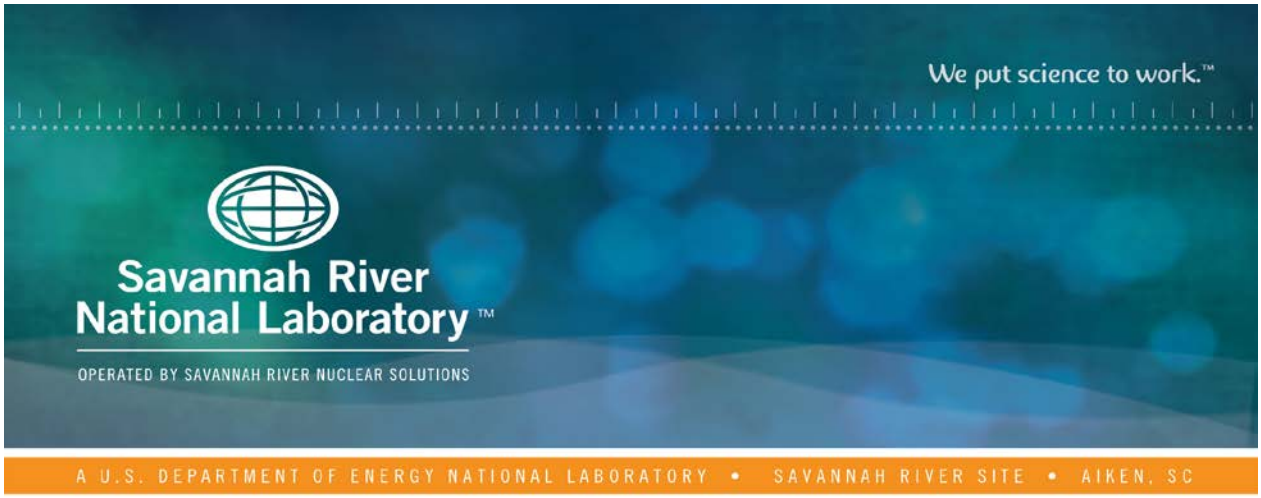

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GUM-compliant uncertainty propagations for Pu and U concentration measurements using the alpha-prototype XOS/LANL hiRX instrument; an SRNL H-Canyon Test Bed performance evaluation project

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DISCLAIMER

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Keywords: XRF, EDXRF, GUM, hiRX

Abbreviations:

ALARA – As low as reasonably achievable; radiation protection concept for worker protection
CCC – Custom calibration curves (results from calibration of hiRX using Pu and U reference materials)
DQO – Data quality objectives; customer requireements
EDXRF – energy dispersive x-ray fluorescence instrument
GUM – Guide to the expression of uncertainty in measurement (international standard JCGM 100)
High-Z – an element with a high mass nuclius; elements with a high mass number or weight
hiRX – High Resolution X-ray instrument; a monochromatic EDXRF
LANL – Los Alamos National Laboratory
NIST – National Institute of Standards and Technology
NNSA – National Nuclear Security Administration
QC – Quality Control; Measurement control practices; component of quality assurance program
ROI – Region of interest
SI – International system of units; the modern metric system
SRE – Sodium Reactor Experiment, SRE research reactor
SRNL – Savannah River National Laboratory
XOS – X-ray Optical Systems, Inc., 15 Tech Valley Drive, East Greenbush, NY 12061

EXECUTIVE SUMMARY

An SRNL H-Canyon Test Bed performance evaluation project was completed jointly by SRNL and LANL on a prototype monochromatic energy dispersive x-ray fluorescence instrument, the hiRX. A series of uncertainty propagations were generated based upon plutonium and uranium measurements performed using the alpha-prototype hiRX instrument. Data reduction and uncertainty modeling provided in this report were performed by the SRNL authors. Observations and lessons learned from this evaluation were also used to predict the expected uncertainties that should be achievable at multiple plutonium and uranium concentration levels provided instrument hardware and software upgrades being recommended by LANL and SRNL are performed.

Table 1 provides a summary of the propagated uncertainties for the alpha-prototype hiRX instrument using LANL-designed microcells. GUM-compliant uncertainty estimates were generated using the model equations described in Appendix A of this report and applied to various mixtures of plutonium and uranium at multiple concentration levels:

Table 1. Uncertainty propagations for alpha-prototype hiRX instrument, tested using LANL microcells

Analyte Concentrations (Sum of Pu + U)	Pu g/L ± Expanded Uncertainty (relative) [1]	U g/L ± Expanded Uncertainty (relative) [1]
1 gPu/L & 0.1 gU/L (Σ = 1.1 g/L)	1.000 ± 9.6 %	0.100 ± 15 %
3.5 gPu/L & 5 gU/L (Σ = 8.5 g/L)	3.50 ± 9.8 %	5.00 ± 9.8 %
10 gPu/L & 0.1 gU/L (Σ = 10.1 g/L)	10.0 ± 10 %	0.100 ± 16 %
0.1 gPu/L & 10 gU/L (Σ = 10.1 g/L)	0.100 ± 10 %	10.0 ± 10 %
9 gPu/L & 9 gU/L (Σ = 18 g/L)	9.00 ± 10 %	9.00 ± 9.5 %
45 gPu/L & 45 gU/L (Σ = 90 g/L)	45.0 ± 14 %	45.0 ± 14 %
0.5 gPu/L & 100 gU/L (Σ = 100.5 g/L)	0.500 ± 13 %	100. ± 13 %
0.5 gPu/L & 250 gU/L (Σ = 250.5 g/L)	0.50 ± 23 %	250. ± 23 %
[1] Coverage factors and confidence intervals	K=2 and 95% (normal)	K=2 and 95% (normal)

The optimum performance level for the hiRX instrument was in the 1-20 g/L total plutonium and uranium when using a LANL-designed disposable microcell with a sample chamber effective thickness of 0.125 cm. The optimum concentration range for the hiRX system can be moved easily by manufacturing a different thickness microcell or an alternative fixed-geometry sample chambers of a different thickness. The variation in the effective thickness between each of the disposable microcells and its impact on the fundamental-parameters shielding calculations proved to be the largest single component of the expanded uncertainty for the hiRX instrument. As a result, the potential benefits of the hiRX instrument design could not be optimized when using disposable microcells.

For comparison purposes the same GUM model equations were applied to a proposed beta-prototype hiRX instrument. The uncertainty distributions for key input parameters were adjusted to simulate the performance of new instrument assuming that recommended improvements to hardware and software were incorporated in a beta-prototype hiRX instrument, including a fixed-geometry sample chamber. These recommendations for improvements are detailed within in this report. Table 2 provides a summary of anticipated uncertainties that could be realized if a proposed beta-prototype hiRX instrument were manufactured. A performance improvement that exceeds these estimates may be possible, but it could not be demonstrated based upon available information.

Table 2. Uncertainty propagation for a proposed beta-prototype hiRX with upgrades including a flowcell

Analyte Concentrations (Sum of Pu + U)	Pu g/L ± Expanded Uncertainty (relative) [1]	U g/L ± Expanded Uncertainty (relative) [1]
1 gPu/L & 0.1 gU/L (Σ = 1.1 g/L)	1.0000 ± 0.96 %	0.1000 ± 3.8 %
3.5 gPu/L & 5 gU/L (Σ = 8.5 g/L)	3.500 ± 0.76 %	5.000 ± 0.86 %
10 gPu/L & 0.1 gU/L (Σ = 10.1 g/L)	10.000 ± 0.80 %	0.1000 ± 4.1 %
0.1 gPu/L & 10 gU/L (Σ = 10.1 g/L)	0.1000 ± 1.1 %	10.000 ± 0.86 %
9 gPu/L & 9 gU/L (Σ = 18 g/L)	9.00 ± 0.87 %	9.00 ± 0.88 %
45 gPu/L & 45 gU/L (Σ = 90 g/L)	45.0 ± 6.0 %	45.0 ± 6.1 %
0.5 gPu/L & 100 gU/L (Σ = 100.5 g/L)	0.500 ± 6.7 %	100.0 ± 6.9 %
0.5 gPu/L & 250 gU/L (Σ = 250.5 g/L)	0.50 ± 20 %	250. ± 20 %
[1] Coverage factors and confidence intervals	K=2 and 95% (normal)	K=2 and 95% (normal)

INTRODUCTION

Los Alamos National Laboratory (LANL) contracted with X-ray Optical Systems, Inc. (XOS), 15 Tech Valley Drive, East Greenbush, NY 12061, to design, fabricate, and deliver a prototype High Resolution X-ray (hiRX) instrument. SRNL collaborated with LANL and XOS on the design and testing of the prototype instrument. This GUM-compliant measurement uncertainty analysis provides an evaluation of the uncertainty in plutonium and uranium concentration measurements from the performance testing of the system. Also incorporated in the GUM uncertainty propagation is a prediction of the uncertainties for uranium and plutonium concentration that should be achievable for a next generation hiRX instrument with improved hardware and software based upon lessons learned from the testing of the system at SRNL, including improvements in sample introduction using a flowcell or similar fixed-geometry (fixed-thickness) sample chamber.

The instrument evaluation project was funded by NNSA NA-241 and tested by SRNL was performed under the SRNL H-Canyon Test Bed Project at SRNL's nuclear facility laboratory in F-Area.

The original design GUM uncertainty propagation, SRNL-L4700-2013-00012, identified positioning and thickness of the sample chambers (originally envisioned to be a microfluidic cell) as the input variable most likely to have the largest variance contribution). This determination was based upon engineering/scientific judgment provided by Zewu Chen, XOS (with concurrence from LANL and SRNL staff). It was recognized at the time of the design that this uncertainty would be reduced if a flowcell arrangement or an in-line configuration were used. However, the cost of ruggedizing the prototype hiRX for radiological containment or at-line installation exceeded available project funding. Furthermore, if a flowcell were used then the entire instrument would have been installed in containment at the SRNL F-Area Laboratory, which would have impacted costs and prevented returning of the system to LANL upon completion of the evaluation. The original design GUM propagation also assumed that the alpha-prototype version of the hiRX instrument would have a detector that monitored the x-ray source, otherwise this variable would have been included as a input variable and would have been a significant contributor to the simulated variance budget. Each of these predictions was validated by testing at SRNL. The original design GUM propagation also considered the impact of interferences from elemental strontium and similar types of spectral interferences. However, the monochromatic nature of the doubly-curved crystals was expected to virtually eliminate interferences. The software and user interface for the alpha-prototype hiRX instrument were not designed to evaluate the spectral appearance of the plutonium and uranium peaks. The off-line data reduction identified a significant interference for the measurement of trace-level plutonium in a uranium spent nuclear fuel being processed in the H-Canyon during the testing of the hiRX instrument.

GUM METHODOLOGY / SRNL IMPLEMENTATION

This propagation does not assume any correlations between input variables.
This propagation does not include input variables for potential interferences from known or unknown sources, but observed and expected interferences are discussed so that a future software upgrade can address mechanisms for identifying interferences when present and to the extent possible correcting for their impact. [**Recommendation**]

The international standard JCGM 100:2008 *Guide to the espression of uncertainty in measurement*, is a systematic process for evaluating well-characterized measurement sytems to determine the combined standard uncertainty (and expanded uncertainty) of the system. The individual sources of uncertainty from the key parameters and components of the measurement system are combined in a manner that generates a measurand (the result of the measurement) and the uncertainty in this measurement along with a coverage factor or confidence interval. This process is controlled within the SRNL Analytical Laboratories using the *Conduct of Analytical Measurements Manual* procedure L3.26-07031 *Measuring and Calculating Method Uncertainty*. This procedure implements the GUM standard and authorizes GUM Workbench™ commercial software for performing the calculations in accordance with JCGM 100. The GUM propagation process involves:

- Specifying and explaining the Measurand.
- Identifying the sources of measurement uncertainty.
- Determining which sources of uncertainty are significant.
- Determining the type of analysis to be performed for key uncertainty components (i.e., Type A or B)
  - Type A – calculation of the standard deviation and the degrees of freedom for a variable, using experimental data generated by the measurement system or from experiments conducted by the performing laboratory (both case-specific measurement results and pooled statistics may be applied)

  - Type B – calculation process based on identifying the applicable population distributions and determining the parameters for that distribution, using other practices including information taken from experiments conducted by others, open literature, expert knowledge/judgement, assumptions, bounding values
- Quantifying each of the significant uncertainty components in terms of statistical parameters (actual data or summary statistics) or uncertainty distributions (type of distribution, mean, and magnitude).
- Creating a Model Equation or a series of Model Equations that describes the Measurand and the measurement system
- Propagating the combined standard uncertainty using a Taylor-Series expansion that combines the partial derivatives from the model equation with the value of each variable.
  - The Calculus associated with propagation process is performed automatically by the GUM Workbench™ software.
- Applying a coverage factor to generate an expanded uncertainty, i.e., assigning a confidence interval.
- Reporting the results in a standardized manner, including rounding of the measurand and the uncertainty to an appropriate number of significant figures.
  - Rounding of the measurand and the expanded uncertainty is performed automatically by the GUM Workbench™ software.

hiRX Measurand

The hiRX was designed to generate both plutonium concentration and uranium concentration on a mass basis. The measurement of mass of analyte per mass of solution, is typically expressed with units of "gram-per-gram" (g g^{-1}), which is a "quantity of dimension one" (i.e., dimensionless) since these units cancel. The results on a mass basis are also reported at mg g^{-1} and µg g^{-1}. The Measurand is often multipled by the solution density of the sample or reference material (determined by independent means) with typical units of grams per cubic centimeter, g cm^{-3}, i.e., grams per milliliter, g mL^{-1}, are generated. The plutonium and uranium concentrations expressed on a volume basis are also reported with units of grams of analyte per unit volume of solution in liters, g L^{-1} (or in the more formal, SI-compliant units of grams per cubic decimeter, g dm^{-3}).

