961
		R.234.238	6.177E-05	1.01	34.60	1.000E+00	6.267E-07	5.597E+01	
		CF.234.238	1.000E+00	0.50	1000.00	6.177E-05	3.088E-07	1.359E+01	
		b.tot.238	2.222E-01	48.24	1000.00	6.651E-11	7.130E-12	7.246E-09	
		b.tot.234	2.222E-01	48.24	1000.00	-4.311E-06	-4.621E-07	3.044E+01	
		Result	6.177E-05	1.36	110.44				1.982
		R.233.238	2.272E-03	0.25	34.68	1.000E+00	5.647E-06	1.978E+01	
		CF.233.238	1.000E+00	0.50	1000.00	2.272E-03	1.136E-05	8.009E+01	
		b.tot.238	2.222E-01	48.24	1000.00	2.446E-09	2.622E-10	4.265E-08	
		b.tot.233	2.222E-01	48.24	1000.00	-4.311E-06	-4.621E-07	1.325E-01	
		Result	2.272E-03	0.56	886.26				1.963

PNNL Sample Number	NBL Sample Number	Quantity	Estimate	Relative Error (%)	DOF	Sensitivity Coefficient	Uncertainty Contribution	Index	K value
U83600	10431	R.236.238	3.755E-04	0.41	30.92	1.000E+00	1.555E-06	2.966E+01	
		CF.236.238	1.000E+00	0.50	1000.00	3.755E-04	1.877E-06	4.322E+01	
		b.tot.238	5.208E-01	77.92	1000.00	3.440E-10	1.396E-10	2.390E-07	
		b.tot.236	5.208E-01	77.92	1000.00	-3.665E-06	-1.487E-06	2.712E+01	
		Result	3.755E-04	0.76	351.32				1.967
		R.235.238	4.946E-03	0.19	30.98	1.000E+00	9.595E-06	1.304E+01	
		CF.235.238	1.000E+00	0.50	1000.00	4.946E-03	2.473E-05	8.665E+01	
		b.tot.238	5.208E-01	77.92	1000.00	4.532E-09	1.839E-09	4.791E-07	
		b.tot.235	5.208E-01	77.92	1000.00	-3.665E-06	-1.487E-06	3.134E-01	
		Result	4.946E-03	0.54	1821.78				1.961
		R.234.238	2.476E-04	0.59	30.91	1.000E+00	1.471E-06	3.663E+01	
		CF.234.238	1.000E+00	0.50	1000.00	2.476E-04	1.238E-06	2.594E+01	
		b.tot.238	5.208E-01	77.92	1000.00	2.269E-10	9.207E-11	1.435E-07	
		b.tot.234	5.208E-01	77.92	1000.00	-3.665E-06	-1.487E-06	3.744E+01	
		Result	2.476E-04	0.98	230.43				1.970
		R.233.238	1.390E-02	0.13	30.98	1.000E+00	1.831E-05	6.491E+00	
		CF.233.238	1.000E+00	0.50	1000.00	1.390E-02	6.948E-05	9.347E+01	
		b.tot.238	5.208E-01	77.92	1000.00	1.273E-08	5.167E-09	5.168E-07	
		b.tot.233	5.208E-01	77.92	1000.00	-3.665E-06	-1.487E-06	4.282E-02	
		Result	1.390E-02	0.52	7354.02				1.960
U83601	27727	R.236.238	8.470E-05	0.83	30.93	1.000E+00	7.031E-07	6.597E+01	
		CF.236.238	1.000E+00	0.50	1000.00	8.470E-05	4.235E-07	2.394E+01	
		b.tot.238	4.170E-02	175.78	1000.00	7.946E-11	5.824E-12	4.527E-09	
		b.tot.236	4.170E-02	175.78	1000.00	-3.752E-06	-2.751E-07	1.010E+01	
		Result	8.470E-05	1.02	71.07				1.994

PNNL Sample Number	NBL Sample Number	Quantity	Estimate	Relative Error (%)	DOF	Sensitivity Coefficient	Uncertainty Contribution	Index	K value
		R.235.238	6.687E-03	0.15	30.97	1.000E+00	1.036E-05	8.764E+00	
		CF.235.238	1.000E+00	0.50	1000.00	6.687E-03	3.343E-05	9.123E+01	
		b.tot.238	4.170E-02	175.78	1000.00	6.273E-09	4.598E-10	1.726E-08	
		b.tot.235	4.170E-02	175.78	1000.00	-3.752E-06	-2.751E-07	6.174E-03	
		Result	6.687E-03	0.52	4032.13				1.961
		R.234.238	7.209E-05	0.94	30.84	1.000E+00	6.798E-07	6.921E+01	
		CF.234.238	1.000E+00	0.50	1000.00	7.209E-05	3.604E-07	1.946E+01	
		b.tot.238	4.170E-02	175.78	1000.00	6.762E-11	4.957E-12	3.680E-09	
		b.tot.234	4.170E-02	175.78	1000.00	-3.752E-06	-2.751E-07	1.133E+01	
		Result	7.209E-05	1.13	64.38				1.998
		R.233.238	5.017E-03	0.23	30.96	1.000E+00	1.167E-05	1.778E+01	
		CF.233.238	1.000E+00	0.50	1000.00	5.017E-03	2.508E-05	8.221E+01	
		b.tot.238	4.170E-02	175.78	1000.00	4.706E-09	3.450E-10	1.555E-08	
		b.tot.233	4.170E-02	175.78	1000.00	-3.752E-06	-2.751E-07	9.885E-03	
		Result	5.017E-03	0.55	979.14				1.962
U84104	UCAR 25-B	R.236.238	2.996E-05	1.41	33.92	1.000E+00	4.226E-07	9.607E+00	
		CF.236.238	1.000E+00	0.50	1000.00	2.996E-05	1.498E-07	1.207E+00	
		b.tot.238	4.815E-01	67.81	1000.00	2.953E-11	9.641E-12	4.999E-09	
		b.tot.236	4.815E-01	67.81	1000.00	-3.944E-06	-1.288E-06	8.919E+01	
		Result	2.996E-05	4.55	3674.90				1.961

PNNL Sample Number	NBL Sample Number	Quantity	Estimate	Relative Error (%)	DOF	Sensitivity Coefficient	Uncertainty Contribution	Index	K value
		R.235.238	5.748E-03	0.23	34.93	1.000E+00	1.347E-05	1.798E+01	
		CF.235.238	1.000E+00	0.50	1000.00	5.748E-03	2.874E-05	8.185E+01	
		b.tot.238	4.815E-01	67.81	1000.00	5.670E-09	1.851E-09	3.397E-07	
		b.tot.235	4.815E-01	67.81	1000.00	-3.944E-06	-1.288E-06	1.643E-01	
		Result	5.748E-03	0.55	1079.97				1.962
		R.234.238	3.377E-05	1.19	34.32	1.000E+00	4.027E-07	8.773E+00	
		CF.234.238	1.000E+00	0.50	1000.00	3.377E-05	1.688E-07	1.542E+00	
		b.tot.238	4.815E-01	67.81	1000.00	3.328E-11	1.087E-11	6.387E-09	
		b.tot.234	4.815E-01	67.81	1000.00	-3.944E-06	-1.288E-06	8.969E+01	
		Result	3.377E-05	4.03	4458.71				1.960
		R.233.238	4.391E-04	0.54	34.89	1.000E+00	2.357E-06	4.617E+01	
		CF.233.238	1.000E+00	0.50	1000.00	4.391E-04	2.195E-06	4.005E+01	
		b.tot.238	4.815E-01	67.81	1000.00	4.331E-10	1.414E-10	1.662E-07	
		b.tot.233	4.815E-01	67.81	1000.00	-3.944E-06	-1.288E-06	1.378E+01	
		Result	4.391E-04	0.79	163.68				1.975
U84105	UCAR 41-B	R.236.238	1.528E-05	8.09	11.54	1.000E+00	1.236E-06	7.867E+01	
		CF.236.238	1.000E+00	0.50	1000.00	1.528E-05	7.640E-08	3.005E-01	
		b.tot.238	2.963E-01	47.69	1000.00	1.739E-11	2.458E-12	3.110E-10	
		b.tot.236	2.963E-01	47.69	1000.00	-4.523E-06	-6.391E-07	2.103E+01	
		Result	1.528E-05	9.12	18.64				2.096