Sources of Uncertainty

Sources of uncertainty have been divided into three groups of variables. The first group of variables are those that are common to the process of collecting and submitting samples to an analytical laboratory. The second group of variables are those specific to the preparation of disposable microcells used only in the current configuration of the alpha-prototype hiRX supplied by XOS and LANL for testing and evaluation at SRNL's Analytical Laboratory in F-Area. The third set of variables are instrument specific parameters of the prototype hiRX system being evaluated.

<u>Sampling and laboratory handling processes</u>

A. **Sample collection, $\Delta_{Sampling}$,** (outside of the analytical laboratory) – This component of uncertainty is expected to be performed in a manner that ensures that the samples collected for laboratory analysis are representative of the bulk material being sampled within the performance standards specified in the International Target Values. This component should also include sample stability after collection but before delivery to the laboratory.
   - Sampling process and equipment – Sampling uncertainty is an importing uncertainty consideration for all measurement systems because it creates a bounding condition for the creation of the data quality objects (DQO) for the laboratory measurement method(s). There is little practical value for the laboratory customer (or a stakeholder / regulator) to create measurement method DQO that are significantly more demanding than the reliability of samples being submitted for analysis.
   - While important, this uncertainty component will not be included in the GUM analysis for the performance of the hiRX system since the instrument is not directly tied to a specific sample process or streams and does not match the intent of this GUM propagation.
   - Furthermore, all comparisons between the hiRX instrument and other measurement methods were compared on the same sample solution.
   - The full scope of standard preparations and handling of QC and calibration reference materials is often similar to the reliability of a well-controlled sampling process.

B. **Reference materials, Δ_{RM},** used for instrument calibration and measurement qualify control – This component of uncertainty considers traceability to SI and the ability of the laboratory to provide satisfactory quality reference materials in a suitable chemical form and at the desired concentrations need for instrument calibration and measurement quality control.
   - As separate variable for this parameter was not created for this uncertainty propagation. See the discussion on the custom calibration variables CCC_{slope} and $CCC_{sensitivity}$ for an explanation.

C. **Subsampling/Evaporation, Δ_{Evap},** into headspace, – Samples containing high concentrations of fission or activation products are handled in shielded analytical cell.
   - The hiRX instrument was not designed for placement within the shielded cells and the microcells were not designed for solution loading within the shielded cells and the subsequent removal from containment for measurement. Unless analytical subsamples (and dilutions when appropriate) are performed within the shielded analytical cells, small portions of each test sample must be removed from the shielded cells in container that preserve the concentration of the solution and prevent or minimize any significant evaporation of the solution within the headspace inside the container. The microcells being tested in combination with the prototype hiRX instrument have the advantage of needing only 7µL of highly radioactive solution. However, the practical considerations associated with removing small portions of the test solution from the shield cells have required that at least 100 µL of sample solution be removed from the shielded cells and promptly delivered to microcells for measurement.
   - Although handling of solutions from the shielded analytical cells was complicated, the manner in which these solutions were handled did not introduce significant added uncertainty to the preparation of microcells, so a separate term for this parameter was not included in the uncertainty propagation.
   - Improvement Opportunity: Design syringes (no headspace containers) that can be handled with manipulators, having a small capacity that supports ALARA principle with a capability to make appropriate additions directly into a flowcell mounted on the hiRX instrument (or to deliver 7µL portions to a microcell if desired). [**Recommendation**]

<u>Preparation of microcell for introducing test sample solution into the hiRX</u>

A. Sample chamber thickness, $\Delta_{shielding\_from\_thickness}$ – The effective height of the sample cavity and the variation in its volume of solution loaded in the microcell. The designed cavity depth is 1.00 mm and the machining tolerance was very reliable. The height and variation for multiple microcells were measured by P. E. O'Rourke using a calibrated depth gauge and found to be 1.00 mm ± 0.01 mm, K=1 (assumed to be Gaussian, 1.0 %). However, the effective height and variation was estimated by P. E. O'Rourke from hiRX spectral measurement and found to be ~1.227 mm ± 0.056 mm, K=1 (±4.6% K=1 Gaussian). This variable directly impacts the shielding calculation by approximately ± 3.5 % K=1, and thus also affects the final Pu and U concentration results in this manner.
   - The uncertainty in this variable, based upon a Type B evaluation, has been assigned a value of 1.000 ± 0.049 (K=1, based upon Gaussian, ± 3.5 % K=1).
   - This variable is actually the larger source of uncertainty in the variance budget because it also significantly impacts the determination of the slope and sensitivity factors obtained during the custom calibration process. (The values for the CCC terms were assigned uncertainties that considered this relationship).
   - See Figure A for a graphical representation of x-ray shielding and absorption and Figure B for a graphic representation of the impact of sample chamber thickness on the calculation of the correction factor for shielding and absorption.

B. Sample density, $\Delta_{shielding\_from\_lab\_density}$ – This parameter would impact the shielding correction significantly if the laboratory solution density measurements were not both precise and accurate. The uncertainty associated with the laboratory density is small and a term was included in the uncertainty propagation to model this parameter. The uncertainty associated with this Δ-term can be adjusted if solution density was obtained with process instrumentation or is based upon historical or other forms of process knowledge.

C. Bubble formation, Δ_{Bubble} in microcells – After the test sample solution is pipetted and the microcell is sealed, each microcell is inspected for bubbles by back lighting the sample cavity using a flashlight. If any bubbles are detected, the microcell is rejected. When bubbles are visible upon inspection the measurement of

uranium and plutonium on the hiRX are significantly biased low in proportion to the size of the bubbles. The inspection process has added reliability to the acceptance of loaded microcells. It is not known if the inspection process is 100% effective at detecting all bubbles of a size that are capable of impacting the hiRX measurements to a detectable extent.

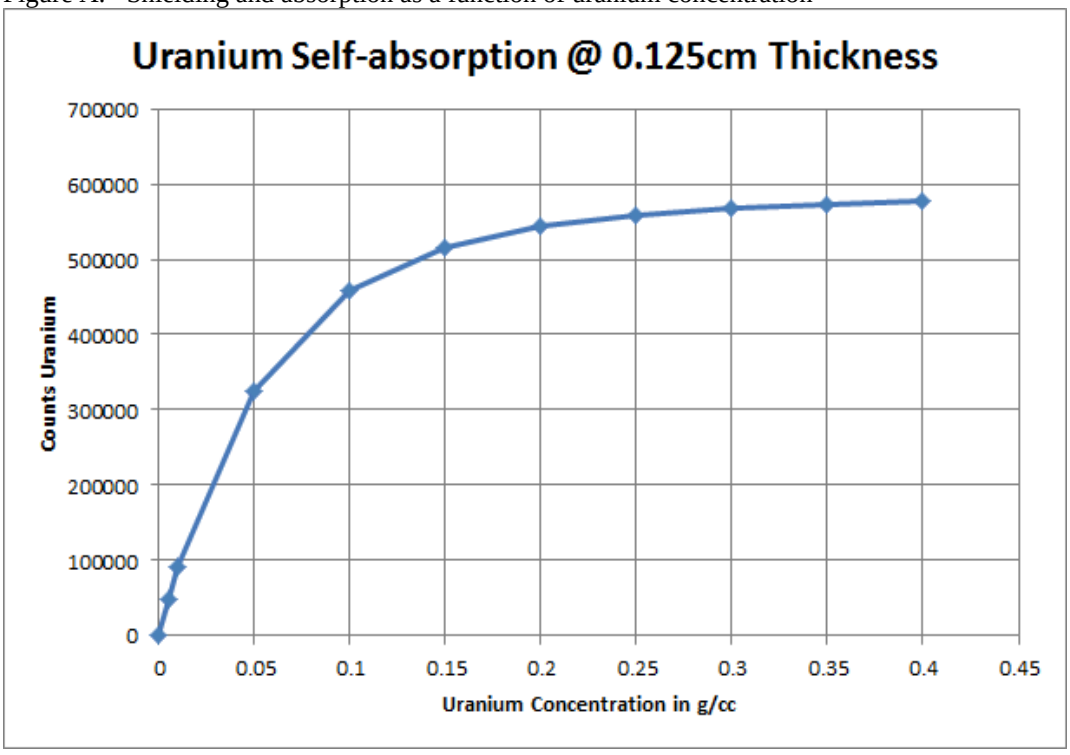
- This potential source of uncertainty is believed to be negligible compared the uncertainty in the variables that impact the shielding and thickness corrections for microcells, and thus does not need to be included in the propagation as it will not alter the calculation of the expanded uncertainty.

Measurement using hiRX

A. Correlation between plutonium and uranium concentration measurements:
   - The Pu and U concentration results depend upon a fundamental parameters shielding correction that uses a properly scaled sum of Pu and U net count rates to iteratively calculate shielding corrections for both elements.
   - These calculations introduce correlation between the two final results, but they do not necessitate identifying correlation coefficients for the input variables, which are all treated as independent in this uncertainty propagation.

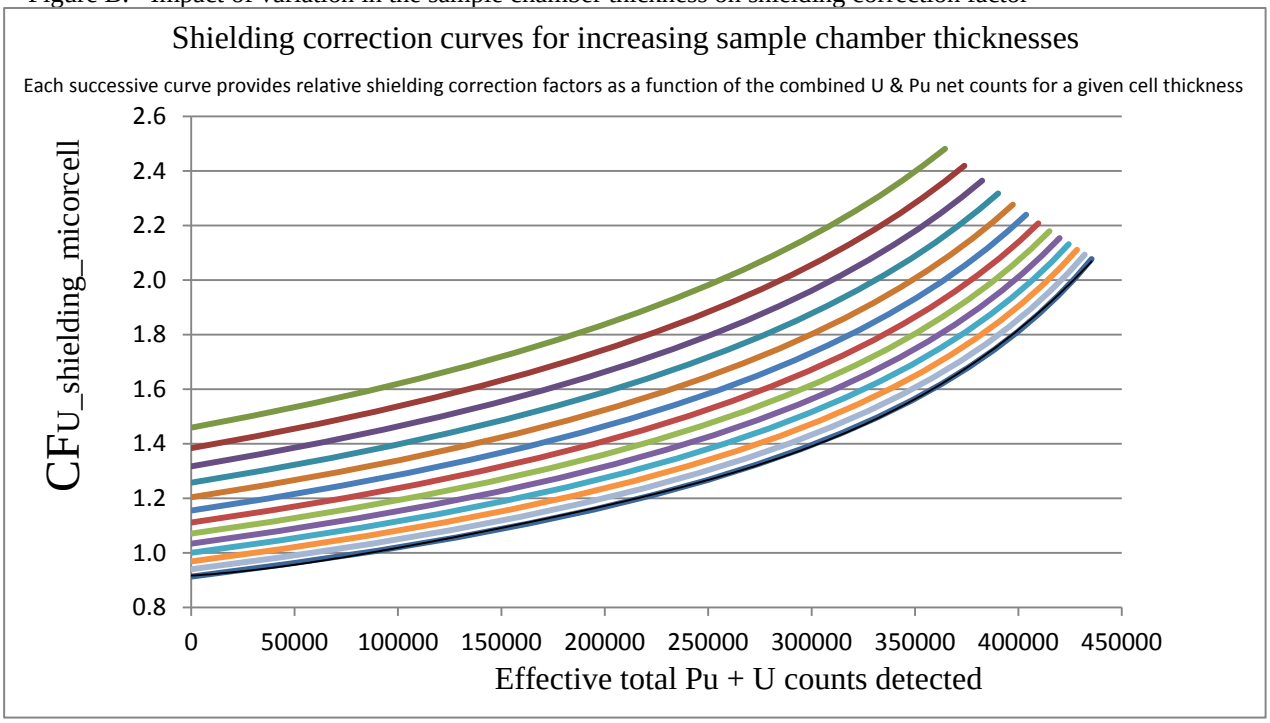
B. Fundamental parameter calculation – The fundamental parameters calculation is performed by the hiRX instrument to correct the observed Pu and U x-ray signals for two similar effects: (1) the loss of available excitation x-rays because the x-ray interacts with the other analytes or with another element in solution before they have an opportunity to intact with the analyte of interest and (2) and the loss of emitted x-rays from the element of interest that do not reach the detector because they are instead captured by the other analyte or another element in the solution.
   - The extent to which the fundamental parameter calculation corrects for x-ray absorption and shielding dictates the linearity of the instrument response versus analyte concentration
   - Absorption and shielding are the effects that cause a nonlinear relationship between the amount of x-rays from the source tube delivered to the test sample solution and the proportional amount of x-rays reaching the detector from plutonium and uranium in the test sample. See Figure A for a graphical representation of the effect of shielding and absorption.