PNNL Sample Number	NBL Sample Number	Quantity	Estimate	Relative Error (%)	DOF	Sensitivity Coefficient	Uncertainty Contribution	Index	K value
		R.235.238	6.222E-03	0.42	32.61	1.000E+00	2.599E-05	4.109E+01	
		CF.235.238	1.000E+00	0.50	1000.00	6.222E-03	3.111E-05	5.888E+01	
		b.tot.238	2.963E-01	47.69	1000.00	7.104E-09	1.004E-09	6.130E-08	
		b.tot.235	2.963E-01	47.69	1000.00	-4.523E-06	-6.391E-07	2.485E-02	
		Result	6.222E-03	0.65	193.10				1.972
		R.234.238	3.986E-05	1.30	32.39	1.000E+00	5.193E-07	3.756E+01	
		CF.234.238	1.000E+00	0.50	1000.00	3.986E-05	1.993E-07	5.533E+00	
		b.tot.238	2.963E-01	47.69	1000.00	4.537E-11	6.411E-12	5.727E-09	
		b.tot.234	2.963E-01	47.69	1000.00	-4.523E-06	-6.391E-07	5.690E+01	
		Result	3.986E-05	2.13	229.55				1.970
		R.233.238	4.138E-04	0.65	32.47	1.000E+00	2.694E-06	6.074E+01	
		CF.233.238	1.000E+00	0.50	1000.00	4.138E-04	2.069E-06	3.584E+01	
		b.tot.238	2.963E-01	47.69	1000.00	4.717E-10	6.666E-11	3.720E-08	
		b.tot.233	2.963E-01	47.69	1000.00	-4.523E-06	-6.391E-07	3.420E+00	
		Result	4.138E-04	0.84	88.00				1.987
U84106	UCAR 57-B	R.236.238	8.949E-06	3.50	25.76	1.000E+00	3.134E-07	8.040E-01	
		CF.236.238	1.000E+00	0.50	1000.00	8.949E-06	4.475E-08	1.639E-02	
		b.tot.238	9.259E-01	83.26	1000.00	9.902E-12	7.633E-12	4.768E-10	
		b.tot.236	9.259E-01	83.26	1000.00	-4.516E-06	-3.481E-06	9.918E+01	
		Result	8.949E-06	39.06	398492.23				1.960

PNNL Sample Number	NBL Sample Number	Quantity	Estimate	Relative Error (%)	DOF	Sensitivity Coefficient	Uncertainty Contribution	Index	K value
		R.235.238	6.771E-03	0.48	32.83	1.000E+00	3.271E-05	4.802E+01	
		CF.235.238	1.000E+00	0.50	1000.00	6.771E-03	3.385E-05	5.143E+01	
		b.tot.238	9.259E-01	83.26	1000.00	7.828E-09	6.034E-09	1.634E-06	
		b.tot.235	9.259E-01	83.26	1000.00	-4.516E-06	-3.481E-06	5.439E-01	
		Result	6.771E-03	0.70	142.33				1.977
		R.234.238	4.721E-05	1.42	30.22	1.000E+00	6.727E-07	3.583E+00	
		CF.234.238	1.000E+00	0.50	1000.00	4.721E-05	2.361E-07	4.413E-01	
		b.tot.238	9.259E-01	83.26	1000.00	5.284E-11	4.074E-11	1.314E-08	
		b.tot.234	9.259E-01	83.26	1000.00	-4.516E-06	-3.481E-06	9.598E+01	
		Result	4.721E-05	7.53	23537.43				1.960
		R.233.238	3.916E-04	0.82	32.50	1.000E+00	3.219E-06	3.938E+01	
		CF.233.238	1.000E+00	0.50	1000.00	3.916E-04	1.958E-06	1.457E+01	
		b.tot.238	9.259E-01	83.26	1000.00	4.502E-10	3.471E-10	4.578E-07	
		b.tot.233	9.259E-01	83.26	1000.00	-4.516E-06	-3.481E-06	4.606E+01	
		Result	3.916E-04	1.31	209.60				1.971