Figure A. Shielding and absorption as a function of uranium concentration



- This calculation is very dependent upon the "thickness" of the sample solution.
- This Type A uncertainty has been assigned a value of 1.000 ± 0.060, rectangular distribution, ± 3.5 % K=1.
- Capabilities to include the contributions from other high-Z elements such as thorium, neptunium, and americium when known to be present above trace levels should be included in the beta-prototype software. [**Recommendation**]
- Other common elements that are sometimes present in significant molar quantities that should be modeled for shielding include aluminum and zirconium from cladding materials. These elements are only partly considered by the Δshielding_from_lab_density term used in the uncertainty propagation. [**Recommendation**]
- See Figure B for a graphic representation of the impact of sample chamber thickness on the calculation of the fundamental parameters shielding correction factor.

Figure B. Impact of variation in the sample chamber thickness on shielding correction factor



C. Instrument custom calibration CCC_{slope} and $CCC_{sensitivity}$ – The value and uncertainty associated with these variables are based hiRX instrument performance and the off-line data reduction performed by P. E. O'Rourke.
   - The CCC values are generated based upon measurements of reference materials and include the uncertainty in the reference materials, ΔRM, and each of the variables impacting microcell preparation and the fundamental parameters calculations.
   - The CCC values are expected to be 30-50% of the variance budget depending upon the calibration range and the number of measurements used to generate the calibration curve from which the slope and sensitivity are calculated.
   - The beta-prototype hiRX software needs to consider the fact that a standard linear regression is not properly weighted since significant weight is given to the smallest and the largest values on the calibration curve. In the case of the EDXRF technologies, the greater the correction for shielding, the larger the uncertainty in the x-y location of the largest value and the greater the uncertainty in the resulting slope and sensitivity terms. Calibration curves containing data point(s) that were adjusted with shielding correction(s) that are greater than 10% should be carefully vetted to evaluate their impact on the uncertainty in the calculated CCC_{slope} and $CCC_{sensitivity}$ terms.

D. Counting time, C_{Time} – The required duration depends on the concentration of uranium and plutonium and the thickness of the sample chamber. The uncertainty in counting is a function of counting statistics (Poisson distribution). The variable "counting time" is measured by the hiRX with sufficient reliability to be negligible provided the counting time is sufficient to generate an adequate number of analyte counts.

E. Counting dead time, C_{DT} – The hiRX instruments corrects results for detector dead time. The residual uncertainty from this uncertainty component is negligible.

F. Spectral overlap between Pu and U peaks $\Delta_{Overlap}$ – The current instrument configuration focuses both the uranium and plutonium x-ray signals on the same detector and depends upon detector resolution and spectral corrections to correct for spectral interferences.
   - This Type B uncertainty (and source of bias) was not included in the GUM uncertainty propagation as an evaluation of the hiRX spectra indicated that resolution was satisfactory. However, as beta-prototype system improvements are considered this small error source could be further reduced.
   - Improvement opportunity; refocus the doubly-curved optical crystal segment so that the Pu and U x-ray signals are focused on different detectors. [**Recommendation**]
   - This improvement opportunity should be considered for the beta-prototype hiRX instrument to reduce source of uncertainty that are entirely instrument driven. [**Recommendation**]

G. Spectral interference, elemental strontium, Δ_{Sr} – Strontium can be used as a surrogate for plutonium on the hiRX instrument. Strontium isotopes are present as fission products, but these radioactive elements are not typically present at concentrations that are important as elemental interferences.
   - When elemental strontium is present as interference in plutonium solutions, the hiRX instrument software or off-line calculations should be capable of making a spectral correction to the plutonium measurement with reliability consistent with the confidence to which the strontium concentration is known. [**Recommendation**]
   - If strontium is known to not be present or is known to be present in amounts that are insignificant then spectral fitting correction should not be applied to the data as more uncertainty will be introduced than will be eliminated. [**Recommendation**]
   - This propagation does not include a Δ_{Sr} term.

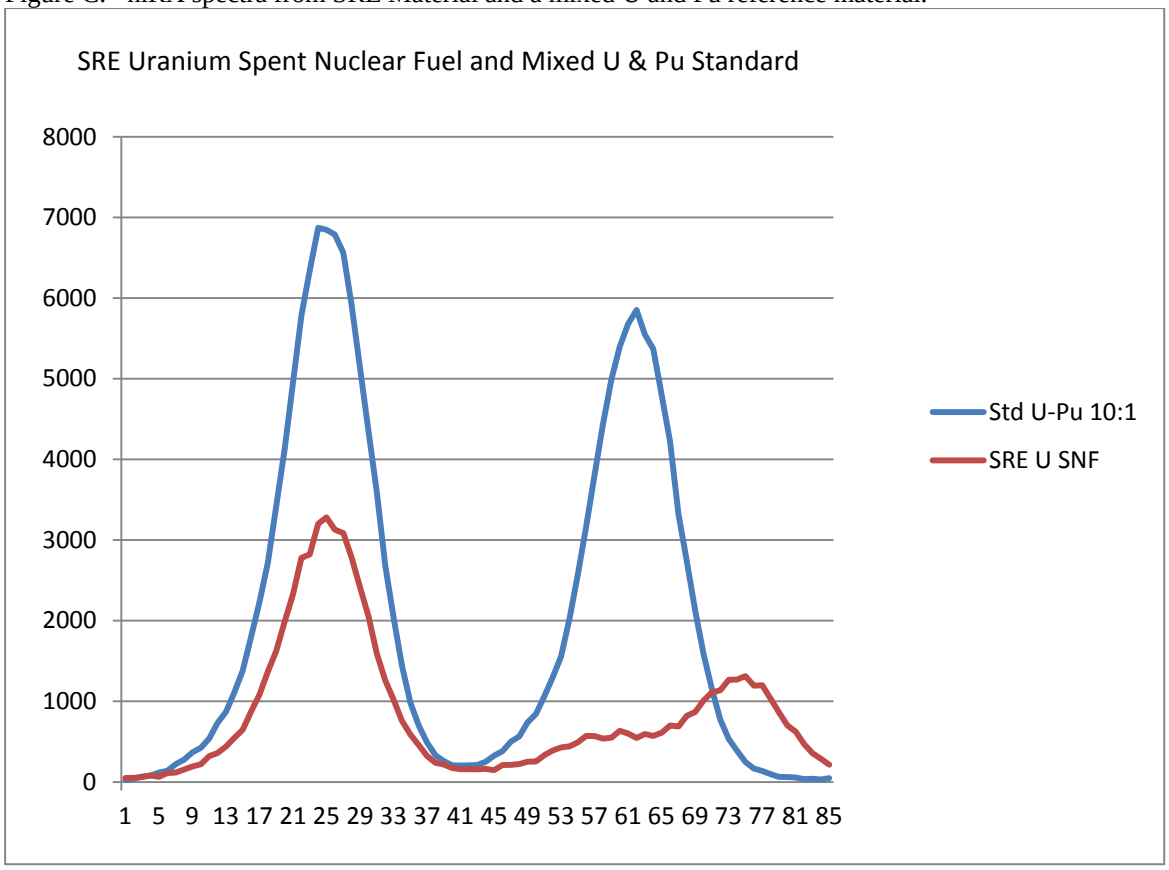
H. Counts from background x-rays, and scattered source x-rays, δC_{Bg} & $\delta C_{Scatter}$ – negligible based on measurements at SRNL
   - The design and shielding within the hiRX instrument is effective at minimizing the sources of background and scattered x-rays.
   - Terms for Pu and U background counts, $C_{\Xi BgforU}$ and $C_{\Xi BgforPu}$ are included in the uncertainty propagation that covers detector background, x-ray scattering, and β-emissions as a single Type A term with a Poisson distribution.

I. Counts from fission products (β-emissions) in irradiated samples, δ_{FP} – negligible based on measurements at SRNL
   - The design and shielding between the sample and the detector is effective at shielding the detector from beta emission from irradiated samples.
   - The hiRX is capable of measuring the background emission from irridiated sample materials (i.e., sample in chamber measured with instrument x-ray source off).

J. Spectral interferences – the quantity having the most impact on determining the extent of absorption and shielding is the mass absorption coefficients, μ_s.
   - The absorption and shielding for a test solution is calculated as the sum on the products of the mass fractions of each element, f_{mi}, times the mass absorption coefficients for each element at the excitation and emission energies, i.e.:
   - $\mu_s = \Sigma [f_{mi} * (\mu_{i,ex} + \mu_{i,em})]$ The physical constants $\mu_{i,ex}$ and $\mu_{i,em}$ are available from NIST.
   - Only solution components with a significant product of mass fraction times the absorption coefficients matter. Aluminum and especially zirconium matter in dissolved spent nuclear fuels, while fission products and stainless steel corrosion products are much less significant. Another example of an important component is iron when added in significant quantities as a reductant before solvent extraction.

K. Spectral interferences have been observed but the source of the interference still requires investigation.
- Refer to the hiRX spectrum in Figure C, collected on samples from the H-Canyon SRE Campaign (a uranium spent nuclear fuel being dissolved while the hiRX instrument was being evaluated). Overlaid on this same figure is the spectrum from a mixed uranium and plutonium standard.
- This source of Type B uncertainty (bias) was not assigned to a variable in this uncertainty propagation.
- Improved detection and handling of interferences is essential in the beta-prototype hiRX instrument. [**Recommendation**]

Figure C. hiRX spectra from SRE Material and a mixed U and Pu reference material.



L. X-ray tube reproducibility and aging Δ_{Rh_source} – This variable was identified during the original design review as a potential source of uncertainty that could be addressed by adding a detector to monitor the x-ray intensity from the x-ray tube and normalize measurement results based upon the average x-ray intensity measured during each standard and sample measurement, including calibration measurements. The XOS instrument designers did not consider this variable to be a source of variation that should be considered as sufficiently important for the alpha-prototype hiRX model because the instrument layout design had already been completed and the "engine" for the system had already been fabricated before this design review item had been identified.
- This improvement opportunity should be considered for the beta-prototype hiRX instrument to reduce source of uncertainty that are entirely instrument driven. [**Recommendation**]

Identification of key source of uncertainty

The following input variables are included in the GUM uncertainty model equations. They are discussed in detail in Appendix A.

$C_{\Xi UROI\_microcell}$ – *This variable is modified to repeat the propagation at different U and Pu concentrations*

$C_{\Xi BGforU\_microcell}$

$\Delta_{Rh\_source\_NotQuantified}$

$t_{count\_time\_microcell}$

$C_{\Xi PuROI\_microcell}$ – *This variable is modified to repeat the propagation at different U and Pu concentrations*

$C_{\Xi BGforPu\_microcell}$

$CCC_{U\_sensitivity\_microcell}$

$CCC_{Pu\_sensitivity\_microcell}$

a_{4U},

a_{3U},

a_{2U},

a_{1U},

a_{0U}

k_{1Pu},

k_{0Pu}

$\Delta_{shielding\_from\_lab\_density}$

$\Delta_{shielding\_from\_microcell\_thickness}$

$D_{lab\_density}$

$C_{\Xi UROI\_flowcell}$ – *This variable is modified to repeat the propagation at different U and Pu concentrations*

$C_{\Xi BGforU\_flowcell}$

$\Delta_{Rh\_source\_Quantified}$

$t_{count\_time\_flowcell}$

$C_{\Xi PuROI\_flowcell}$ – *This variable is modified to repeat the propagation at different U and Pu concentrations*

$C_{\Xi BGforPu\_flowcell}$

$CCC_{U\_sensitivity\_flowcell}$

$CCC_{Pu\_sensitivity\_flowcell}$

$\Delta_{shielding\_from\_flowcell\_thickness}$

Basis for the selecting sources of measurement uncertainty (variables) included in the GUM model equations:

The constraints on the design of the prototype hiRX instrument by XOS did not allow for including features that would have facilitated installing the instrument in radiological containment in a manner that would have allowed the system to be returned to LANL for future application or testing. This proof-in-concept prototype hiRX instrument was installed at SRNL in a benchtop configuration and samples containing microliter quantities in radiologically-sealed microcell were introduced into the sample chamber and analyzed. In this configuration, the sources of uncertainty from the hiRX technology and instrument design would be tested in combination with sources of uncertainty introduced from using a microcell for test sample introduction. Potential sources of uncertainty from introducing a test solution using a microcell include: consistency in introducing and aligning test solution and sample chamber within the instrument, the uniformatity of critical dimensions within each microcell, variation in the test solution handling and loading into the microcells. Sources of uncertainty that are independent of the specific type of sample holder or flowcell are: protocols for the collection of sample solutions (outside of the laboratory), the handling of the test solution following receipt into the laboratory, and the reliability and traceability of the calibration standard solutions. While all variables impact measurement uncertainty, some variables can not be tested separately and others if found to be a major contributor to the total uncertainty will prevent modeling and calculating a refined estimate for the some of the minor contributors to total uncertianty.

Based on the evalution of calibration and test data, the effective depth of the microcell sample solution cavity appear to be the largest source of measurement uncertainty. The sample cell cavity in each of the microcells is machined very precisely. The sample cell depth was measured by P. E. O'Rourke, SRNL, using a calibrated depth guage. The sample cell depth was found to be 0.100 cm ± 0.001 cm (±1%), in excellent agreement with the design depth. However, an apparent cell thickness of 0.1227 cm ± .006 cm or ±4.9% best explains the hiRX measurement data when it was modelled to determine the fundamental parameters calibration. O'Rourke postulates that the apparent increases in the cell thickness is real and is caused by variation in the microcell's snap cap and closure process. In order for the o-ring to ensure an effective liquid seal around the cell cavity, the sample cell o-ring must be at least slightly compressed, thus it must be slightly thicher than the height of the cell cavity. When the seal presses on the inner disk it likely pushes it away from the top of the cell cavity and against the snap cap, instead of compressing until the inner disk contacts the top of the cell cavity. Seating of the o-ring during its installation shortly before loading the microcell with a test solution may be part of the source of the variation and the observed variation in bubble formation.

The cell cavity has a volume that should be filled by 5 µL of solution. However, when quantities ranging from 5 µL to 6 µL were pipetted into the chamber bubbles were observed routinely. A 7 µL volume was found to be the more effective at avoiding bubbles, but not entirely effective. The effective volume of the sample chamber was approximately 40 % larger than the design volume. A 7 µL portion of a test solution appears to contact the o-ring and wet the area of the seal, but did not appear to spread beyond the sealling surface of the o-ring. It should be noted that while the visual observation of the sealed microcell using a flashlight to provide back lighting was generally effective at detecting bubbles within the sample chamber, this was not a microscopic examination of the cell and it could only be performed on the bottom not the top of the microcell. The microcell provided a reliable radiological barrier that prevented the spread of contamination, but migration of nanoliter portions of test solution at the inner sealing surface do not challenge the the effectiveness of the microcell to prevent the spread of contamination.

Assigning all observed variation in measured counts to the variation in the apparent cell thickness does not give recognition to other components of uncertainty that are likely to be less significant, but cannot be separately evaluated as their contribution would impact the count rate in a similar manner. These variable include: the spread of excess liquid across the surface of the o-ring seal and ensuring that each 7 µL portion of test solution is consistently located within the x-ray beam.

In addition to thickness of the cell cavity within the microcell, other parameters impacting measurement control and uncertainty are: traceability and reliability standards solutions used for instrument calibration; the process of collecting test samples conducted outside of the laboratory; subsequent laboratory sample handling and splitting; techniques that prevent concentration due to evaporation within the headspace of the sample container, especially when small volumes of highly radioactive solutions are removed from shielded analytical cells; consistent microcell positioning within the x-ray spot; variation in the x-ray intensity generated by the hiRX x-ray source, and x-ray self-absorption. Count rate and counting time will impact counting statistics For the microcell thickness being used, the FP model appears to be effective for samples containing a total actinide concentration of up to 100 g/L (0.1 g/cm^3).

Conclusions and Recommendations

Testing and evaluation of the hiRX instrument at SRNL was effective at assessing system performance. Technical details from this evaluation are provided in LANL technical report LA-UR-16-20357, Version 2, *hiRX performance testing at SRNL using spent nuclear fuel* authored by Kathryn G. McIntosh and George J. Havrilla of LANL, and Robert F. Gilmore, Jr. and Michael K. Holland of SRNL. Technical report SRNL-L4110-2016-00001, Revision 0, *hiRX Hybrid XRF Calibration*, was generated by Patrick E. O'Rourke to document fundamental parameters corrections and instrument calibration capabilities for the current hiRX system and to predict instrument performance under conditions where the data reduction software and the instrument hardware and sample chamber are modified to optimize instrument performance. The information in these two reports were combined to generate this GUM-compliant uncertainty analysis for the hiRX system in it current configuration and as a beta-prototype system.

As currently configured, the hiRX instrument using microcells for the sample chamber provides measurement results that have an expanded uncertainty of 10% with a coverage factor of 2 (i.e., 95% confidence interval) for the optimum Pu and U concentration ranges. The largest portion of this measurement uncertainty is caused by varation in the effective thickness of the microcell sample chamber, not in the implementation of the monochromatic EDXRF capability provided by the alpha-prototype hiRX instrument. The XOS corporation incorporated numerous novel design features and a reasonable user interface for this alpha-prototype instrument. Instrument source noise and detector x-ray background level are very low. Lessons learned from evaluating the instrument have identified several key aspects of the current hardware and data-reduction software design that need to be addressed in combination with a flowcell sample chamber to achieve an expanded uncertainties of 1% or less (K=2). These recommendations are identified within this uncertainty propagation report

It is appropriate to note that the optimum range for the instrument can be easily shifted by changing the thickness of the flowcell sample chamber. It must be recognized that the application of flowcell technology will require that the beta-prototype instrument will need to be installed in radiological containment in order to operate or test the system using plutonium and uranium and levels of interest for nuclear material processing. Alternative, radiological containment unit could be modified to interface a contained flowcell with the instrument, but this arrangement is also expensive.

References

SRNL-L4700-2013-00012, Revision 0, Michael K. Holland and Patrick E. O'Rourke, SRNL, *HiRX Pu (and U) concentration measurements; GUM uncertainty propagation*, November 2013.

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LA-UR-16-20357, Version 2, Kathryn G. McIntosh[1], George J. Havrilla[1], Robert F. Gilmore, Jr.[2] and Michael K. Holland[2], *hiRX performance testing at SRNL using spent nuclear fuel*, March 2016. [[1]LANL, [2]SRNL]

Appendices

A. GUM Uncertainty Propagation, example [using appropriate Pu and U counts yielding 3.5 gPu/L and 5.0 gU/L]
B. GUM Outputs using different Pu and U counts, but same model equations [provided in Appendix A.]

Appendix A
GUM Uncertainty Propagation, example
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Model Equations:

Equations for alpha-prototype XOS hiRX Instrument using disposable microcell sample chamber

Net Count Rates, NCR, for samples containing Pu and U are calculated by subtracting the background counts from the total counts in the region of interest, ROI, then dividing by the counting time:

$$U_{NCR\_microcell} = (C_{\Xi UROI\_microcell} - C_{\Xi BGforU\_microcell}) * \Delta_{Rh\_source\_NotQuantified} / t_{count\_time\_microcell}$$
$$Pu_{NCR\_microcell} = (C_{\Xi PuROI\_microcell} - C_{\Xi BGforPu\_microcell}) * \Delta_{Rh\_source\_NotQuantified} / t_{count\_time\_microcell}$$

Factors for Custom Calibration Curves, CCC, as Sensitivity Factors (i.e., NCR per unit concentration, mass basis) and as Calibration Slopes (i.e., Analyte Conc., mass basis vs. NCR):

$$CCC_{U\_slope\_microcell} = 1 / CCC_{U\_sensitivity\_microcell}$$
$$CCC_{Pu\_slope\_microcell} = 1 / CCC_{Pu\_sensitivity\_microcell}$$
$$K_{Equivalency\_Factor\_microcell} = CCC_{U\_sensitivity\_microcell} / CCC_{Pu\_sensitivity\_microcell}$$

Correction factors for shielding (at a fixed sample solution density and a fixed microcell thickness) are calculated based upon the combined Pu and U expressed as an "effective" total counts, which considers the increased sensitivity or response of the hiRX instrument for plutonium concentration:

$$E_{Total\_NCR\_microcell} = U_{NCR\_microcell} + (Pu_{NCR\_microcell} * K_{Equivalency\_Factor\_microcell})$$
$$CF_{U\_microcell} = (a4_U * E_{Total\_NCR\_microcell}\text{^}4 + a3_U * E_{Total\_NCR\_microcell}\text{^}3 + a2_U * E_{Total\_NCR\_microcell}\text{^}2 + a1_U * E_{Total\_NCR\_microcell} + a0_U)$$
$$CF_{Pu\_microcell} = k1_{Pu} * CF_{U\_microcell} + k0_{Pu}$$

Shielding propagation, with Δ-terms for variables that impact the uncertainty in the correction factor for shielding, i.e., uncertainty in the measured sample solution density, variation in microcell thickness, and rhodium x-ray source stability. Each Δ-term has a value equal to one (1), and is assigned a ± relative uncertainty, expressed as a fraction:

$$CF_{U\_shielding\_microcell} = CF_{U\_microcell} * \Delta_{shielding\_from\_lab\_density} * \Delta_{shielding\_from\_microcell\_thickness} * \Delta_{Rh\_source\_NotQuantified}$$
$$CF_{Pu\_shielding\_microcell} = CF_{Pu\_microcell} * \Delta_{shielding\_from\_lab\_density} * \Delta_{shielding\_from\_microcell\_thickness} * \Delta_{Rh\_source\_NotQuantified}$$

Fundamental Parameters correction of the U and Pu net count rates:

$$FP\_U_{NCRsample\_microcell} = U_{NCR\_microcell} * CF_{U\_shielding\_microcell}$$
$$FP\_Pu_{NCRsample\_microcell} = Pu_{NCR\_microcell} * CF_{Pu\_shielding\_microcell}$$

U and Pu concentrations, on a mass basis, are calculated by multiplying the appropriate FP net count rate by the slope of the custom calibration curve for U and Pu, respectively:

$$U_{mg\_per\_g\_microcell} = FP\_U_{NCRsample\_microcell} * CCC_{U\_slope\_microcell}$$
$$Pu_{mg\_per\_g\_microcell} = FP\_Pu_{NCRsample\_microcell} * CCC_{Pu\_slope\_microcell}$$

U and Pu concentrations, on a volume basis, are calculated by multiplying the U and Pu concentrations on a mass basis by the sample solution density (measured separately by the laboratory):

$$U_{g\_per\_L\_microcell} = U_{mg\_per\_g\_microcell} * D_{lab\_density}$$
$$Pu_{g\_per\_L\_microcell} = Pu_{mg\_per\_g\_microcell} * D_{lab\_density}$$

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GUM Uncertainty Propagation, example
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Model Equations, continued:

Equations for beta-prototype XOS hiRX Instrument with upgraded hardware including internal detector for the rhodium x-ray source and a flowcell sample chamber as well as upgraded user interface and data reduction software

Net Count Rates, NCR, for samples containing Pu and U are calculated by subtracting the background counts from the total counts in the region of interest, ROI, then dividing by the counting time:

$$U_{NCR\_flowcell} = (C_{\Sigma UROI\_flowcell} - C_{\Sigma BGforU\_flowcell}) * \Delta_{Rh\_source\_Quantified} / t_{count\_time\_flowcell}$$
$$Pu_{NCR\_flowcell} = (C_{\Sigma PuROI\_flowcell} - C_{\Sigma BGforPu\_flowcell}) * \Delta_{Rh\_source\_Quantified} / t_{count\_time\_flowcell}$$

Factors for Custom Calibration Curves, CCC, as Sensitivity Factors (i.e., NCR per unit concentration, mass basis) and as Calibration Slopes (i.e., Analyte Conc., mass basis vs. NCR):

$$CCC_{U\_slope\_flowcell} = 1 / CCC_{U\_sensitivity\_flowcell}$$
$$CCC_{Pu\_slope\_flowcell} = 1 / CCC_{Pu\_sensitivity\_flowcell}$$
$$K_{Equivalency\_Factor\_flowcell} = CCC_{U\_sensitivity\_flowcell} / CCC_{Pu\_sensitivity\_flowcell}$$

Correction factors for shielding (at a fixed sample solution density and a fixed flowcell thickness) are calculated based upon the combined Pu and U expressed as an "effective" total counts, which considers the increased sensitivity or response of the hiRX instrument for plutonium concentration:

$$E_{Total\_NCR\_flowcell} = U_{NCR\_flowcell} + (Pu_{NCR\_flowcell} * K_{Equivalency\_Factor\_flowcell})$$
$$CF_{U\_flowcell} = (a4_U * E_{Total\_NCR\_flowcell}\text{^}4 + a3_U * E_{Total\_NCR\_flowcell}\text{^}3 + a2_U * E_{Total\_NCR\_flowcell}\text{^}2 + a1_U * E_{Total\_NCR\_flowcell} + a0_U)$$
$$CF_{Pu\_flowcell} = k1_{Pu} * CF_{U\_flowcell} + k0_{Pu}$$

Shielding propagation, with Δ-terms for variables that impact the uncertainty in the correction factor for shielding, i.e., uncertainty in the measured sample solution density, uncertainty in the measured thickness of the flowcell, and uncertainty in the measured rhodium x-ray source output. Each Δ-term has a value equal to one (1) and is assigned a ± relative uncertainty, expressed as a fraction. The Δ-term for the uncertainty in the rhodium x-ray source assumes that the beta-prototype hiRX instrument has been upgraded with a detector to correct for the difference in the x-ray tube output at the time of the sample measurement versus the x-ray tube output during instrument calibration:

$$CF_{U\_shielding\_flowcell} = CF_{U\_flowcell} * \Delta_{shielding\_from\_lab\_density} * \Delta_{shielding\_from\_flowcell\_thickness} * \Delta_{Rh\_source\_Quantified}$$
$$CF_{Pu\_shielding\_flowcell} = CF_{Pu\_flowcell} * \Delta_{shielding\_from\_lab\_density} * \Delta_{shielding\_from\_flowcell\_thickness} * \Delta_{Rh\_source\_Quantified}$$

Fundamental Parameters correction of the U and Pu net count rates:

$$FP\_U_{NCRsample\_flowcell} = U_{NCR\_flowcell} * CF_{U\_shielding\_flowcell}$$
$$FP\_Pu_{NCRsample\_flowcell} = Pu_{NCR\_flowcell} * CF_{Pu\_shielding\_flowcell}$$

U and Pu concentrations, on a mass basis, are calculated by multiplying the appropriate FP net count rate by the slope of the custom calibration curve for U and Pu, respectively:

$$U_{mg\_per\_g\_flowcell} = FP\_U_{NCRsample\_flowcell} * CCC_{U\_slope\_flowcell}$$
$$Pu_{mg\_per\_g\_flowcell} = FP\_Pu_{NCRsample\_flowcell} * CCC_{Pu\_slope\_flowcell}$$

U and Pu concentrations, on a volume basis, are calculated by multiplying the U and Pu concentrations on a mass basis by the sample solution density (measured separately by the laboratory):

$$U_{g\_per\_L\_flowcell} = U_{mg\_per\_g\_flowcell} * D_{lab\_density}$$
$$Pu_{g\_per\_L\_flowcell} = Pu_{mg\_per\_g\_flowcell} * D_{lab\_density}$$

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GUM Uncertainty Propagation, example
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List of Quantities:

Quantity	Unit	Definition
$U_{NCR\_microcell}$	s^{-1}	Net count rate for uranium in a microcell, corrected for background activity
$C_{\Xi UROI\_microcell}$		Analyte counts in the uranium region-of-interest (ROI) in a microcell
$C_{\Xi BGforU\_microcell}$		Background counts in the uranium ROI in a microcell
$\Delta_{Rh\_source\_NotQuantified}$		Δ-term for the uncertainty in the long-term variation in the x-ray tube stability (no source intensity correction, but monitored to determine when custom calibration should be repeated)
$t_{count\_time\_microcell}$	s	Typical counting time used for hiRX evaluation using microcells
$Pu_{NCR\_microcell}$	s^{-1}	Net count rate for plutinium in a microcell, corrected for background activity
$C_{\Xi PuROI\_microcell}$		Analyte counts in the plutonium region-of-interest (ROI) in a microcell
$C_{\Xi BGforPu\_microcell}$		Background counts in the plutonium ROI in a microcell
$CCC_{U\_slope\_microcell}$	$s * mg * g^{-1}$	Slope of the uranium custom calibration curve with uncertainty associated with microcells
$CCC_{U\_sensitivity\_microcell}$	$g * mg^{-1} * s^{-1}$	Sensitivity of the uranium based upon the custom calibration curve, i.e., Sensitivity = $CCC_{U\_slope\_microcell}^{-1}$
$CCC_{Pu\_slope\_microcell}$	$s * mg * g^{-1}$	Slope of the plutonium custom calibration curve with uncertainty associated with microcells
$CCC_{Pu\_sensitivity\_microcell}$	$g * mg^{-1} * s^{-1}$	Sensitivity of the uranium based upon the custom calibration curve, i.e., Sensitivity = $CCC_{Pu\_slope\_microcell}^{-1}$
$K_{Equivalency\_Factor\_microcell}$		Equivalency factor (ratio) between uranium sensitivity and plutonium sensitifity, with uncertainty component based on measurements in a microcell
$E_{Total\_NCR\_microcell}$	s^{-1}	Equivalent total net count rate for microcell measurements
$CF_{U\_microcell}$		Shielding correction factor for uranium in a microcell
$a4_U$	s^4	coefficient for the fourth-order term using a fourth order polynomial regression curve relating the uranium shielding correction factor and the plutonium shielding correction factor (independent of microcell or flowcell)
$a3_U$	s^3	coefficient for the third-order term using a fourth order polynomial regression curve relating the uranium shielding correction factor and the plutonium shielding correction factor (independent of microcell or flowcell)
$a2_U$	s^2	coefficient for the second-order term using a fourth order polynomial regression curve relating the uranium shielding correction factor and the plutonium shielding correction factor (independent of microcell or flowcell)
$a1_U$	s^1	coefficient for the first-order term using a fourth order polynomial regression curve relating the uranium shielding correction factor and the plutonium shielding correction factor (independent of microcell or flowcell)
$a0_U$	s^0	coefficient for the zero-order term using a fourth order polynomial regression curve relating the uranium shielding correction factor and the plutonium shielding correction factor (independent of microcell or flowcell)
$CF_{Pu\_microcell}$		Shielding correction factor for plutonium in a microcell

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GUM Uncertainty Propagation, example
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List of Quantities, continued:

Quantity	Unit	Definition
$k1_{Pu}$		coefficient for the first-order term using a linear regression curve relating the uranium shielding correction factor and the plutonium shielding correction factor (independent of microcell or flowcell)
$k0_{Pu}$		coefficient for the zero-order term using a linear regression curve relating the uranium shielding correction factor and the plutonium shielding correction factor (independent of microcell or flowcell)
$CF_{U\_shielding\_microcell}$		Correction factor for shielding of uranium propagated with the $\Delta_{uncertainty}$ components that impact shielding including test sample density, microcell thickness, and stability of the rhodium x-ray source
$\Delta_{shielding\_from\_lab\_density}$		Δ-term for shielding caused by the uncertainty in the density of the test sample (measured using a laboratory quality solution density meter)
$\Delta_{shielding\_from\_microcell\_thickness}$		Δ-term for shielding caused by the uncertainty in the thickness of the sample chamber when using a microcell
$CF_{Pu\_shielding\_microcell}$		Correction factor for shielding of plutonium propagated with the $\Delta_{uncertainty}$ components that impact shielding including test sample density, microcell thickness, and stability of the rhodium x-ray source
$FP\_U_{NCRsample\_microcell}$	s^{-1}	Fundamental parameters calculation of the uranium net count rate for a microcell
$FP\_Pu_{NCRsample\_microcell}$	s^{-1}	Fundamental parameters calculation of the plutonium net count rate for a microcell
$U_{mg\_per\_g\_microcell}$	$mg * g^{-1}$	Uranium concentration on a mass basis (mg g^{-1}) for a microcell
$Pu_{mg\_per\_g\_microcell}$	$mg * g^{-1}$	Plutonium concentration on a mass basis (mg g^{-1}) for a microcell
$U_{g\_per\_L\_microcell}$	$mg * mL^{-1}$	Uranium concentration on a volume basis (g L^{-1}) for a microcell
$D_{lab\_density}$	$g * mL^{-1}$	Density of test sample solution, measured using a laboratory quality solution density meter (densitometer)
$Pu_{g\_per\_L\_microcell}$	$mg * mL^{-1}$	Plutonium concentration on a volume basis (g L^{-1}) for a microcell
$U_{NCR\_flowcell}$	s^{-1}	Net count rate for uranium in a flowcell, corrected for background activity
$C_{ΞUROI\_flowcell}$		Analyte counts in the uranium region-of-interest (ROI) in a flowcell
$C_{ΞBGforU\_flowcell}$		Background counts in the uranium ROI in a flowcell
$\Delta_{Rh\_source\_Quantified}$		Δ-term for the uncertainty in the residual variation remaining after a correction for the intensity of the rhodium x-ray has been applied to the counts in ROI.
$t_{count\_time\_flowcell}$	s	Optimum counting time based on the evaluation of the prototye hiRX instrument, assuming upgrades in hardware and software design and the addition of a flowcell
$Pu_{NCR\_flowcell}$	s^{-1}	Net count rate for plutonium in a flowcell, corrected for background activity
$C_{ΞPuROI\_flowcell}$		Analyte counts in the plutonium region-of-interest (ROI) in a flowcell
$C_{ΞBGforPu\_flowcell}$		Background counts in the plutonium ROI in a flowcell

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GUM Uncertainty Propagation, example
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List of Quantities, continued:

Quantity	Unit	Definition
$CCC_{U\_slope\_flowcell}$	$s * mg * g^{-1}$	Slope of the uranium custom calibration curve, CCC, with uncertainty associated with flowcells
$CCC_{U\_sensitivity\_flowcell}$	$g * mg^{-1} * s^{-1}$	Sensitivity of the uranium based upon the custom calibration curve, i.e., Sensitivity = $CCC_{U\_slope\_flowcell}^{-1}$
$CCC_{Pu\_slope\_flowcell}$	$s * mg * g^{-1}$	Slope of the plutonium custom calibration curve, CCC, with uncertainty associated with flowcells
$CCC_{Pu\_sensitivity\_flowcell}$	$g * mg^{-1} * s^{-1}$	Sensitivity of the uranium based upon the custom calibration curve, i.e., Sensitivity = $CCC_{Pu\_slope\_flowcell}^{-1}$
$K_{Equivalency\_Factor\_flowcell}$		Equivalency factor (ratio) between uranium sensitivity and plutonium sensitifity, with an uncertainty component based on measurements in a flowcell
$E_{Total\_NCR\_flowcell}$	s^{-1}	Equivalent total net count rate for microcell measurements
$CF_{U\_flowcell}$		Shielding correction factor for shielding of uranium in a flowcell
$CF_{Pu\_flowcell}$		Shielding correction factor for shielding of plutonium in a flowcell
$CF_{U\_shielding\_flowcell}$		Correction factor for shielding of uranium propagated with the $\Delta_{uncertainty}$ components that impact shielding including test sample density, flowcell thickness, and stability of the rhodium x-ray source
$\Delta_{shielding\_from\_flowcell\_thickness}$		Δ-term for shielding cause by the uncertainty in the thickness of the sample chamber when using a flowcell
$CF_{Pu\_shielding\_flowcell}$		Correction factor for shielding of plutonium propagated with the $\Delta_{uncertainty}$ components that impact shielding including test sample density, flowcell thickness, and stability of the rhodium x-ray source
$FP\_U_{NCRsample\_flowcell}$	s^{-1}	Fundamental parameters calculateion of the uranium net count rate for a flowcell
$FP\_Pu_{NCRsample\_flowcell}$	s^{-1}	Fundamental parameters calculation of the plutonium net count rate for a flowcell
$U_{mg\_per\_g\_flowcell}$	$mg * g^{-1}$	Uranium concentration on a mass basis ($mg\ g^{-1}$) for a flowcell
$Pu_{mg\_per\_g\_flowcell}$	$mg * g^{-1}$	Plutonium concentration on a mass basis ($mg\ g^{-1}$) for a flowcell
$U_{g\_per\_L\_flowcell}$	$mg * mL^{-1}$	Uranium concentration on a volume basis ($g\ L^{-1}$) for a flowcell
$Pu_{g\_per\_L\_flowcell}$	$mg * mL^{-1}$	Plutonium concentration on a volume basis ($g\ L^{-1}$) for a flowcell

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GUM Uncertainty Propagation, example
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Quantity Values:

$U_{NCR\_microcell}$:
Interim Result

The sources of background activity include: detector background counts, scatter of rhodium x-rays from the source, fission product beta emissions. Testing of the hiRX prototype indicated that all of these sources of background counts are negligible.

$C_{\Xi UROI\_microcell}$:
Type B Poisson
Expectation Value (λ): 43772

$C_{\Xi BGforU\_microcell}$:
Type B Poisson
Expectation Value (λ): 1000

$\Delta_{Rh\_source\_NotQuantified}$:
Type B rectangular distribution
Value: 1.000
Halfwidth of Limits: 0.017

The current hiRX design and calibration methodology are based upon an assumption that the x-ray tube will be stable over time. Based on testing of the prototype hiRX instrument, this assumption is true over the short-term. It is likely that over the long-term the output of the x-ray tube will slowly decrease. The custom calibration would need to be repeated regularly to keep this effect within control limits established based upon data quality objectives, DQO. For this GUM uncertainty propagation it was assumed that a DQO of 1% at k=1 could be used. This corresponds to a $\Delta_{Rh\_source\_}$ (rectangular) would correspond with this DQO.
It is assumed that a hiRX instrument with the current design with all of the doubly curved crystals focused on the microcell, and the relative output of the rhodium x-ray source is not measured during each test sample measurement. hiRX instrument control would need to monitor the long-term performance of the x-ray tube using a solid strontium disk or similar quality control check, and the instrument would need to be re-calibrated when a change in the output of the x-ray tube is larger than the Δ-value cited for this uncertainty component. Alternatively a full recalibration may not be required if an intensity correction could be applied to the net counts.
The $\Delta_{Rh\_source\_NotQualified}$ input variable is included twice in the series of model equations for the calculation of a single uranium or plutonium concentration result. The net count rate is affected by this source of uncertainty and the shielding correction is also impacted by this source of uncertainty.

$t_{count\_time\_microcell}$:
Type B rectangular distribution
Value: 100 s
Halfwidth of Limits: 0.028 s

Assume that live counting time is within one electrical cycle. $\pm$ 1 / 60 Hz = $\pm$ 0.1667 s. Convert to a rectangular distribution: $\pm$ 0.1667 s x $3^{0.5}$ = $\pm$ 0.028 s.

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GUM Uncertainty Propagation, example
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Quantity Values, continued:

$Pu_{NCR\_microcell}$:
Interim Result

The sources of background activity include: detector background counts, scatter of rhodium x-rays from the source, fission product beta emissions. Testing of the hiRX prototype indicated that all of these sources of background counts are negligible.

$C_{\Xi PuROI\_microcell}$:
Type B Poisson
Expectation Value (λ): 250070

$C_{\Xi BGforPu\_microcell}$:
Type B Poisson
Expectation Value (λ): 1000

$CCC_{U\_sensitivity\_microcell}$:
Type B rectangular distribution
Value: 108.53 g * mg^{-1} * s^{-1}
Halfwidth of Limits: 6.62 g * mg^{-1} * s^{-1}

Uncertainty in the slope of the uranium custom calibration curve, mass basis: ± 3.5 % x $3^{0.5}$ = ± 6.1%.
108.53 x 0.061 = 6.62

$CCC_{Pu\_sensitivity\_microcell}$:
Type B rectangular distribution
Value: 898.2 g * mg^{-1} * s^{-1}
Halfwidth of Limits: 51.2 g * mg^{-1} * s^{-1}

Uncertainty in the slope of the plutonium custom calibration curve, mass basis: ± 3.3 % x $3^{0.5}$ = ± 5.7%.
898.20 x 0.057 = 51.2

$K_{Equivalency\_Factor\_microcell}$:
Interim Result

A larger percentage of the doubly-curved crystals are devoted to collecting and focusing plutonium x-rays compared to uranium x-rays. This feature of the instrument caused the net count rate to be higher for plutonium compared to uranium. However, the shielding correction factors need to be computed based upon the combined Pu and U elemental concentration not the sum of their net count rates. An equivalency term is used to convert the Pu net count rate to an effective uranium count rate so that it can be combined to generate an effective total count rate. The ratio of the slopes of the plutonium and uranium calibration curves is 0.1208 based upon a U_{slope} of 1.0853E+07 and a Pu_{slope} of 8.9824E+07. The U_{slope} and Pu_{slope} variables are positively correlated, and the uncertainty in their ratio is assumed to be small. A 5% uncertainty does not cause this term to be a significant budget contributor.

$a4_U$:
Type B rectangular distribution
Value: 0 s^4
Halfwidth of Limits: $4.8 \cdot 10^{-16}$ s^4

$a3_U$:
Type B rectangular distribution
Value: 0 s^3
Halfwidth of Limits: $1 \cdot 10^{-12}$ s^3

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Quantity Values, continued:

$a2_U$:
Type B rectangular distribution
Value: $6.740 \cdot 10^{-8}$ s^2
Halfwidth of Limits: $1 \cdot 10^{-9}$ s^2

$a1_U$:
Type B rectangular distribution
Value: $6.485 \cdot 10^{-5}$ s^1
Halfwidth of Limits: $1 \cdot 10^{-6}$ s^1

$a0_U$:
Type B rectangular distribution
Value: $1.003 \cdot 10^{+0}$ s^0
Halfwidth of Limits: $1 \cdot 10^{-5}$ s^0

$k1_{Pu}$:
Constant
Value: 0.93

$k0_{Pu}$:
Constant
Value: 0.0705

The coefficients $k1_{Pu}$ and $k0_{Pu}$ were generated based upon an Excel™ correlation plot and the associated equation for the trend line. However, the $k1_{Pu}$ term should be handled in GUM as a constant. The actual uncertainties in calculating both the $U_{shielding}$ and $Pu_{shielding}$ are very similar. These calculations use the individual physical properties of each element as described in technical report SRNL-L4110 -2016- 00001, Rev. 0."hiRX Hybrid XRF Calibration" by Patrick E. O'Rourke, January 2016. For convenience, the GUM uncertainty propagation calculates the $Pu_{shielding}$ correction from the $U_{shielding}$ correction, but this conversion should not be modelled to propagate additional uncertainty. The relative uncertainty associated with the $CF_{U\_}$ should be the same.

$\Delta_{shielding\_from\_lab\_density}$:
Type B rectangular distribution
Value: 1.00000
Halfwidth of Limits: .00027

The density of test sample solutions can be measured in the laboratory with an uncertainty of ±0.0005 g/cm^3 (k=2). In-line density or specific gravity instrumentation can achieve ± 0.01 g/cm^3 (k=2), or better. These relative small measurement uncertainties in the density of the test sample solution have a minimal impact on the uncertainty in the correction factor for the shielding of U and Pu. A Δ nominal density of 1.200 g/cm^3 with an uncertainty of ± 0.005 g/cm^3 (i.e., ± 0.42 % relative) will impact the correction factor for shielding by ± 0.27% (relative). This relationship can be scaled to calculate the term $\Delta_{shielding\_from\_density}$.

- For a typical laboratory measurement of solution density with an uncertainty of r = ± 0.0005 (rectangular) the impact on shielding term is: 1 ± 0.00027 (± 0.027 % (relative). [0.27 % x 0.0005 / 0.005 = 0.027 %].
- For an at-line density instrumentation with an uncertainty of r = ± 0.01 (rectangular) the impact on shielding term is: 1 ± 0.0054 (± 0.54 % (relative). [0.27 % x 0.01 / 0.005 = 0.54 %]

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Quantity Values, continued:

$\Delta_{shielding\_from\_microcell\_thickness}$:
Type B rectangular distribution
Value: 1.000
Halfwidth of Limits: 0.049

The variation in effectiveness thickness of the microcells used during hiRX testing was found to be 0.1227 cm ± 0.0056 cm (k=1), or 4.6 %. A fixed geometry flowcell with a diameter of 0.100 cm should have a known (measured) thickness of ± 0.0005 cm (k=1), or better.

- A $\Delta_{thickness}$ term was modeled by P. E. O'Rourke in Excel™: At a nominal thickness of 0.125 cm a deviation of + 0.005 cm (i.e., ± 4.0 % relative) the impact on the correction factor for shielding was - 2.5 %.
- An uncertainty in microcell thickness of 0.1227 cm ± 0.0056 (k=1) should have a very similar effect on the correction factor for shielding of ± 2.5 % x .0056 / 0.005 = ± 2.8 % (k=1). Converting from a Gaussian distribution to a rectangular distribution yields: $\Delta_{shielding\_from\_microcell\_thickness}$ = 1.000 ± 0.049 (rectangular)
- For the proposed flowcell with a thickness of 0.100 cm ± 0.0003 cm (k=1), the uncertainty in the correction factor for shielding would be ± 2.5 % x .0003 / 0.005 = ± 0.15 % (k=1). Converting from a Gaussian distribution to a rectangular distribution yields: $\Delta_{shielding\_from\_flowcell\_thickness}$ = 1.000 ± 0.003 (rectangular)

Nested polynomials were used for both solution density and cell thickness measurement in relation to x-ray absorption correction factors. An error in density of +0.005 g/cm^3 at 1.2 g/cm^3 results in an error of -0.27% in the x-ray absorption correction factor. An error in thickness of +0.005 cm in a measurement cell with a thickness of 0.125 cm results in an error of -2.5%. -- Dr. Patrick O'Rourke, Advisory Scientist, SRNL

$D_{lab\_density}$:
Type B rectangular distribution
Value: 1.1681 g * mL^{-1}
Halfwidth of Limits: 0.0005 g * mL^{-1}

$U_{NCR\_flowcell}$:
Interim Result

The sources of background activity include: detector background counts, scatter of rhodium x-rays from the source, fission product beta emissions. Testing of the hiRX prototype indicated that all of these sources of background counts should be negligible and independent of the type of sample chamber.

$C_{\Sigma UROI\_flowcell}$:
Type B Poisson
Expectation Value (λ): 437720

$C_{\Sigma BGforU\_flowcell}$:
Type B Poisson
Expectation Value (λ): 10000

$\Delta_{Rh\_source\_Quantified}$:
Type B rectangular distribution
Value: 1.000
Halfwidth of Limits: 0.001

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Quantity Values, continued:

It is assumed that the hiRX instrument design would be modified so that only a fraction (perhaps 60% to 80%) of the doubly-curved crystals will focus the rhodium excitation x-ray on the sample chamber and the remaining fraction (20% to 40%) would focus the x-ray on a dedicated detector, instead of the current design where all of the x-rays from the source are focused on the sample chamber (flowcell). The fraction of the excitation x-rays and the minimum counting time should be set so that the net counts from the excitation x-rays (Poison distribution) should be measured with a negligible uncertainty from counting statistics since the overall quality of the plutonium and uranium concentration will be scaled using the ratio of the net count rate from the excitation x- rays during test sample measurement and the net count rate during instrument calibration. The $\Delta_{Rh\_source\_Qualified}$ input variable is included twice in the series of model equations for the calculation of a single uranium or plutonium concentration result. The net count rate is affected by this source of uncertainty and the shielding correction is also impacted by this source of uncertainty.

$t_{count\_time\_flowcell}$:
Type B rectangular distribution
Value: 1000 s
Halfwidth of Limits: 0.028 s

$Pu_{NCR\_flowcell}$:
Interim Result

The sources of background activity include: detector background counts, scatter of rhodium x-rays from the source, fission product beta emissions. Testing of the hiRX prototype indicated that all of these sources of background counts should be negligible and independent of the type of sample chamber.

$C_{\Xi PuROI\_flowcell}$:
Type B Poisson
Expectation Value (λ): 2500700

$C_{\Xi BGforPu\_flowcell}$:
Type B Poisson
Expectation Value (λ): 10000

$CCC_{U\_sensitivity\_flowcell}$:
Type B rectangular distribution
Value: 108.53 g * mg^{-1} * s^{-1}
Halfwidth of Limits: 0.65 g * mg^{-1} * s^{-1}

Uncertainty in the slope of the uranium custom calibration curve, mass basis: ± 0.35 % x $3^{0.5}$ = ± 0.6%.
108.53 x 0.006 = 0.65

$CCC_{Pu\_sensitivity\_flowcell}$:
Type B rectangular distribution
Value: 898.2 g * mg^{-1} * s^{-1}
Halfwidth of Limits: 4.5 g * mg^{-1} * s^{-1}

Uncertainty in the slope of the plutonium custom calibration curve, mass basis: ± 0.3 % x $3^{0.5}$ = ± 0.5 %.
898.20 x 0.005 = 4.5

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Quantity Values, continued:

$\Delta_{shielding\_from\_flowcell\_thickness}$:
Type B rectangular distribution
Value: 1.0000
Halfwidth of Limits: 0.003

The variation in effectiveness thickness of the microcells used during hiRX testing was found to be 0.1227 cm ± 0.0056 cm (k=1), or 4.6 %. A fixed geometry flowcell with a diameter of 0.100 cm should have a known (measured) thickness of ± 0.0005 cm (k=1), or better.

- A $\Delta_{thickness}$ term was modeled by P. E. O'Rourke in Excel™: At a nominal thickness of 0.125 cm a deviation of + 0.005 cm (i.e., ± 4.0 % relative) the impact on the correction factor for shielding was - 2.5 %.
- An uncertainty in microcell thickness of 0.1227 cm ± 0.0056 (k=1) should have a very similar effect on the correction factor for shielding of ± 2.5 % x .0056 / 0.005 = ± 2.8 % (k=1). Converting from a Gaussian distribution to a rectangular distribution yields: $\Delta_{shielding\_from\_microcell\_thickness}$ = 1.000 ± 0.049 (rectangular).
- For the proposed flowcell with a thickness of 0.100 cm ± 0.0003 cm (k=1), the uncertainty in the correction factor for shielding would be ± 2.5 % x .0003 / 0.005 = ± 0.15 % (k=1). Converting from a Gaussian distribution to a rectangular distribution yields: $\Delta_{shielding\_from\_flowcell\_thickness}$ = 1.000 ± 0.003 (rectangular).

Nested polynomials were used for both solution density and cell thickness measurement in relation to x-ray absorption correction factors. An error in density of +0.005 g/cm^3 at 1.2 g/cm^3 results in an error of -0.27% in the x-ray absorption correction factor. An error in thickness of +0.005 cm in a measurement cell with a thickness of 0.125 cm results in an error of -2.5%. -- Dr. Patrick O'Rourke, Advisory Scientist, SRNL

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Uncertainty Budgets:

$U_{g\_per\_L\_microcell}$: Uranium concentration on a volume basis (g L^{-1}) for a microcell

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Corr.-Coeff.	Index
$U_{NCR\_microcell}$	427.80 s^{-1}	4.68 s^{-1}	∞					
$C_{\Xi UROI\_microcell}$	42880	207	∞	Poisson	$120 \cdot 10^{-6}$	0.026 mg * mL^{-1}	0.1051	1.1 %
$C_{\Xi BGforU\_microcell}$	100.0	10.0	∞	Poisson	$-120 \cdot 10^{-6}$	$-1.2 \cdot 10^{-3}$ mg * mL^{-1}	$-5.1 \cdot 10^{-3}$	0.0 %
$\Delta_{Rh\_source\_NotQuantified}$	1.00000	$9.81 \cdot 10^{-3}$	∞	rectangular	11	0.10 mg * mL^{-1}	0.4225	17.8 %
$t_{count\_time\_microcell}$	100.0000 s	0.0162 s	∞	rectangular	-0.055	$-900 \cdot 10^{-6}$ mg * mL^{-1}	$-3.7 \cdot 10^{-3}$	0.0 %
$Pu_{NCR\_microcell}$	2489.0 s^{-1}	24.9 s^{-1}	∞					
$C_{\Xi PuROI\_microcell}$	$249.000 \cdot 10^{3}$	499	∞	Poisson	$910 \cdot 10^{-9}$	$450 \cdot 10^{-6}$ mg * mL^{-1}	$1.8 \cdot 10^{-3}$	0.0 %
$C_{\Xi BGforPu\_microcell}$	100.0	10.0	∞	Poisson	$-910 \cdot 10^{-9}$	$-9.1 \cdot 10^{-6}$ mg * mL^{-1}	0.0	0.0 %
$CCC_{U\_slope\_microcell}$	$9.214 \cdot 10^{-3}$ s * mg * g^{-1}	$325 \cdot 10^{-6}$ s * mg * g^{-1}	∞					
$CCC_{U\_sensitivity\_microcell}$	108.53 g * mg^{-1} * s^{-1}	3.82 g * mg^{-1} * s^{-1}	∞	rectangular	-0.044	-0.17 mg * mL^{-1}	-0.6871	47.2 %
$CCC_{Pu\_sensitivity\_microcell}$	898.2 g * mg^{-1} * s^{-1}	29.6 g * mg^{-1} * s^{-1}	∞	rectangular	$-250 \cdot 10^{-6}$	$-7.4 \cdot 10^{-3}$ mg * mL^{-1}	-0.0304	0.0 %
$K_{Equivalency\_Factor\_microcell}$	0.12083	$5.83 \cdot 10^{-3}$	∞					
$E_{Total\_NCR\_microcell}$	728.5 s^{-1}	16.3 s^{-1}	∞					
$CF_{U\_microcell}$	1.08602	$4.33 \cdot 10^{-3}$	∞					
$a4_U$	0.0 s^4	$279 \cdot 10^{-18}$ s^4	∞	rectangular	$1.3 \cdot 10^{12}$	$360 \cdot 10^{-6}$ mg * mL^{-1}	$1.5 \cdot 10^{-3}$	0.0 %
$a3_U$	0.0 s^3	$1.46 \cdot 10^{-15}$ s^3	∞	rectangular	$1.8 \cdot 10^{9}$	$2.6 \cdot 10^{-6}$ mg * mL^{-1}	0.0	0.0 %
$a2_U$	$67.40 \cdot 10^{-9}$ s^2	$3.89 \cdot 10^{-9}$ s^2	∞	rectangular	$2.4 \cdot 10^{6}$	$9.5 \cdot 10^{-3}$ mg * mL^{-1}	0.0388	0.2 %
$a1_U$	$64.85 \cdot 10^{-6}$ s^1	$3.74 \cdot 10^{-6}$ s^1	∞	rectangular	3400	0.013 mg * mL^{-1}	0.0513	0.3 %
$a0_U$	1.00300000 s^0	$5.79 \cdot 10^{-6}$ s^0	∞	rectangular	4.6	$27 \cdot 10^{-6}$ mg * mL^{-1}	0.0	0.0 %
$CF_{U\_shielding\_microcell}$	1.0860	0.0332	∞					
$\Delta_{shielding\_from\_lab\_density}$	1.000000	$156 \cdot 10^{-6}$	∞	rectangular	5.0	$780 \cdot 10^{-6}$ mg * mL^{-1}	$3.2 \cdot 10^{-3}$	0.0 %
$\Delta_{shielding\_from\_microcell\_thickness}$	1.0000	0.0283	∞	rectangular	5.0	0.14 mg * mL^{-1}	0.5773	33.3 %
$FP\_U_{NCRsample\_microcell}$	464.6 s^{-1}	16.6 s^{-1}	∞					
$U_{mg\_per\_g\_microcell}$	4.281 mg * g^{-1}	0.210 mg * g^{-1}	∞					
$D_{lab\_density}$	1.168100 g * mL^{-1}	$289 \cdot 10^{-6}$ g * mL^{-1}	∞	rectangular	4.3	$1.2 \cdot 10^{-3}$ mg * mL^{-1}	$5.0 \cdot 10^{-3}$	0.0 %
$U_{g\_per\_L\_microcell}$	5.000 mg * mL^{-1}	0.245 mg * mL^{-1}	∞					

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Uncertainty Budgets, continued:

$Pu_{g\_per\_L\_microcell}$: Plutonium concentration on a volume basis (g L^{-1}) for a microcell

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Corr.-Coeff.	Index
$U_{NCR\_microcell}$	427.80 s^{-1}	4.68 s^{-1}	∞					
$C_{\Xi UROI\_microcell}$	42880	207	∞	Poisson	$4.9 \cdot 10^{-6}$	$1.0 \cdot 10^{-3}$ mg * mL^{-1}	$5.9 \cdot 10^{-3}$	0.0 %
$C_{\Xi BGforU\_microcell}$	100.0	10.0	∞	Poisson	$-4.9 \cdot 10^{-6}$	$-49 \cdot 10^{-6}$ mg * mL^{-1}	0.0	0.0 %
$\Delta_{Rh\_source\_NotQuantified}$	1.00000	$9.81 \cdot 10^{-3}$	∞	rectangular	7.4	0.072 mg * mL^{-1}	0.4193	17.6 %
$t_{count\_time\_microcell}$	100.0000 s	0.0162 s	∞	rectangular	-0.039	$-620 \cdot 10^{-6}$ mg * mL^{-1}	$-3.6 \cdot 10^{-3}$	0.0 %
$Pu_{NCR\_microcell}$	2489.0 s^{-1}	24.9 s^{-1}	∞					
$C_{\Xi PuROI\_microcell}$	$249.000 \cdot 10^{3}$	499	∞	Poisson	$15 \cdot 10^{-6}$	$7.3 \cdot 10^{-3}$ mg * mL^{-1}	0.0425	0.2 %
$C_{\Xi BGforPu\_microcell}$	100.0	10.0	∞	Poisson	$-15 \cdot 10^{-6}$	$-150 \cdot 10^{-6}$ mg * mL^{-1}	0.0	0.0 %
$CCC_{U\_sensitivity\_microcell}$	108.53 g * mg^{-1} * s^{-1}	3.82 g * mg^{-1} * s^{-1}	∞	rectangular	$1.4 \cdot 10^{-3}$	$5.2 \cdot 10^{-3}$ mg * mL^{-1}	0.0302	0.0 %
$CCC_{Pu\_slope\_microcell}$	$1.1133 \cdot 10^{-3}$ s * mg * g^{-1}	$36.7 \cdot 10^{-6}$ s * mg * g^{-1}	∞					
$CCC_{Pu\_sensitivity\_microcell}$	898.2 g * mg^{-1} * s^{-1}	29.6 g * mg^{-1} * s^{-1}	∞	rectangular	$-4.1 \cdot 10^{-3}$	-0.12 mg * mL^{-1}	-0.6978	48.7 %
$K_{Equivalency\_Factor\_microcell}$	0.12083	$5.83 \cdot 10^{-3}$	∞					
$E_{Total\_NCR\_microcell}$	728.5 s^{-1}	16.3 s^{-1}	∞					
$CF_{U\_microcell}$	1.08602	$4.33 \cdot 10^{-3}$	∞					
$a4_U$	0.0 s^4	$279 \cdot 10^{-18}$ s^4	∞	rectangular	$850 \cdot 10^{9}$	$240 \cdot 10^{-6}$ mg * mL^{-1}	$1.4 \cdot 10^{-3}$	0.0 %
$a3_U$	0.0 s^3	$1.46 \cdot 10^{-15}$ s^3	∞	rectangular	$1.2 \cdot 10^{9}$	$1.7 \cdot 10^{-6}$ mg * mL^{-1}	0.0	0.0 %
$a2_U$	$67.40 \cdot 10^{-9}$ s^2	$3.89 \cdot 10^{-9}$ s^2	∞	rectangular	$1.6 \cdot 10^{6}$	$6.2 \cdot 10^{-3}$ mg * mL^{-1}	0.0361	0.1 %
$a1_U$	$64.85 \cdot 10^{-6}$ s^1	$3.74 \cdot 10^{-6}$ s^1	∞	rectangular	2200	$8.2 \cdot 10^{-3}$ mg * mL^{-1}	0.0477	0.2 %
$a0_U$	1.00300000 s^0	$5.79 \cdot 10^{-6}$ s^0	∞	rectangular	3.0	$17 \cdot 10^{-6}$ mg * mL^{-1}	0.0	0.0 %
$CF_{Pu\_microcell}$	1.08050	$4.19 \cdot 10^{-3}$	∞					
$k1_{Pu}$	0.93							
$k0_{Pu}$	0.07050	$1.15 \cdot 10^{-3}$	∞	rectangular	3.2	$3.7 \cdot 10^{-3}$ mg * mL^{-1}	0.0217	0.0 %
$\Delta_{shielding\_from\_lab\_density}$	1.000000	$156 \cdot 10^{-6}$	∞	rectangular	3.5	$550 \cdot 10^{-6}$ mg * mL^{-1}	$3.2 \cdot 10^{-3}$	0.0 %
$\Delta_{shielding\_from\_microcell\_thickness}$	1.0000	0.0283	∞	rectangular	3.5	0.099 mg * mL^{-1}	0.5748	33.0 %
$CF_{Pu\_shielding\_microcell}$	1.0805	0.0330	∞					
$FP\_Pu_{NCRsample\_microcell}$	2689.4 s^{-1}	94.9 s^{-1}	∞					
$Pu_{mg\_per\_g\_microcell}$	2.994 mg * g^{-1}	0.147 mg * g^{-1}	∞					
$D_{lab\_density}$	1.168100 g * mL^{-1}	$289 \cdot 10^{-6}$ g * mL^{-1}	∞	rectangular	3.0	$860 \cdot 10^{-6}$ mg * mL^{-1}	$5.0 \cdot 10^{-3}$	0.0 %
$Pu_{g\_per\_L\_microcell}$	3.497 mg * mL^{-1}	0.172 mg * mL^{-1}	∞					

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Uncertainty Budgets, continued:

$U_{g\_per\_L\_flowcell}$: Uranium concentration on a volume basis (g L^{-1}) for a flowcell

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Corr.-Coeff.	Index
$a4_U$	0.0 s^4	$279\cdot10^{-18}$ s^4	∞	rectangular	$1.3\cdot10^{12}$	$360\cdot10^{-6}$ mg * mL^{-1}	0.0122	0.0 %
$a3_U$	0.0 s^3	$1.46\cdot10^{-15}$ s^3	∞	rectangular	$1.8\cdot10^{9}$	$2.6\cdot10^{-6}$ mg * mL^{-1}	0.0	0.0 %
$a2_U$	$67.40\cdot10^{-9}$ s^2	$3.89\cdot10^{-9}$ s^2	∞	rectangular	$2.4\cdot10^{6}$	$9.5\cdot10^{-3}$ mg * mL^{-1}	0.3204	10.3 %
$a1_U$	$64.85\cdot10^{-6}$ s^1	$3.74\cdot10^{-6}$ s^1	∞	rectangular	3400	0.013 mg * mL^{-1}	0.4231	17.9 %
$a0_U$	1.00300000 s^0	$5.79\cdot10^{-6}$ s^0	∞	rectangular	4.6	$27\cdot10^{-6}$ mg * mL^{-1}	0.0	0.0 %
$\Delta_{shielding\_from\_lab\_density}$	1.000000	$156\cdot10^{-6}$	∞	rectangular	5.0	$780\cdot10^{-6}$ mg * mL^{-1}	0.0263	0.0 %
$D_{lab\_density}$	1.168100 g * mL^{-1}	$289\cdot10^{-6}$ g * mL^{-1}	∞	rectangular	4.3	$1.2\cdot10^{-3}$ mg * mL^{-1}	0.0416	0.2 %
$U_{NCR\_flowcell}$	427.725 s^{-1}	0.701 s^{-1}	∞					
$C_{\Xi UROI\_flowcell}$	$428.725\cdot10^{3}$	655	∞	Poisson	$12\cdot10^{-6}$	$8.1\cdot10^{-3}$ mg * mL^{-1}	0.2744	7.5 %
$C_{\Xi BGforU\_flowcell}$	1000.0	31.6	∞	Poisson	$-12\cdot10^{-6}$	$-390\cdot10^{-6}$ mg * mL^{-1}	-0.0133	0.0 %
$\Delta_{Rh\_source\_Quantified}$	1.000000	$577\cdot10^{-6}$	∞	rectangular	11	$6.1\cdot10^{-3}$ mg * mL^{-1}	0.2051	4.2 %
$t_{count\_time\_flowcell}$	1000.0000 s	0.0162 s	∞	rectangular	$-5.5\cdot10^{-3}$	$-90\cdot10^{-6}$ mg * mL^{-1}	$-3.0\cdot10^{-3}$	0.0 %
$Pu_{NCR\_flowcell}$	2490.70 s^{-1}	2.14 s^{-1}	∞					
$C_{\Xi PuROI\_flowcell}$	$2.49170\cdot10^{6}$	1580	∞	Poisson	$91\cdot10^{-9}$	$140\cdot10^{-6}$ mg * mL^{-1}	$4.8\cdot10^{-3}$	0.0 %
$C_{\Xi BGforPu\_flowcell}$	1000.0	31.6	∞	Poisson	$-91\cdot10^{-9}$	$-2.9\cdot10^{-6}$ mg * mL^{-1}	0.0	0.0 %
$CCC_{U\_slope\_flowcell}$	$9.2140\cdot10^{-3}$ s * mg * g^{-1}	$37.3\cdot10^{-6}$ s * mg * g^{-1}	∞					
$CCC_{U\_sensitivity\_flowcell}$	108.530 g * mg^{-1} * s^{-1}	0.439 g * mg^{-1} * s^{-1}	∞	rectangular	-0.044	-0.019 mg * mL^{-1}	-0.6501	42.3 %
$CCC_{Pu\_sensitivity\_flowcell}$	898.20 g * mg^{-1} * s^{-1}	3.18 g * mg^{-1} * s^{-1}	∞	rectangular	$-250\cdot10^{-6}$	$-800\cdot10^{-6}$ mg * mL^{-1}	-0.0269	0.0 %
$K_{Equivalency\_Factor\_flowcell}$	0.120831	$649\cdot10^{-6}$	∞					
$E_{Total\_NCR\_flowcell}$	728.68 s^{-1}	1.80 s^{-1}	∞					
$CF_{U\_flowcell}$	1.08604	$3.44\cdot10^{-3}$	∞					
$CF_{U\_shielding\_flowcell}$	1.08604	$4.43\cdot10^{-3}$	∞					
$\Delta_{shielding\_from\_flowcell\_thickness}$	1.00000	$2.48\cdot10^{-3}$	∞	rectangular	5.0	0.012 mg * mL^{-1}	0.4181	17.5 %
$FP\_U_{NCRsample\_flowcell}$	464.53 s^{-1}	2.09 s^{-1}	∞					
$U_{mg\_per\_g\_flowcell}$	4.2802 mg * g^{-1}	0.0254 mg * g^{-1}	∞					
$U_{g\_per\_L\_flowcell}$	4.9997 mg * mL^{-1}	0.0297 mg * mL^{-1}	∞					

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Uncertainty Budgets, continued:

$Pu_{g\_per\_L\_flowcell}$: Plutonium concentration on a volume basis (g L^{-1}) for a flowcell

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Corr.-Coeff.	Index
$a4_U$	0.0 s^4	$279\cdot10^{-18}$ s^4	∞	rectangular	$850\cdot10^{9}$	$240\cdot10^{-6}$ mg * mL^{-1}	0.0120	0.0 %
$a3_U$	0.0 s^3	$1.46\cdot10^{-15}$ s^3	∞	rectangular	$1.2\cdot10^{9}$	$1.7\cdot10^{-6}$ mg * mL^{-1}	0.0	0.0 %
$a2_U$	$67.40\cdot10^{-9}$ s^2	$3.89\cdot10^{-9}$ s^2	∞	rectangular	$1.6\cdot10^{6}$	$6.2\cdot10^{-3}$ mg * mL^{-1}	0.3164	10.0 %
$a1_U$	$64.85\cdot10^{-6}$ s^1	$3.74\cdot10^{-6}$ s^1	∞	rectangular	2200	$8.2\cdot10^{-3}$ mg * mL^{-1}	0.4177	17.5 %
$a0_U$	1.00300000 s^0	$5.79\cdot10^{-6}$ s^0	∞	rectangular	3.0	$17\cdot10^{-6}$ mg * mL^{-1}	0.0	0.0 %
$k1_{Pu}$	0.93							
$k0_{Pu}$	0.07050	$1.15\cdot10^{-3}$	∞	rectangular	3.2	$3.7\cdot10^{-3}$ mg * mL^{-1}	0.1901	3.6 %
$\Delta_{shielding\_from\_lab\_density}$	1.000000	$156\cdot10^{-6}$	∞	rectangular	3.5	$550\cdot10^{-6}$ mg * mL^{-1}	0.0277	0.0 %
$D_{lab\_density}$	1.168100 g * mL^{-1}	$289\cdot10^{-6}$ g * mL^{-1}	∞	rectangular	3.0	$860\cdot10^{-6}$ mg * mL^{-1}	0.0440	0.2 %
$U_{NCR\_flowcell}$	427.725 s^{-1}	0.701 s^{-1}	∞					
$C_{\Xi UROI\_flowcell}$	$428.725\cdot10^{3}$	655	∞	Poisson	$490\cdot10^{-9}$	$320\cdot10^{-6}$ mg * mL^{-1}	0.0163	0.0 %
$C_{\Xi BGforU\_flowcell}$	1000.0	31.6	∞	Poisson	$-490\cdot10^{-9}$	$-16\cdot10^{-6}$ mg * mL^{-1}	0.0	0.0 %
$\Delta_{Rh\_source\_Quantified}$	1.000000	$577\cdot10^{-6}$	∞	rectangular	7.4	$4.2\cdot10^{-3}$ mg * mL^{-1}	0.2159	4.7 %
$t_{count\_time\_flowcell}$	1000.0000 s	0.0162 s	∞	rectangular	$-3.9\cdot10^{-3}$	$-62\cdot10^{-6}$ mg * mL^{-1}	$-3.2\cdot10^{-3}$	0.0 %
$Pu_{NCR\_flowcell}$	2490.70 s^{-1}	2.14 s^{-1}	∞					
$C_{\Xi PuROI\_flowcell}$	$2.49170\cdot10^{6}$	1580	∞	Poisson	$1.5\cdot10^{-6}$	$2.3\cdot10^{-3}$ mg * mL^{-1}	0.1175	1.4 %
$C_{\Xi BGforPu\_flowcell}$	1000.0	31.6	∞	Poisson	$-1.5\cdot10^{-6}$	$-46\cdot10^{-6}$ mg * mL^{-1}	$-2.4\cdot10^{-3}$	0.0 %
$CCC_{U\_sensitivity\_flowcell}$	108.530 g * mg^{-1} * s^{-1}	0.439 g * mg^{-1} * s^{-1}	∞	rectangular	$1.4\cdot10^{-3}$	$600\cdot10^{-6}$ mg * mL^{-1}	0.0304	0.0 %
$CCC_{Pu\_slope\_flowcell}$	$1.11334\cdot10^{-3}$ s * mg * g^{-1}	$3.94\cdot10^{-6}$ s * mg * g^{-1}	∞					
$CCC_{Pu\_sensitivity\_flowcell}$	898.20 g * mg^{-1} * s^{-1}	3.18 g * mg^{-1} * s^{-1}	∞	rectangular	$-4.1\cdot10^{-3}$	-0.013 mg * mL^{-1}	-0.6555	43.0 %
$K_{Equivalency\_Factor\_flowcell}$	0.120831	$649\cdot10^{-6}$	∞					
$E_{Total\_NCR\_flowcell}$	728.68 s^{-1}	1.80 s^{-1}	∞					
$CF_{U\_flowcell}$	1.08604	$3.44\cdot10^{-3}$	∞					
$CF_{Pu\_flowcell}$	1.08052	$3.40\cdot10^{-3}$	∞					
$\Delta_{shielding\_from\_flowcell\_thickness}$	1.00000	$2.48\cdot10^{-3}$	∞	rectangular	3.5	$8.7\cdot10^{-3}$ mg * mL^{-1}	0.4417	19.5 %
$CF_{Pu\_shielding\_flowcell}$	1.08052	$4.39\cdot10^{-3}$	∞					
$FP\_Pu_{NCRsample\_flowcell}$	2691.2 s^{-1}	11.4 s^{-1}	∞					
$Pu_{mg\_per\_g\_flowcell}$	2.9963 mg * g^{-1}	0.0168 mg * g^{-1}	∞					
$Pu_{g\_per\_L\_flowcell}$	3.4999 mg * mL^{-1}	0.0197 mg * mL^{-1}	∞					

Appendix A
GUM Uncertainty Propagation, example
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Results at 3.5 gPu/L and 5 gU/L [total Pu+U 8.5 g/L]:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
$U_{g\_per\_L\_microcell}$	5.00 mg * mL^{-1}	9.8 % (relative)	2.00	95% (normal)
$Pu_{g\_per\_L\_microcell}$	3.50 mg * mL^{-1}	9.8 % (relative)	2.00	95% (normal)
$U_{g\_per\_L\_flowcell}$	5.000 mg * mL^{-1}	1.2 % (relative)	2.00	95% (normal)
$Pu_{g\_per\_L\_flowcell}$	3.500 mg * mL^{-1}	1.1 % (relative)	2.00	95% (normal)

Appendix B
GUM Outputs using different Pu and U counts, but same model equations
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Results at 1 gPu/L and 0.1 gU/L [total Pu+U 1.1 g/L]:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
$U_{g\_per\_L\_microcell}$	0.100 mg * mL^{-1}	15 % (relative)	2.00	95% (normal)
$Pu_{g\_per\_L\_microcell}$	1.000 mg * mL^{-1}	9.6 % (relative)	2.00	95% (normal)
$U_{g\_per\_L\_flowcell}$	0.1000 mg * mL^{-1}	3.8 % (relative)	2.00	95% (normal)
$Pu_{g\_per\_L\_flowcell}$	1.0000 mg * mL^{-1}	0.76 % (relative)	2.00	95% (normal)

Results at 3.5 gPu/L and 5 gU/L [total Pu+U 8.5 g/L]:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
$U_{g\_per\_L\_microcell}$	5.00 mg * mL^{-1}	9.8 % (relative)	2.00	95% (normal)
$Pu_{g\_per\_L\_microcell}$	3.50 mg * mL^{-1}	9.8 % (relative)	2.00	95% (normal)
$U_{g\_per\_L\_flowcell}$	5.000 mg * mL^{-1}	0.86 % (relative)	2.00	95% (normal)
$Pu_{g\_per\_L\_flowcell}$	3.500 mg * mL^{-1}	0.76 % (relative)	2.00	95% (normal)

Results at 10 gPu/L and 0.1 gU/L [total Pu+U 10.1 g/L]:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
$U_{g\_per\_L\_microcell}$	0.100 mg * mL^{-1}	16 % (relative)	2.00	95% (normal)
$Pu_{g\_per\_L\_microcell}$	10.0 mg * mL^{-1}	10 % (relative)	2.00	95% (normal)
$U_{g\_per\_L\_flowcell}$	0.1000 mg * mL^{-1}	4.1 % (relative)	2.00	95% (normal)
$Pu_{g\_per\_L\_flowcell}$	10.000 mg * mL^{-1}	0.80 % (relative)	2.00	95% (normal)

Results at 0.1 gPu/L and 10 gU/L [total Pu+U 10.1 g/L]:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
$U_{g\_per\_L\_microcell}$	10.0 mg * mL^{-1}	10 % (relative)	2.00	95% (normal)
$Pu_{g\_per\_L\_microcell}$	0.100 mg * mL^{-1}	10 % (relative)	2.00	95% (normal)
$U_{g\_per\_L\_flowcell}$	10.000 mg * mL^{-1}	0.86 % (relative)	2.00	95% (normal)
$Pu_{g\_per\_L\_flowcell}$	0.1000 mg * mL^{-1}	1.1 % (relative)	2.00	95% (normal)

Appendix B
GUM Outputs using different Pu and U counts, but same model equations
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Results at 9 gPu/L and 9 gU/L[total Pu+U 18 g/L]:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
$U_{g\_per\_L\_microcell}$	9.00 mg * mL^{-1}	9.5 % (relative)	2.00	95% (normal)
$Pu_{g\_per\_L\_microcell}$	9.00 mg * mL^{-1}	10 % (relative)	2.00	95% (normal)
$U_{g\_per\_L\_flowcell}$	9.000 mg * mL^{-1}	0.88 % (relative)	2.00	95% (normal)
$Pu_{g\_per\_L\_flowcell}$	9.000 mg * mL^{-1}	0.87 % (relative)	2.00	95% (normal)

Results at 45 gU/L and 45 gPu/L[total Pu+U 90 g/L]:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
$U_{g\_per\_L\_microcell}$	45.0 mg * mL^{-1}	14 % (relative)	2.00	95% (normal)
$Pu_{g\_per\_L\_microcell}$	45.0 mg * mL^{-1}	14 % (relative)	2.00	95% (normal)
$U_{g\_per\_L\_flowcell}$	45.0 mg * mL^{-1}	6.1 % (relative)	2.00	95% (normal)
$Pu_{g\_per\_L\_flowcell}$	45.0 mg * mL^{-1}	6.0 % (relative)	2.00	95% (normal)

Results at 0.5 gPu/L and 100 gU/L [total Pu+U 100 g/L]:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
$U_{g\_per\_L\_microcell}$	100 mg * mL^{-1}	13 % (relative)	2.00	95% (normal)
$Pu_{g\_per\_L\_microcell}$	0.500 mg * mL^{-1}	13 % (relative)	2.00	95% (normal)
$U_{g\_per\_L\_flowcell}$	100.0 mg * mL^{-1}	6.9 % (relative)	2.00	95% (normal)
$Pu_{g\_per\_L\_flowcell}$	0.500 mg * mL^{-1}	6.7 % (relative)	2.00	95% (normal)

Results at 0.5 gPu/L and 250 gU/L [total actinides 100 g/L]:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
$U_{g\_per\_L\_microcell}$	250 mg * mL^{-1}	23 % (relative)	2.00	95% (normal)
$Pu_{g\_per\_L\_microcell}$	0.50 mg * mL^{-1}	23 % (relative)	2.00	95% (normal)
$U_{g\_per\_L\_flowcell}$	250 mg * mL^{-1}	20 % (relative)	2.00	95% (normal)
$Pu_{g\_per\_L\_flowcell}$	0.50 mg * mL^{-1}	20 % (relative)	2.00	95% (normal)